DET : Detection Principles

THERMIONIC SURFACE IONIZATION – Samples form gas phase negative ions by extraction of electrons from a hot, catalytically active solid surface. Key parameters are the surface composition, surface temperature, gas composition around the surface, and polarization of the surface relative to a surrounding ion collector. Multiple detection modes are obtained through systematic changes in these four parameters. Some modes combine reactive gas phase chemistry to decompose incoming samples, and then ionize the decomposition products by interaction with the surface. In other modes, intact sample molecules are ionized by direct impact with the surface with no intervening reactive gas phase chemistry. Some modes are non-destructive so that sample aromas can be sensed at the detector exit, and series combinations with other detectors are possible. Several modes use Air as the main detector gas, so that stand-alone applications involving selective detection of samples in ambient Air streams is possible.

FLAME IONIZATION - Samples decompose and form ions in gas phase reactions with radical species such as H, O, and OH that are present in self-sustained flames. A polarizer voltage and ion collector located near the flame effectively measures ions formed by combustion of most organic compounds. Polarizer and collector electrodes located more remotely downstream of the flame selectively measure only long-lived ion species.

REACTOR THERMIONIC IONIZATION ANALYSIS (RTIA) - In a non-GC implementation of thermionic detection, a thermionic ionization transducer is preceded by a heated reactor chamber. The transducer detects selective vapors thermally evolved from liquid or solid samples placed in the reactor. When the gas flowing through the reactor and transducer is Air or Oxygen, detected vapors include volatilized sample constituents as well as products of oxidation of the sample constituents.

CATALYTIC COMBUSTION IONIZATION - A hot catalytic ceramic surface operated in a detector environment containing Oxygen momentarily ignites a burst of ionization when an individual combustible compound containing a high concentration of Methylene groups elutes through the detector. The detection method provides selectivity of Alkanes vs. Alkenes, as well as saturated vs. unsaturated FAMEs, and the onset of combustion ionization is associated with the thermionic emission character of the ceramic surface.

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Ion Sources

STRUCTURE OF ION SOURCES - Thermionic sources are small (0.062 inch diameter x 0.40 inch long) ceramic cylinders composed of a loop of wire coated with layers of ceramic materials. Additives in the ceramic determine its activity. Source types are identified as TID-1, TID-2, TID-3, TID-4, TID-5, TID-6, and CFID, according to their chemical formulations and their work functions for the emission of thermionic electrons. Also available is an FID Probe consisting of an uncoated loop of wire.

SOURCE MOUNTING CONFIGURATIONS - A standard source mounting is a hexagonal shaped stainless steel flange which fits all DET structures as well as the Agilent 6890/7890 NPD structure. Also available is a 1/4 inch tube mounting for use in other customer-designed NPDs such as those in the Thermo Electron Trace GC and the SRI Instruments GC. Sources mounted in a round flange that fits the Finnigan/Tremetrics 9001 GC are also available.

SOURCE RECYCLING SERVICE - Return depleted DET or Agilent 6890/7890 NPD ion sources to DET for an environmental friendly disposal. Electrical connector and Aluminum connector holder can be reused with other new parts in a RECYCLED ION SOURCE ASSEMBLY priced lower than a new source, but with the same performance.

PRICES (hex or 1/4 tube mounts with connector):
$350 each (new), $315 each (recycled)

Designed Uses of the Ion Source Types:

- **TID-1**, low work function for operation in Nitrogen, Air, or Oxygen; detects electronegative compounds.
- **TID-2**, moderate work function for NPD-like operation in dilute Hydrogen/Air; detects N or P compounds with minimal tailing of P peaks.
- **TID-3**, moderate work function for operation in Nitrogen, Air, or Oxygen; detects volatile Halogenates.
- **TID-4**, moderate work function for NPD-like operation in dilute Hydrogen/Air; provides the best N response for the NPD.
- **TID-5**, high work function for operation in dilute Hydrogen/Air; selective for Br and I.
- **CFID**, high work function for operation downstream of Hydrogen/Air flame; in Remote FID detector provides selectivity for Pb, Sn, P, or Si.
- **TID-6**, high work function for operation in pre-mixed high flow of Hydrogen/Air; used in PTID for selectivity and very high sensitivity for P.

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Modes

TID-1-NITROGEN: selective for some **Nitro** and **Halogenated compounds** at **femtogram** and **picogram** levels, **most Oxygenates** at **picogram** and **nanogram** levels with especially large responses for **Phenols**, **Carboxylic Acids**, and **Glycols**.

TID-1-AIR(OXYGEN): selective for **Halogenates** and **Nitro** compounds at **picogram** levels, **some Oxygenates** at **picrogram** and **nanogram** levels, **water vapor** at **ppm** levels, and **microgram** levels of **Methylene groups** in **Linear Chain Hydrocarbons**.

TID-3-NITROGEN: selective for **volatile Halogenates** such as **Trihalomethanes** with minimal peak tailing.

TID-2-HYDROGEN/AIR (**NPD**): selective for **N** or **P** compounds at **sub-picogram** levels with **minimal tailing of P peaks**.

TID-4-HYDROGEN/AIR (**NPD**): our **best N-response** (**femtogram detectivity**).

PTID: selective for **P compounds** with very large signals and suppressed N-response.

FTID (**Flame Thermionic Ionization**): selective for **Nitrogen** or **Halogen compounds** at **nanogram levels** and **above**.

REMOTE FID: selective for **Pb**, **Sn**, **P, or Si compounds** with **picogram detection**.

FID: **universal response** to all organics.

TANDEM TID/NPD(TID) and **TID/FID**: **simultaneous signals** from **two detectors** with many possible combinations.

Examples of some applications:

- **drugs of abuse** with NPD (TID-4).
- **pesticides** and **environmental pollutants** with NPD (TID-2 or TID-4).
- **nitro explosives** with TID-1 and NPD (TID-4).
- **phenols** and **carboxylic acids in foods and flavors** analyses with TID-1.
- **oxygenates** and **N-compounds in petroleum** samples with TID-1 and NPD.
- **trihalomethanes** with TID-3.
- **Pb** or **Sn in complex matrices** with REMOTE FID and organic-fueled flame.

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GC Equipment

Detector Hardware for Retrofit on Thermo Trace, Agilent 6890, Varian, HP 5890, or SRI GC Models - Compact detector towers made of stainless steel and ceramic mount onto the existing FID or NPD base on the GC, and use the GC's existing controls for setting detector temperature and gas flows. Ion Sources identical to those used for the Agilent 6890/7890 NPD are on a self-aligning flange that fits the tower top.

Electronics - A stand-alone **DET Current Supply** provides a precision controlled constant heating current for the Ion Source for best response stability versus time, plus a selection of Ion Source polarization for optimum response in all modes. **Thermo Trace NPD electronics** provide the most versatile control of heating current and polarization, while Agilent, Varian, and SRI NPD electronics are more limited. The **Thermo Trace and Agilent 6890/7890 NPD Electrometers, Varian TSD Electrometer, and SRI NPD Amplifier** suffice for signal measurement. Otherwise, a **Keithley Model 6485 Picoammeter** provides a stand-alone unit for signal measurement for DET hardware mounted on HP5890 or the Agilent 6890/7890 FID detector base, as well as all DET stand-alone Transducer equipment.

Compact GC Analyzer - DET tower hardware, ceramic Ion Sources, and a Detector Current Supply are combined with a compact SRI model 310 GC. Analyzer features a glass lined flash vaporization injector, and a 15 m or 30 m x 0.32 mm fused silica column. Connection to a laptop computer provides data analysis and time programming of column temperature and carrier gas pressure.

Stand-alone Transducers and **Detection Modules** - TID/NPD transducers are hardware assemblies fitted with Tube or Swage-type inlet fittings for easy attachment to standard gas line connections. Detection modules include these transducers in a thermally insulated box containing a temperature controller and pneumatics controls where required. An **RTIA (Reactor Thermionic Ionization Analyzer)** module includes a heated reactor chamber as the inlet for the TID/NPD transducer.

Some examples of DET equipment uses:

- inexpensive, best performance, highest quality ion source replacements for the Agilent 6890/7890 NPD - TID-2 (black ceramic for sharp P peaks) or TID-4 (white ceramic for best N-response), $350. each new or $315 each recycled.
- more stable Constant Current type ion source heating power for the Agilent 6890/7890 NPD - substitute DET Current Supply ($1760) for the 6890/7890 Bead Voltage (Constant Voltage type) - other modes of thermionic detection also accessible with this equipment change.
- convert Agilent 6890/7890 NPD to selective detection of Oxygenates or volatile Halogenates - use DET Current Supply as above and replace NP ion source with TID-1 or TID-3 ($350. ea.).
- replace Varian TSD with DET NPD/TID hardware for lower cost ion sources and much improved P-peak shapes - DET NPD/TID/FID tower ($1650), TID-2 or TID-4 source ($350), and use compatible Varian TSD electronics. Add a DET Current Supply for detection modes other than NPD.

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NOVEL GC DETECTION BY DETECTOR ENGINEERING & TECHNOLOGY

TRANSFORM AN NPD TO OXYGENATE SELECTIVE DETECTION

greatly expand applications for the same basic equipment (O, N, P - the most common heteroatoms in organic chemistry)

DET supplies Agilent Technologies, Thermo Scientific, and SRI Instruments with Ceramic Ion Sources (beads) for their NPDs. For selectivities beyond NP compounds, DET has developed a family of 8 electrically heated, ceramic surfaces having different ionizing/catalytic activities. One ceramic is identified by the nomenclature "TID-1", and it provides selective ionization for Oxygenated compounds like Alcohols, Phenols, Carboxylic Acids, Glycols, Phthalates, Water, etc. Whereas NPD applications are mainly pesticide and drug analyses, Oxygenate selectivity applies to a much broader range of Food, Flavor, Fragrance, and Fuel analyses.

1.) CONVERTING AN AGILENT NPD TO OXYGENATE SELECTIVITY:

a.) replace the NP ion source with a TID-1 ceramic;

b.) change the detector gases from Hydrogen/Air to Nitrogen or Air;

c.) improve signal-to-noise for Oxygenates by a factor of 10 by substituting a stand-alone DET Current Supply for Agilent's Bead Voltage as the means of ion source power.

2.) CONVERTING A THERMO NPD TO OXYGENATE SELECTIVITY:

a.) replace the NP ion source by Thermo's "TS-1 source for ENS mode" (this is DET's TID-1 ceramic);

b.) change the detector gases as described above;

c.) use Thermo's NPD electronics to achieve optimum response in all modes of thermionic surface ionization;

Thermo NPD hardware with DET's NPD/TID/FID tower structure which is compatible with Thermo's NPD electronics - DET hardware mounts easily onto Thermo's detector base, and provides a better gas seal, more stream-lined gas flow, and more efficient ion collection within the detection volume – DET hardware also uses the same universal style ion source mountings as on Agilent GC models.

3.) CONVERTING AN SRI NPD TO OXYGENATE SELECTIVITY:

a.) replace the NP ion source with SRI's TID ion source (this is DET's TID-1 ceramic);

b.) change the detector gases as described above;

c.) use SRI's NPD electronics for ion source power and signal measurement;

d.) improve reliability of Oxygenate detection and interchangeability with other detection modes by replacing the SRI detector hardware with DET's NPD/TID/FID tower structure for more stream-lined gas flow and efficient ion collection – DET hardware uses the same universal style ion source mounting as on Agilent GC models.

e.) improve control of ion source power by substituting a stand-alone DET Current Supply for SRI's "Bead Volts" supply.

4.) RETROFIT VARIAN AND HP 5890 GC MODELS FOR OXYGENATE SELECTIVITY AS WELL AS

a.) replace Varian TSD hardware with a DET NPD/TID/FID tower structure which is compatible with Varian's TSD electronics - adjust the detector gases accordingly – substitute a stand-alone DET Current Supply for ion source power for 10 times better signal-to-noise for Oxygenates;

b.) replace HP 5890 NPD hardware and electronics with DET's NPD/TID/Remote FID hardware and DET's stand-alone electronics for ion source power and signal measurement – adjust detector gases.

5.) SOME SPECIFIC APPLICATIONS FOR SELECTIVE TID-1 IONIZATION:

a.) detection of Ethanol and other Alcohols in Petroleum and Biofuels;

b.) detection of Acetic, Formic, and other Carboxylic Acids in Wine and other food and flavor analyses;

c.) picogram detection of BisPhenol A (BPA) and Phthalates in food packaging products;

d.) detection of Glycerol and Glycols in wine and food products;

e.) low picogram detection of Phenols in environmental samples;

f.) low picogram detection of Vanillin and Salicylates in food flavorings;

g.) exceptional femtogram detection for Nitro explosives like TNT and 2,4-Dinitrotoluene, as well as Nitro pesticides like Methyl Parathion;

h.) detection of trace Water in solvents and petroleum samples;

products of oxidative decomposition that build up in motor oil versus miles of automobile usage;

k.) selective detection of Methylene groups in linear chain Hydrocarbons and Fatty Acid Methyl Esters (FAMEs) in petroleum and biofuels.

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THEORY AND OPERATION

OF THE

NPD/TID/CFID DETECTORS

FTID DETECTOR

REMOTE FID DETECTOR

TANDEM TID DETECTOR

FID DETECTOR

NPD	-	NITROGEN PHOSPHORUS DETECTOR
TID	-	THERMIONIC IONIZATION DETECTOR
CFID	-	CATALYTIC FLAME IONIZATION DETECTOR
FTID	-	FLAME THERMIONIC IONIZATION DETECTOR

DET
innovations in chemical detection

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I. GENERAL THEORY

A. BASIC DETECTOR COMPONENTS

The basic configuration of DET detectors is a cylindrically-shaped thermionic/catalytic source positioned on the axis of a cylindrical collector electrode. This configuration provides a stream-lined gas flow through the detection volume, and a radial-shaped electrical field for efficient ion collection. The thermionic source is heated by a constant current power supply, and is biased at a negative voltage with respect to the collector. Negative ionization current is measured with a conventional electrometer. The detector generally mounts onto an NPD or FID type detector base so that at least two sources of detector gases can be supplied. One of the detector gases, and often a third "Makeup" gas, are introduced through the center of a sample conduit tubing, along with the sample carrier gas from the GC. The remaining detector gas sweeps the outer diameter of the sample conduit tubing. In many cases, a conventional FID flame tip suffices as the sample conduit.

The most important parameters in this detector are the composition of the surface of the source, the temperature of the source, the composition of gases surrounding the source, and the magnitude of polarization between the source and collector. Entirely different types of detector responses are obtained through variations in any or all of these key parameters. Consequently, the basic detector hardware provides the capability for a whole family of operating modes.

B. THERMIONIC IONIZATION DETECTION (TID)

Samples impact the heated, alkali activated ceramic surface of the source, and are ionized by the extraction of electrical charge from the surface. This surface ionization process is controlled by the surface work function, the surface temperature, and the composition of gases surrounding the surface. N,P specificity is obtained from a very hot surface of moderate work function operating in a chemically active environment consisting of a dilute concentration of H_2 mixed with air (TID-2-H_2/Air). Very high specificity and sensitivity to certain compounds containing electronegative functional groups is obtained from a low work function source operated at moderate temperatures in an inert environment of pure N_2 (TID-1-N_2), or in an oxygen containing environment (TID-1-Air).

C. CATALYTIC FLAME IONIZATION DETECTION (CFID)

A source comprised of ceramic and a non-alkali additive serves as a combination ignitor, polarizer, and catalytic surface in a H_2/air flame environment. In this CFID, the ionization occurs primarily in a gas phase process, and universal responses similar to those of an FID are obtained. The catalytic surface aids in the combustion process, and provides enhanced responses to certain compounds normally having reduced responses in conventional FIDs.

D. FLAME THERMIONIC IONIZATION DETECTION (FTID)

An alkali activated ceramic source of low work function is operated at moderate temperatures in the effluent stream of a H_2/Air flame. Unlike the CFID, ionization in the flame environment is normally not measured. Instead, the neutral products of combustion are selectively re-ionized by the thermionic transducer placed downstream of the flame. The FTID provides specific responses to heteroatom compounds which yield electronegative products of combustion, especially nitrogen or halogen compounds.

E. REMOTE FLAME IONIZATION DETECTION (REMOTE FID)

Similar to an FTID, a ceramic source structure and ionization collector are located several centimeters downstream of a flame. Unlike an FTID, the thermionic source is operated in a manner that does not produce any additional ionization beyond that originally produced in the flame. Instead, the source functions as a polarizer to produce collection of long lived negative ions emanating from the flame. The REMOTE FID provides specific responses only to compounds which produce very stable negative ions in combustion. Examples are the specific detection of lead, tin, or phosphorus compounds.

F. TANDEM TID

TANDEM TID refers to a series combination of two independently controlled thermionic ionization detection stages. Each stage provides a different response, and both responses are obtained simultaneously for each sample compound.

G. FLAME IONIZATION DETECTION (FID)

FID detection of all organic compounds is achieved by using an uncoated loop of Pt/Rh wire in place of the thermionic source.

H. UNIQUE LAYERED CONSTRUCTION OF THE SOURCE

In the thermionic ionization process, charge lost from the surface of the thermionic source (I_2) must be replaced by a migration of charge through the body of the source (I_1). The present TID sources have a separate non-alkali/ceramic sublayer through which charge migration occurs, and an alkali/ceramic surface layer optimized to provide the type of selective surface ionization desired. There are currently available 7 different type thermionic sources identified as TID-1, TID-2, TID-3, TID-4, TID-5, TID-6, and CFID; and an FID ignitor/polarizer probe which is an uncoated Pt/Rh wire.

I. GENERAL OPERATING CHARACTERISTICS

The TID, CFID, FTID and REMOTE FID are mass flow rate sensitive detectors rather than concentration sensitive detectors. This means that relatively high flows of detector gases can be used to sweep the detector volume without causing reduced response due to sample dilution effects. The composition and flow rates of detector gases, however, do influence the surface temperature of the source. In most modes of operation, the source temperature will be in the general range of 400 - 800°C, whereas the surrounding detector tower will be at a wall temperature of 100 - 400°C as set by the detector heater block controls on the GC. The resultant source temperature is a balance of the electrical heat input to the source and heat losses due to conduction and convection through the gases flowing past the source. Therefore, the source temperature is dependent on the magnitude of source heating current, the detector heater block temperature, the thermal conductivity of the gas mixture flowing past the source, and the magnitude of the total gas flow through the detector. In the CFID, FTID, and REMOTE FID, the source is also heated to some extent by the H_2/Air flame burning around and/or beneath the source.

From the above considerations, the following general operating characteristics can be expected:

1.) At any fixed set of gas flows and detector heater block temperature, the principal means of varying source temperature is via the magnitude of source heating current.

2.) If the gas flows or detector heater block temperature are changed, a readjustment of source heating current restores the source to the same surface temperature it had before the change. Often the magnitude of detector background signal or the response to a standard sample can serve as a guide to the correct readjustment of source heating current.

3.) Helium has a much higher thermal conductivity than nitrogen, so the use of helium as the GC carrier gas generally requires higher settings of source heating current than when nitrogen is used.

4.) As the total gas flow through the detector is increased, generally expect to supply more heating current to obtain the same source temperature. The present detector has a small internal volume, so for most TID modes a total gas flow of 80 - 120mL/min is adequate. For the CFID, FTID, and REMOTE FID, typical gas flows are 200 - 250mL/min.

5.) As the detector heater block temperature is increased, expect to supply less heating current to the source to obtain the same source temperature. The detector has been designed to operate for extended periods of time at detector heater block temperatures of 400°C. As a general rule, it is best to operate the detector heater block temperature as high as is allowable by the application. This minimizes the temperature gradient between the source and the surrounding wall, and helps minimize detector contamination.

TID-1 DETECTION USING VARIAN TSD ELECTRONICS

1.) DET TID-1 detection normally uses a stand-alone DET Current Supply to provide heating power and polarization to the TID-1 Ion Source. In contrast to an NPD where the optimum polarization is a low value (i.e., - 4 or -5 V), best TID-1 sensitivity is obtained with a higher polarization of -45 V which is available from the DET supply.

2.) The polarization or bias voltage on Varian's TSD electronics is normally set at -4 V for NPD detection. However, that bias voltage can be increased to a value of - 12 V by adjusting the bias voltage potentiometer to its maximum (full clockwise) position. This will suffice for providing some of the unique TID-1 selectivity. If better detectivity is required, then the DET supply is always an option.

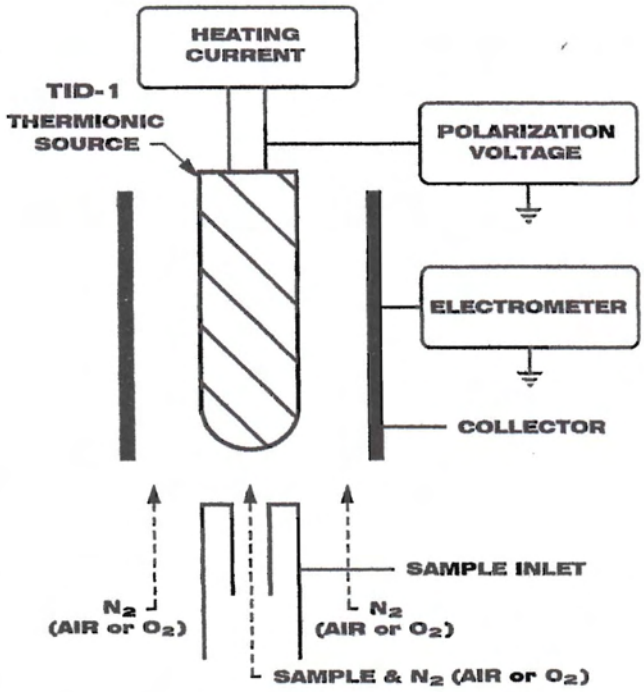
3.) Unlike an NPD which requires a detector gas mixture of Hydrogen and Air, TID-1 detection requires only an inert Nitrogen gas environment, or an oxidizing environment of Air or Oxygen. These can be achieved using the TSD pneumatics controls, by simply connecting the appropriate gas composition to the gas inlets normally supplying "Hydrogen", "Air", and Makeup to the detector. Best selectivity versus Hydrocarbons is generally obtained using Nitrogen as the detector gas. Air or Oxygen environments suppress responses from some compounds while enhancing responses to others.

4.) TID-1 detection does not require as high a heating current for the ion source as is used in an NPD. Varian TSD electronics provide a minimum of 2.400 Amps heating current, and that will be sufficient for many TID-1 applications.

TID-1-N_2(O_2): selective for NITRO, OXYGENATED, or HALOGENATED compounds

Equipment:

This detection mode uses a **TID-1** type thermionic source mounted in either a **TID/FID, REMOTE FID, FTID, PTID,** or **TANDEM TID** tower. The detector gas is N_2 flowed through the gas lines which normally provide "H_2" and "air" to an NPD or FID. (Air or O_2 are other possible choices for the detector gases.) The source is heated by a constant current supply and is polarized at -45 Volts relative to the collector. In most applications, the surface temperature of the source is in the range of 400-600 °C which has no visible glow.



Principle:

This mode uses a low work function surface operated in an inert (or oxidizing) gas environment. The surface functions as a reservoir of electrons. Samples impact the surface and are ionized by a process involving the extraction of electrons from the surface. Gas phase negative ions are formed and collected for the detector signal. The process is extremely selective to compounds containing electronegative functional groups such as the NO_2 group, halogen atoms, or oxygenated functionalities. In some cases there occurs a direct electron attachment to the intact sample molecule. In many other cases, there occurs a dissociative electron attachment to an electronegative fragment of the sample molecule. The manner in which electronegative groups are bound in the structure of the sample molecule strongly influences the response.

Response:

This mode is characterized by primary, secondary, and tertiary levels of response. Primary compounds are detectable at femtogram levels and have selectivities of 10^8 versus hydrocarbons. Examples of primary compounds are 4-nitrophenol, 2,4-dinitrotoluene, TNT, methyl parathion, pentachlorophenol, and heptachlor. Secondary compounds are detectable at picogram levels and have selectivities of 10^7 - 10^5. Examples of secondary responders are atrazine, 2-nitrophenol, 2,4-dichlorophenol, diazepam, chlordane, dieldrin, phenols, carboxylic acids, glycols, vanillin, and methyl salicylate. Tertiary compounds are detectable at 1 - 10 nanogram levels and have selectivities of 10^4 versus hydrocarbons. Examples of tertiary compounds are alcohols, ketones, aldehydes, phthalates, thiols, and the pyrrole functional group.

The TID-1 source can also be used in oxidizing detector gas environments such as air or O_2. The presence of O_2 in the detector reduces the response of some compounds, and enhances others. Examples of compounds which are enhanced are 2,4-dinitro-phenol, endrin, simazine, furan, and water vapor.

IIIA. OPERATION: TID-1-N_2 MODE

1.) BASIC DESCRIPTION

In this mode of operation, a thermionic source (TID-1) of very low work function is operated in a chemically inert gas environment of N_2. Sample compounds are ionized by a surface process involving the extraction of electrons from the heated source and the subsequent formation of gas phase negative ions from the sample compound. This mode of operation is extremely specific to compounds which contain electronegative functional groups. In particular, very large responses (femtogram and picogram detectivity) are obtained for certain compounds containing the nitro (NO_2) group and for some polychlorinated compounds. Lower levels of response (nanogram detectivity) are obtained for many oxygenated compounds such as alcohols and phenols. The manner in which the electronegative groups are bound up in the structure of the sample molecule also has a strong influence on the magnitude of response that is obtained. This mode of operation exhibits its greatest specificity when the source is operated at relatively low source heating currents. As the heating current is increased, some responses are obtained for a wider variety of compounds, although the detector still discriminates strongly against many classes of compounds.

2.) DETECTOR GAS FLOWS

In this mode of operation, N_2 is used for both detector gas 1 and gas 2. The principal function of the detector gases is to maintain a well purged detector volume. A flow rate of 10 - 15 mL/min for detector gas 1 generally suffices, while a flow rate of 50 - 70 mL/min is generally adequate for detector gas 2. N_2 is the preferred GC carrier gas, although He can also be used subject to the considerations described on page I-4.

To minimize excessive jet effects at the small orifice of the sample conduit, the sum of the GC carrier gas and detector gas 1 should normally be less than about 40 mL/min. Gas flows are measured at the exit tube of the detector tower using the flow measuring tubing and fitting that are supplied. (On HP 5890 GC installations, gas flows may be more accurately measured at the detector base before installing the detector tower.)

3.) OPERATION

a.) To become familiar with the response characteristics of the TID-1-N_2 mode, some initial experimentation with high responding test samples is recommended. Examples of good test sample compounds are methyl parathion or 2,4 dinitrotoluene at concentration levels of about 1 - 10 ng. A good source of methyl parathion is Varian TSD test sample #82-005048-04, and a good source of 2,4 dinitrotoluene is 100:1 dilution of Supelco nitroaromatic mixture #4-8742.

b.) Each new TID-1 source is accompanied by a chromatogram of the response of that source to a test sample. The conditions associated with this chromatogram provide a good starting point for examining the source.

c.) GENERAL OPERATING PROCEDURES

1.) Set detector and carrier gas flows in accordance with guidelines in I.I and IIIA.2.

2.) Set the detector heater block at the desired operating temperature. (300°C or higher is generally preferred for this detector.)

3.) Connect the DET electrometer or the electrometer on the GC to a signal recording device (ie., integrator or data system) and disengage any electrometer autozeroing if applicable. In initial setup of the TID, it is helpful to monitor the magnitude of the background signal level as the source heating current is increased. Set the electrometer and data system attenuations and range so the recorded display corresponds to approximately 10^{-11} Amps for full scale signal.

4.) On the DET Current Supply providing heating current to the thermionic source, set the bias voltage switch on the back of the supply at -45 V.

5.) With the Current thumbwheel switch initially set at 0000, turn on the Current Supply. The magnitude of heating current required depends on the operating temperature of the heated detector base, and the thermal gradients in the detector hardware depend to some extent on which GC model is used. Typical heating currents are as follows:

Temperature - - - - - Heating Current - - - - - - - - - - - - -

	VARIAN 3800	Ag 6890/NPD	HP5890/6890 FID
100°C	2.7 - 3.0 Amps	2.6 - 2.8	2.9 - 3.1
200°C	2.5 - 2.7 Amps	2.4 - 2.6	2.7 - 2.9
300°C	2.3 - 2.5 Amps	2.2 - 2.4	2.5 - 2.7

Start at the lower end of these ranges and observe the recorded baseline for an indication of signal increase as the heating current is turned up from zero. Typically an initial signal will rise rapidly from the baseline, reach a peak, and then equilibrate to some lower level. The hot thermionic source radiates some heat to the surrounding detector tower, and the equilibration of the detector tower temperature may require as long as 30 minutes. To minimize this thermal equilibration time, set the detector heater block at as high a temperature as allowed by the application so that the thermal gradient between the thermionic source and the surrounding detector wall is minimized.

5.) Set the injector and column temperature such that the test sample compounds will have a retention time in the range of 2 - 6 minutes.

6.) Inject a volume of about one microliter of the test sample and observe the detector response to the electronegative compounds. Adjust the electrometer attenuation and range if necessary to get an on-scale sample peak and inject the sample again.

7.) Increase the source heating current by an increment of 0.1 Amps and inject the test sample again. Generally, this increase in heating current will increase the magnitude of the background signal as well as the sample response. To ensure on-scale sample peaks, adjust the electrometer range or attenuation to achieve about the same percent of full scale level for the background signal.

8.) Response characteristics of interest in these test sample chromatograms are the solvent response, sample compound responses, and magnitude of the detector background signal. Frequently, as the source heating current is increased, the response of the detector to the solvent will increase relative to the sample response. This indicates that the detector becomes less specific at higher currents. Also the ratio of sample peak heights relative to the magnitude of background signal may change with changes in heating current. Generally expect changes in the ratio of sample response to background signal to be indicative of changes in the detector signal-to-noise ratio (ie., detectivity).

9.) Compare the two chromatograms of c.6 and c.7 to determine which best suits the desired application of the detector. The following guidelines may be useful:

9.1 Lowest detector noise (ie., about 2×10^{-14} Amps) occurs for background signal levels of 10×10^{-12} Amps or less.

9.2 Highest specificity is obtained at lower source heating currents.

9.3 At some loss of specificity, signal-to-noise ratios (ie., detectivity) can often be improved by increasing source heating current until the detector background signal level reaches about 10×10^{-12} Amps.

9.4 The operating lifetime of the source often decreases with increasing source heating current.

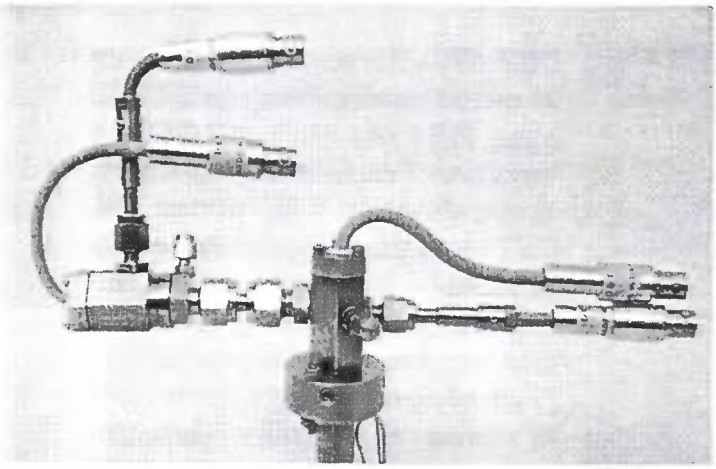
10.) Once the preliminary results of c.6 - c.8 have demonstrated the basic characteristics of the TID-1-N_2 mode, the detector is ready to be applied to any analytical sample of interest. Some experimentation with source heating current and/or detector heater block temperature similar to c.6 - c.8 is often helpful to best optimize the detector for each new type of sample.

IIIAA. OPERATION: TID-1-AIR (O_2) MODE

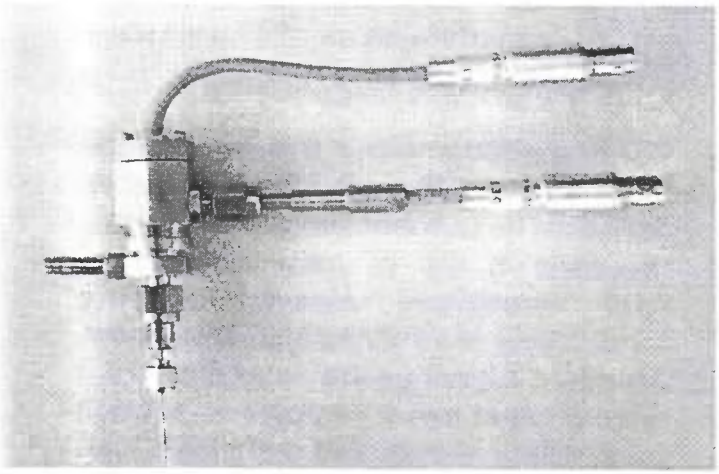
This mode of operation is similar to the TID-1-N_2 mode, except that the detector gases are Air or O_2 instead of N_2. This mode also is specific for electronegative compounds, but the responses differ from the TID-1-N_2 mode because of the presence of the weakly electronegative O_2 molecule in the gas environment. Generally, the magnitudes of gas flow rates used for detector gas 1 and gas 2 are the same as those recommended for the TID-1-N_2 mode. However, there may be specific applications where the most favorable sample responses are obtained from using detector gas combinations such as Air (O_2) for gas 1 and N_2 for gas 2, or vice versa. Therefore, it is frequently instructive to experiment first with the TID-1 source in an N_2 environment, and then to perform the same analyses with an Air (O_2) environment.

NOTE: Long term operation of the TID-1 source at high source heating currents in an oxygen containing environment sometimes causes a change in the TID-1 surface characteristics such that subsequent operation in an N_2 environment may yield reduced sensitivity. Therefore, once it is established which gas environment is best for a given analysis, the TID-1 source should be dedicated to continued operation in either an N_2 or O_2 environment for best results.

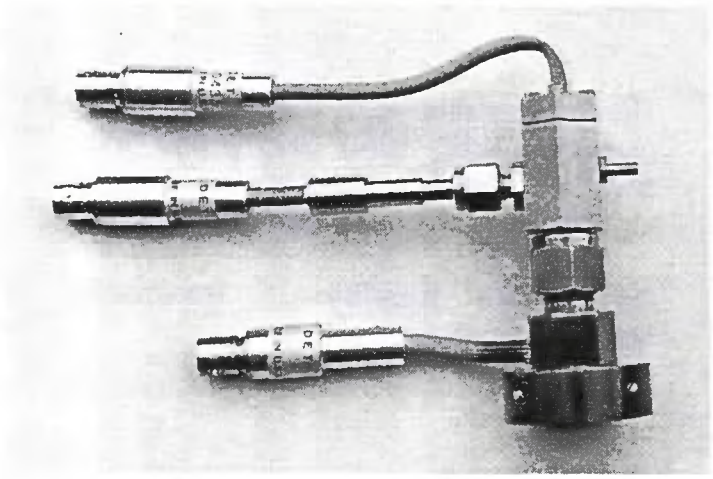
EXAMPLES OF DET HARDWARE STRUCTURES



Tandem TID/FID hardware for custom fit onto Varian GCs. Two gas lines in Varian detector base supply gas environment for TID stage of detection. Third gas inlet after TID detection supplies Hydrogen flow through ceramic jet for second stage FID detection. Fourth gas connection at FID inlet supplies Air flow about outer periphery of FID jet.

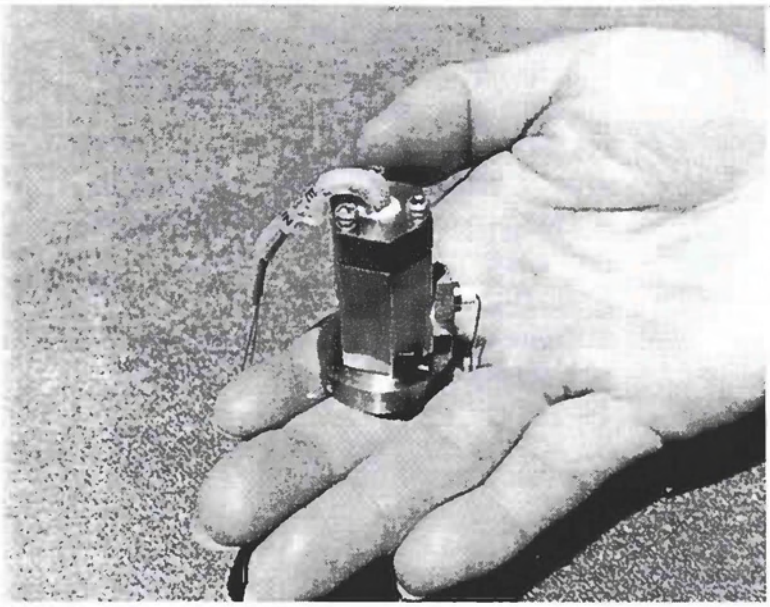


FID transducer for samples in an incoming Air stream. 1/16 inch Swage inlet provides Hydrogen flow through a ceramic lined jet. 1/4 inch tube inlet provides sample and Air flow about outer periphery of FID flame jet.

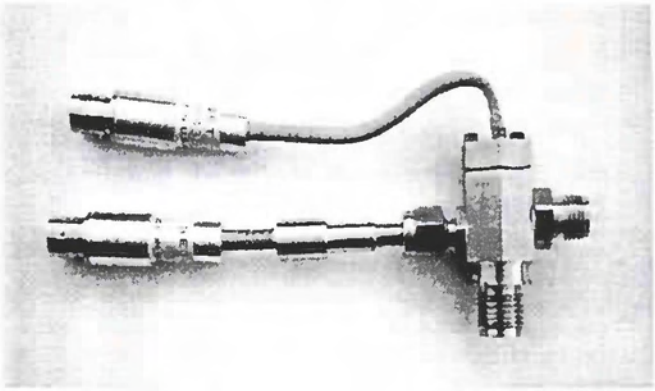


Flame Thermionic Ionization Detector (FTID) structure that fits onto Varian GC detector base. Samples decomposed in flame at short ceramic jet. Polarization voltage supplied at bottom of detector drives flame ions to the surrounding detector wall. Thermionic transducer attached downstream re-ionizes neutral Halogen and/or Nitrogen combustion products from the flame.

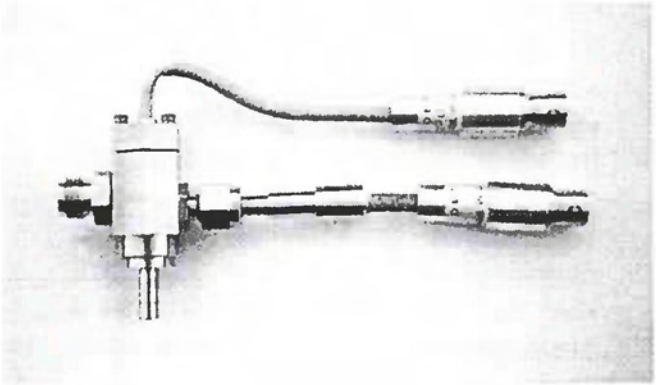
EXAMPLES OF DET HARDWARE STRUCTURES



DET NPD hardware for custom fit onto Bendix Process GC FID base. DET structure is 0.75 inch hexagonal stainless steel stock, approximately 1.50 inches tall. DET structure fits inside Bendix detector housing with ion source power wiring (2 wires) and electrometer signal wiring (1 wire) connecting to terminals in base of Bendix detector housing. Stand-alone DET Current Supply used to power ion sources, and Bendix negative ion electrometer used for signal measurement.



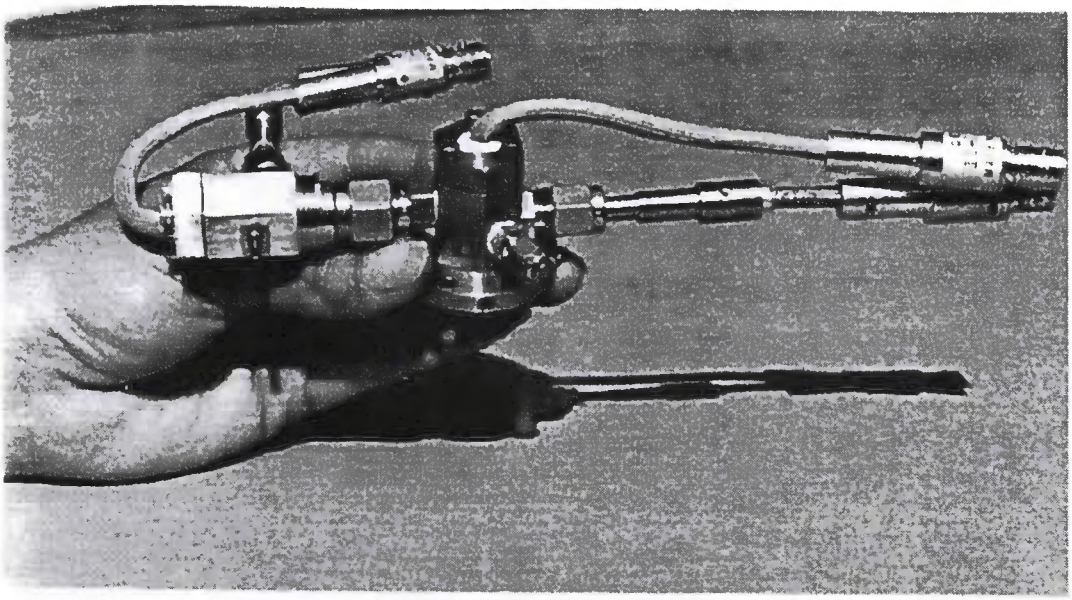
TID Transducer with 0.375 inch Swage inlet and 0.250 inch Swage outlet. Standard hexagonal flanged ion source mounted in top of transducer tower with fiberglass sleeved cabling terminating in a Twinex type connector. Standard signal probe extending from side of tower has a flexible mid section for bending as required and a BNC type connector for cabling to a negative ion electrometer.



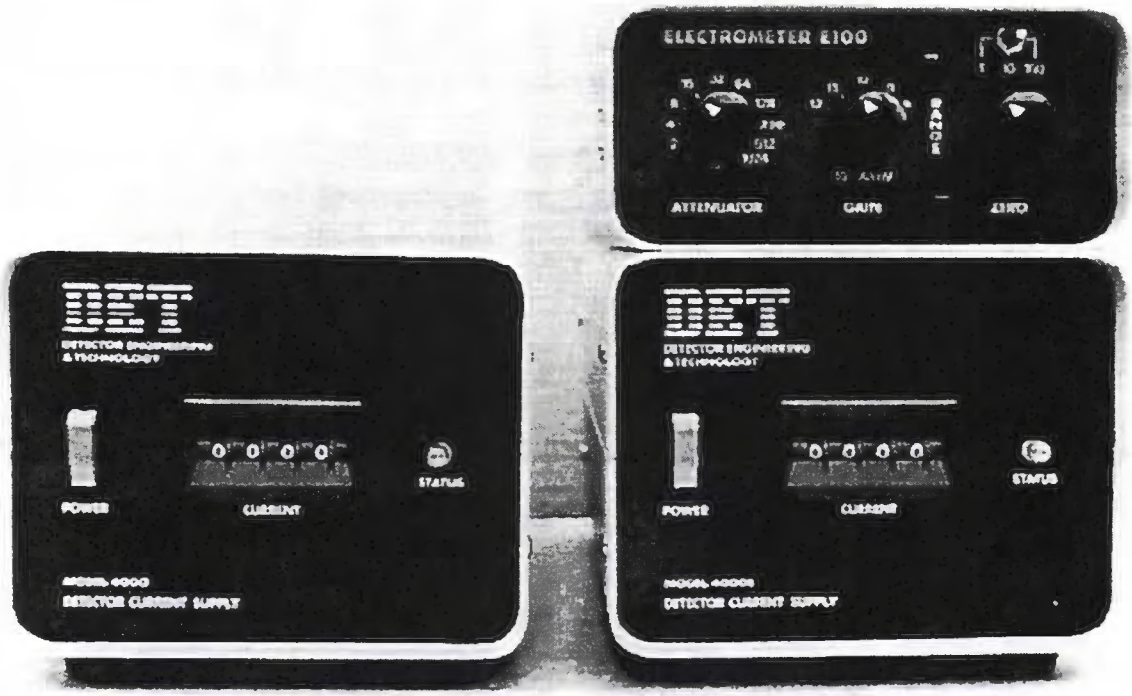
TID Transducer with 0.250 inch outer diameter inlet tube and 0.250 inch Swage outlet. Standard ion source and signal connections as described above.

Other size tube/Swage inlet/outlet fittings are also possible.

DET innovations in chemical detection



TANDEM TID - 2 simultaneous signals



DETECTOR CURRENT SUPPLY

COMBINED CURRENT SUPPLY AND ELECTROMETER

DET
innovations in chemical detection

CHROMalytic ECHnology Pty Ltd
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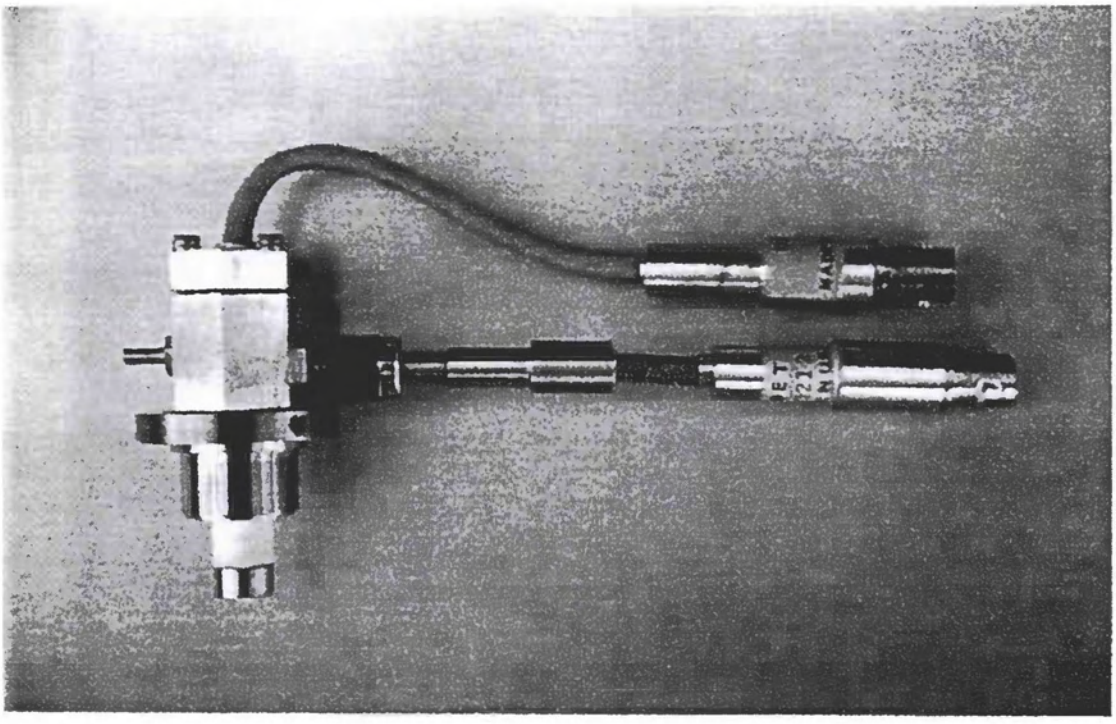
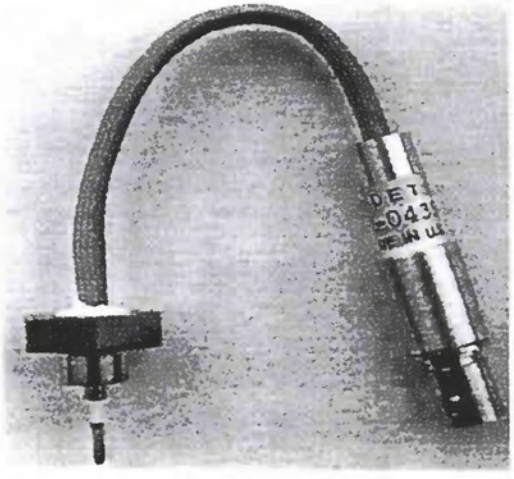
DET innovations in chemical detection



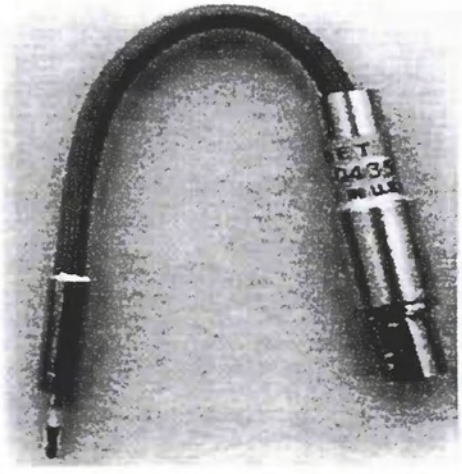
DET NPD/TID/REMOTE FID HARDWARE
MOUNTS ONTO AGILENT 6890 FID BASE OR HP 5890 FID/NPD BASE

THERMIONIC IONIZATION SOURCES

(AVAILABLE WITH OR WITHOUT ELECTRICAL CONNECTOR)



STANDARD HEXAGONAL FLANGE MOUNTING FITS ALL DET HARDWARE AND AGILENT 6890 NPD HARDWARE



1/4 INCH TUBE MOUNTING FOR CUSTOM APPLICATIONS. USED IN THERMO-FINNIGAN AND SRI GCs.

DET
innovations in chemical detection

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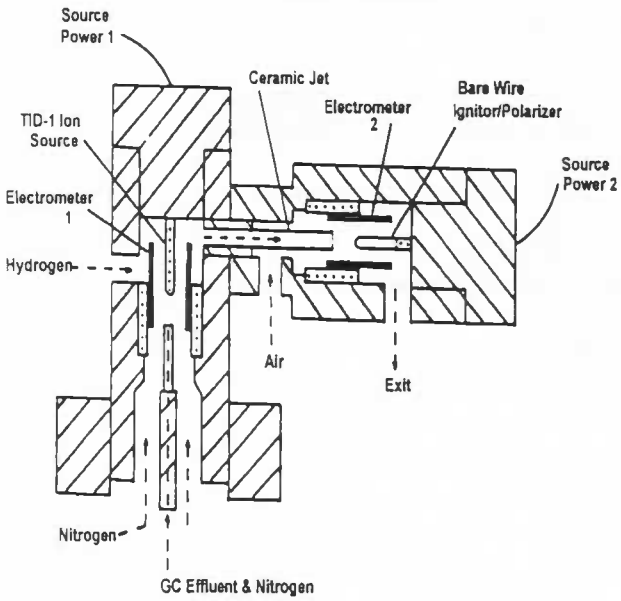
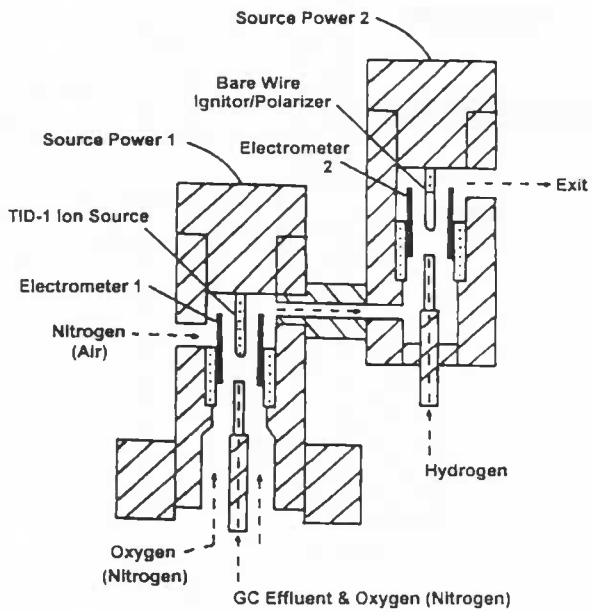
TANDEM TID/FID: SIMULTANEOUS TID and FID SIGNALS

Tandem TID-1-Nitrogen/FID



TANDEM TID-1-Oxygen (Nitrogen)/FID

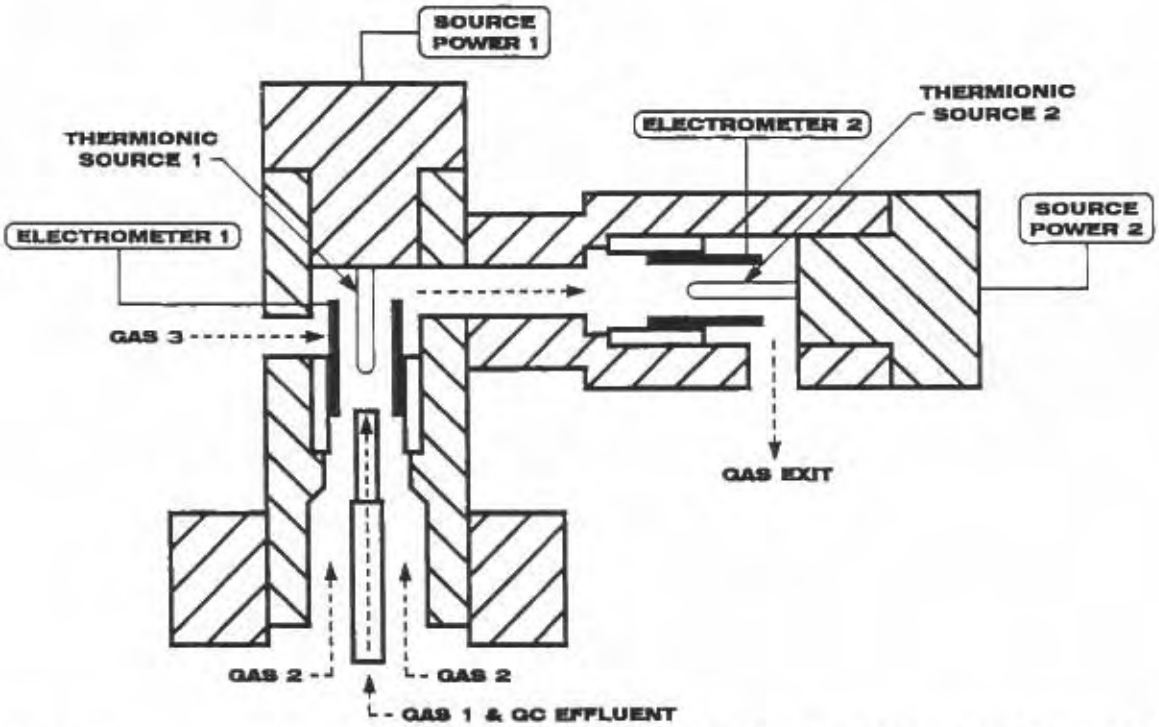


Equipment:

In a **TANDEM TID/FID**, two independently controlled thermionic and flame ionization detection stages are combined in a series combination. The first stage is a **MODIFIED TID/FID** tower (Varian GC models) or a **MODIFIED REMOTE FID** tower (Agilent 6890 and HP 5890 GC models) that mounts onto the existing FID base on the GC. (The mounting configuration illustrated above is that which fits Varian instruments.) The second stage is either an **FID TRANSDUCER/JET ASSEMBLY** for the case where the first stage effluent is carried into the FID in an inert gas stream, or an **FID/AIR SAMPLE TRANSDUCER** for the case where the first stage effluent is carried into the FID in an oxidizing gas stream. In either case, two different detector gases can be supplied through the lines in the detector base that normally supply "H_2" and "Air" to an FID. A third gas inlet in the modified first stage tower provides an additional gas flow between the two stages. The second stage **FID TRANSDUCER/JET ASSEMBLY** includes a fourth gas inlet for Air to sweep the outer periphery of the FID flame jet. The second stage **FID/AIR SAMPLE TRANSDUCER** includes a fourth gas inlet for H_2 to the flame jet. A ceramic coated thermionic ion source such as the **TID-1** or **TID-3** is normally used in the first stage, while a bare wire **FID Probe** is used as the flame ignitor/polarizer in the second stage. Each stage of detection requires a separate heating current and polarization electronic module for powering the ion source/FID probe. The simultaneous TID and FID signals from the two stages require two negative ion electrometers for measurement.

DET innovations in chemical detection

TANDEM TID: 2 SIMULTANEOUS SIGNALS, many signal combinations are possible



Equipment:

In a **TANDEM TID**, two independently controlled thermionic ionization detection stages are combined in a series configuration. The first stage is a **MODIFIED TID/FID** tower (Varian GC models) or a **MODIFIED REMOTE FID** tower (Agilent 6890 and HP 5890 GC models) that mounts onto the existing FID base on the GC. The second stage is a **TID TRANSDUCER** that attaches to the exit port of the first stage. Two different detector gases can be supplied through the lines in the detector base which normally supply "H_2" and "air" to an FID. A third gas inlet in the modified first stage tower provides an additional detector gas flow between the two stages. The two detection stages can be easily decoupled to allow separate operation of each structure. The first detection stage can be purchased separately, and the second stage may be added later as needed.

Each stage requires a thermionic source or FID probe, and their separate heating current and polarization electronics. The simultaneous signals from the two stages require two negative ion electrometers for measurement.

Response:

Many different tandem signal combinations are possible, depending on the type of thermionic sources/FID probe used and the composition of detector gases supplied. Some possibilities are as follows:

TID-1-N_2/HWCID - simultaneous detection of oxygenates and hydrocarbons in gasolines;

TID-1-Air/NPD - simultaneous detection of organochlorine and nitrogen/phosphorus pesticides;

FID/FTID-2 - simultaneous detection of hydrocarbons and high concentration halogenates;

PTID: **(Phosphorus Thermionic Ionization)** selective detection and very large signals for **P** with **suppressed N** response.

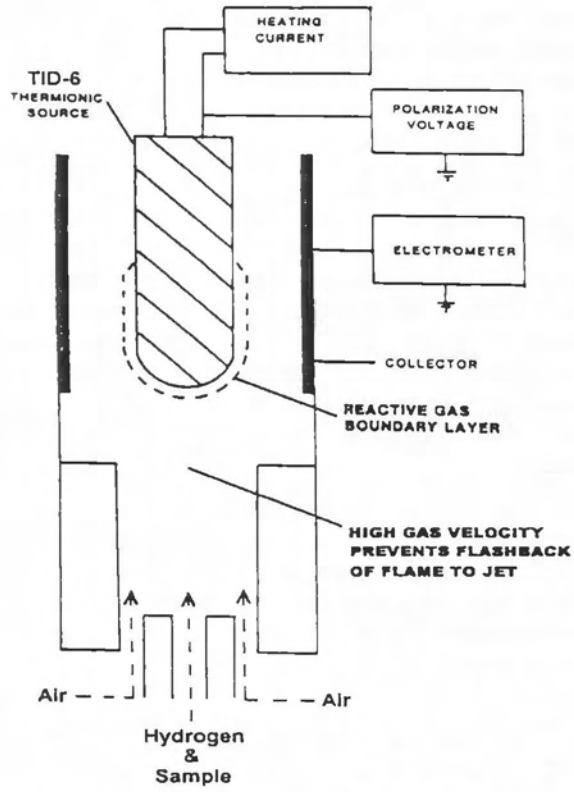
Equipment:

This detection mode uses a **TID-6** type thermionic source mounted in a **PTID Tower**. The **PTID** tower structure is similar to a Remote FID Tower in positioning the thermionic source several centimeters downstream of the jet. However, the **PTID Tower** contains a reduced internal diameter for high gas velocity to prevent flame front flashback from the hot source to the jet. This allows higher Hydrogen and Air gas flows to be used than are possible with an NPD. In the PTID, typical gas flows are H_2 = 20 - 30 mL/min, and Air = 250 - 500 mL/min. The thermionic source is heated by a constant current supply and is polarized at - 15 V with respect to the collector. During operation, the surface temperature of the source is maintained in the range of 600 - 800°C which produces a visible orange glow.

Principle:

This mode uses a thermionic source of high work function operated in an FID-like H_2/air environment. However, unlike an FID, an internal flow restrictor prevents flame front flashback to form a self sustaining flame at the jet orifice where H_2 and Air are initially mixed together. Instead, an ignited, chemically active gas boundary layer is maintained about the hot source surface similar to an NPD. Because of the higher H_2 and Air, this PTID boundary layer has a much higher concentration of chemically active radical species. NPD thermionic sources do not hold up well in this harsher environment, so this mode of detection requires a more durable ceramic source surface. Like an NPD, sample compounds are decomposed in the gaseous boundary layer, and P compounds form

PTID



decomposition products which are converted with high efficiency to gas phase negative ions by extracting electrons from the thermionic surface.

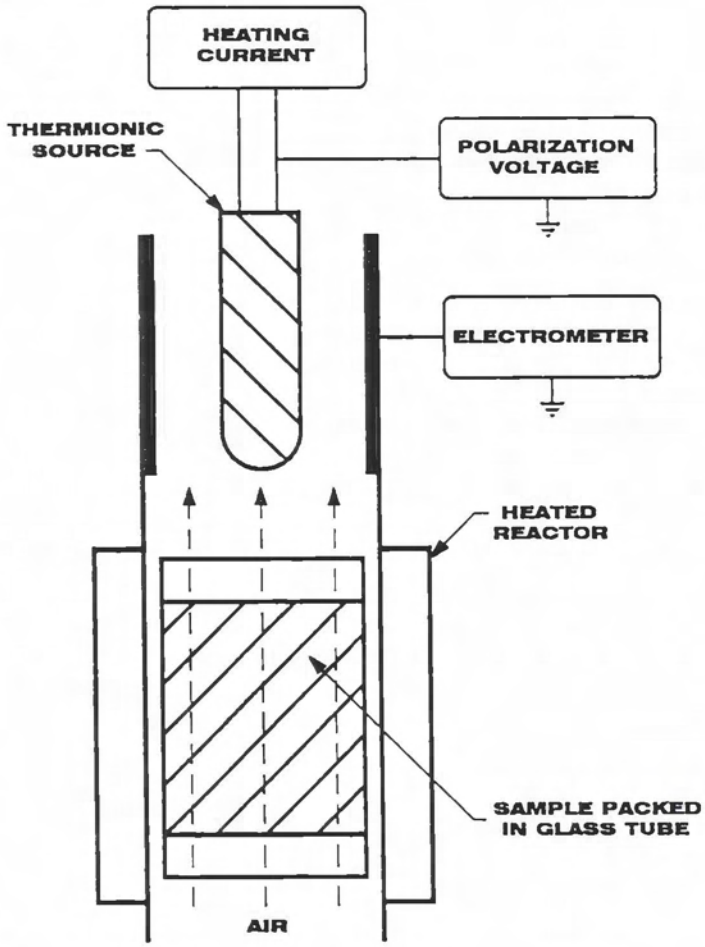
Response:

PTID response to P compounds is generally more than 10 times larger than the corresponding response of an NPD. However, the background and noise are also larger, so detectivity is comparable to an NPD (0.07 pg P/sec). The dynamic range of response of a PTID exceeds 5 orders of magnitude, and it has excellent selectivity vs. hydrocarbons, as well as vs. N, O, Cl, Br, S, and Si compounds.

RTIA: REACTOR THERMIONIC IONIZATION ANALYZER

Equipment:

RTIA modules are stand-alone units containing a thermionic ionization transducer preceded by a heated reactor chamber. Each module has a thermally insulated, temperature controlled (50-400°C) transducer and reactor, and supporting gas flow control elements or an air sample pump as needed. The transducer response is determined by the type of thermionic source used, and the type of gases supplied. Available modes include **TID-1-Air(N_2)**, **TID-3-Air(N_2)**, or **TID-2-H_2/Air** (i.e., NPD). TID-1-Air is an especially simple configuration in which the operating gas may be ambient air drawn in by a pump attached to the module exit port. Power and signal measurement for the transducer is provided by a stand-alone **CURRENT SUPPLY/ELECTROMETER** module.



Applications:

The RTIA selectively detects electronegative or NP vapors which thermally evolve from solid or liquid samples. Applications include a direct inject-vaporize procedure for liquid samples; a desorb-detect procedure for solid samples; and a trap-desorb-detect procedure for vapors in ambient air. The TID-1-Air mode detects nitrogen oxides and halogen/halogen oxides evolved in the thermal oxidation of food products, fabricating materials, oil bearing source rocks, and contaminated soil/water samples.

FID & HWCID & CFID: universal response to ALL ORGANICS

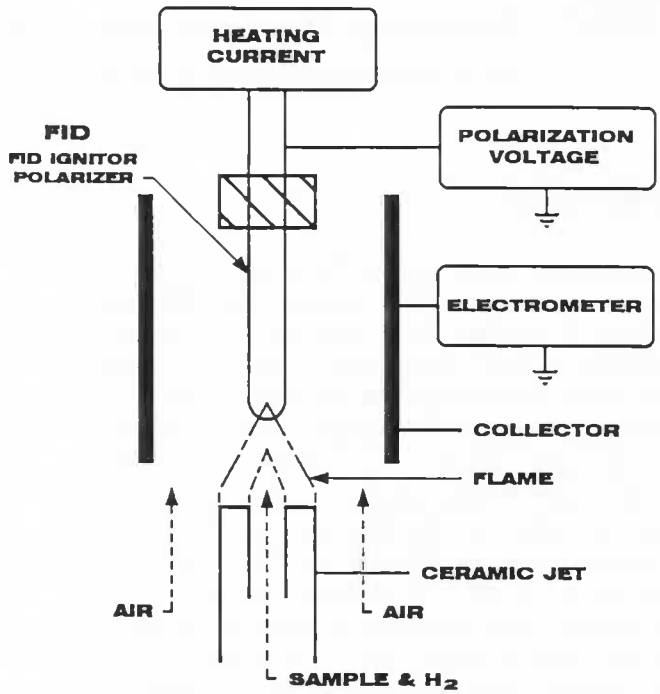
Equipment:

The FID mode uses an **FID Probe** consisting of a bare loop of wire. The Probe is mounted in a **TID/FID** tower which positions it in close proximity to an unpolarized flame jet. The flame jet in this detector is a high purity alumina ceramic (0.062 in. O.D. x 0.031 in. I.D.) which withstands long term operation without deteriorating oxidation, and which can operate at very high temperatures without excessive thermionic electron emission. The FID Probe functions as both flame ignitor and polarizer. H_2 and air are the detector gases, and a self-sustaining flame burns at the jet. The FID Probe is also used in an optional **FID Transducer/JET Assembly** for the second stage of a **Tandem TID** tower configuration. The FID Probe is also used in an exclusive **HWCID** (Hot Wire Combustion Ionization) detection mode to provide jet-less FID type responses using a **TID Transducer** second stage for the Tandem TID tower. In the HWCID, a flame-like environment is maintained by continuously supplying heating current to the probe wire. With standard DET electronics, the FID Probe is normally polarized at -45 Volts, and negative ions are collected. On some GCs, the FID Probe can also be connected to existing positive polarizing voltages in order to collect positive rather than negative ions.

For the **CFID** mode (Catalytic Flame Ionization), a CFID type thermionic source is used instead of the FID Probe. As in the FID, a self-sustaining flame burns at the jet. The CFID source is connected to polarizing and heating current electronics, so the source surface can be electrically heated as well as flame heated. The source in this mode serves the threefold purpose of flame ignitor, polarizer, and catalytic combustion modifier. The CFID source is typically polarized at -5 Volts, and negative ions are collected.

Principle:

Hydrogen-air flames are unique chemical environments characterized by high temperatures and high concentrations of radical or unstable chemical species such as H, O, and OH. Sample molecules are efficiently decomposed in such a reactive environment, and sample fragments are ionized in gas phase reactions with the flame radicals. For organic



samples, an important mechanism is the chemi-ionization reaction,

$$CH + O \Rightarrow CHO^+ + e^-,$$

where two neutral species combine to yield equal concentrations of positive and negative charged species in the gas phase. In addition to the gas phase ionization of an FID, the CFID provides a secondary thermionic ionization mechanism on the CFID source surface. The secondary mechanism selectively affects responses to compounds containing heteroatoms such as Cl and P. The relative magnitude of the secondary ionization is controlled by varying the heating current to the source.

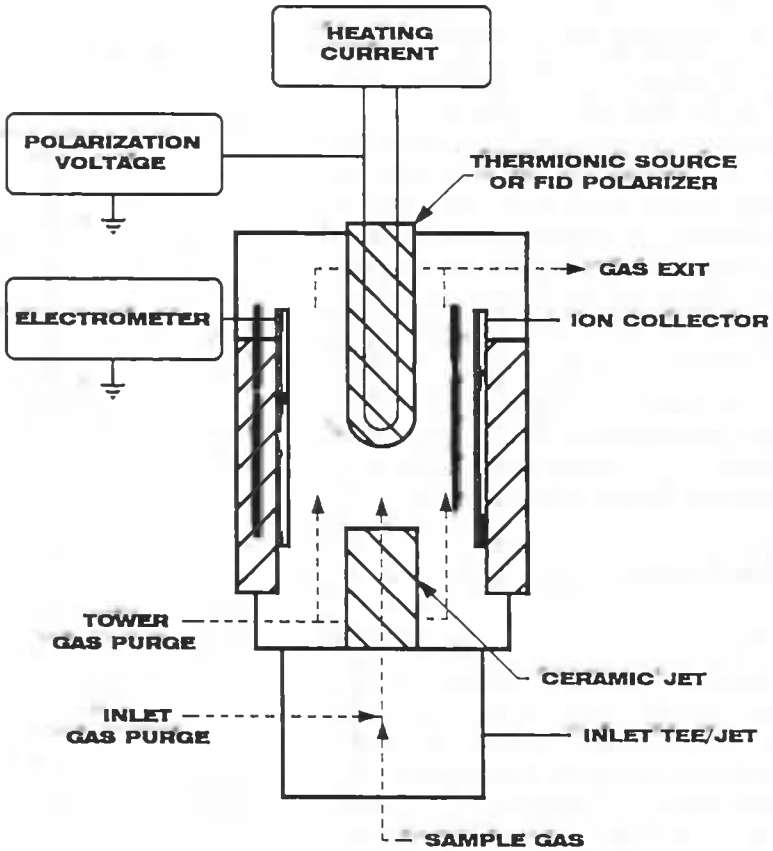
Response:

The FID responds to all organic compounds. In comparison to an FID, the HWCID provides a factor of 2 enhancement for aromatic hydrocarbons relative to alkane hydrocarbons. The HWCID sensitivity is about 100 times less than the FID, but its linearity at high sample concentrations is much better than the FID. By judicious adjustment of the electrical heating of the CFID source, it is possible in the CFID mode to achieve response factors for halogenates which are comparable to hydrocarbons.

TFID: THERMIONIC/FLAME IONIZATION DETECTOR

Equipment:

TFID modules are stand-alone units containing a GC type detector which operates according to the principles of thermionic surface ionization or flame ionization. Each module has a thermally insulated, temperature controlled (50 - 400°C) transducer equipped with a standard Swage type inlet fitting, and supporting gas flow control elements as needed. An air sample pump connected at the module exit port also suffices for the operating gas for some modes. The detector response is determined by the type of thermionic source/FID probe element used, and the type of gases supplied. Available selective modes of thermionic ionization detection include **TID-1-N_2(Air)**, **TID-3-N_2(Air)**, and **NPD**. Available flame ionization modes include a conventional **FID** and the **CFID**. Power and signal measurement for the transducer in the TFID module is provided by a second **CURRENT SUPPLY/ELECTROMETER** module.



Applications:

TFID modules are intended for use in screening sample gas streams evolved from Head Space Analyzers, Thermal Desorbers, Purge and Trap Instrumentation,Super Critical Fluid Extractors, Thermal Analysis Instruments, and any other sample gas generating equipment. When configured with an air pump, the TFID detects electronegatives like NO_2, HF, Cl_2, and I_2 (TID-1-Air mode), or acrylonitrile and methylamine (NPD) in air at ppb levels. The TFID is also a self-contained auxiliary detector system that can be coupled into GCs via heated transfer lines.

CHEMICAL DETECTION by DET

featuring novel applications of the principles of THERMIONIC SURFACE IONIZATION and FLAME IONIZATION

Selective Detection for GC
NPD - BEST N DETECTIVITY
(less than 70 femtograms N/sec)

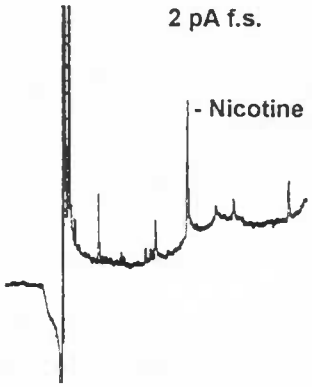
The combination of an Agilent 6890 NPD and a DET TID-4 ceramic ion source (bead) provides state-of-the-art N-selectivity for trace detection of drugs of abuse, pesticides, explosives, and pollutants.

The 6890 NPD hardware features a concentric cylinder ion source - collector electrode geometry for stream-lined gas flow and efficient ion collection. Similar DET equipment is available for HP5890, Varian 3400-3800, and SRI 8610 GC models.

600 femtograms Nicotine

TID-4 in 6890 NPD

2 pA f.s.



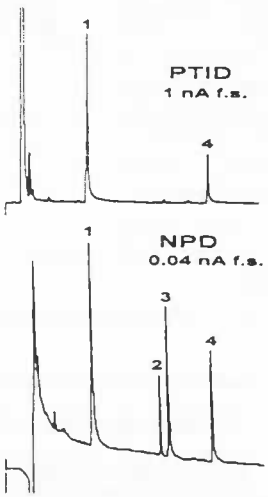
Selective Detection for GC
PHOSPHORUS COMPOUNDS
Very Big Signals with a New PTID

Pesticide Sample:
1-Mevinphos (P)
2-Trifluralin (N)
3-Simazine (N)
4-Methyl Parathion (NP)

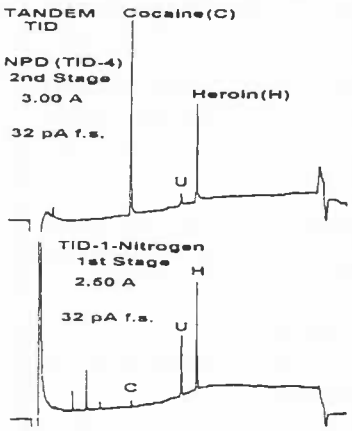
NPD detects both P and N. PTID detects only P with signals 10 times bigger than the NPD.

A Phosphorus Thermionic Ionization Detector (PTID) combines surface ionization principles with high flows of Hydrogen and Air for P/C selectivity of 100,000:1, P/N selectivity of 100:1, detectivity of 70 fg P/sec, and a dynamic response range more than 100,000.

NP pesticides 480 pg each



Tandem Thermionic Detection for GC
COCAINE - HEROIN



NPD and **TID-1** are two different modes of thermionic ionization.

Ceramic **TID-1** surface operates at 400-600°C in a gas environment of Nitrogen or Air. **TID-1** is non-destructive so it can be combined in series with another detector like the **NPD**.

Ceramic **NPD** surface operates at 600-800°C in an ignited, dilute mix of Hydrogen in Air.

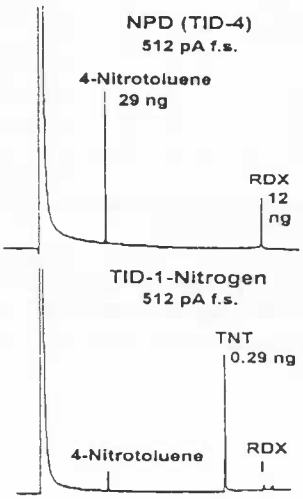
Sample analyzed: NPD detects both Cocaine (C) and Heroin (H). TID-1 detects Heroin and Heroin impurity (U). Tandem combination gives simultaneous TID-1 and NPD signals for each sample injection.

- Femtogram GC Detection -
NITRO-COMPOUNDS like TNT, 2,4-Dinitrotoluene, DNPH-Aldehydes, Methyl Parathion, 4-Nitrophenol, etc.

Unique **TID-1** surface ionization provides better selectivity than ECD and NPD, and needs only Air or N_2 as the detector gas with no requirement for high purity.

TID-1 detection is an inexpensive modification of Agilent 6890 NPD equipment. DET NPD/TID-1 equipment is also available to fit HP 5890, Varian 3400-3800, and SRI 8610 GC models.

EXPLOSIVES Sample: NPD has a big response to RDX and 4-Nitrotoluene. TID-1 has a much larger response to TNT.

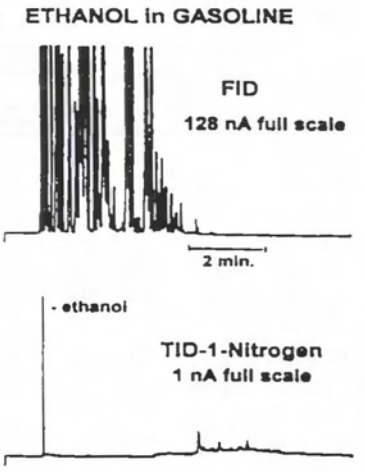


TID-1 and TID-3 modes of detection are simple, inexpensive modifications of Agilent 6890 or DET NPD equipment. Both modes can operate with a detector gas environment of either Nitrogen or Air (no Hydrogen required), with the choice of N_2 or Air depending on the selectivity required. The ceramic coated TID-1 ionization surface is electrically heated to operating temperatures in the range of 400 - 600°C, while the ceramic TID-3 surface operates at 600 - 800°C. Both ion source types are polarized at - 45 Volts with respect to a surrounding ion collector. Ion source polarization and heating power are provided by a stand-alone DET Current Supply module. TID-1 and TID-3 ion source configurations fit into the Agilent 6890 NPD equipment and into DET NPD equipment designed to mount onto HP 5890, SRI 8610, or Varian GCs. Negative ion detection signals can be measured with the Agilent 6890 NPD electrometer, Varian TSD electrometer, SRI FID/NPD electrometer, or with a DET electrometer.

Oxygenate Selective Detection for GC
ETHANOL in GASOLINE

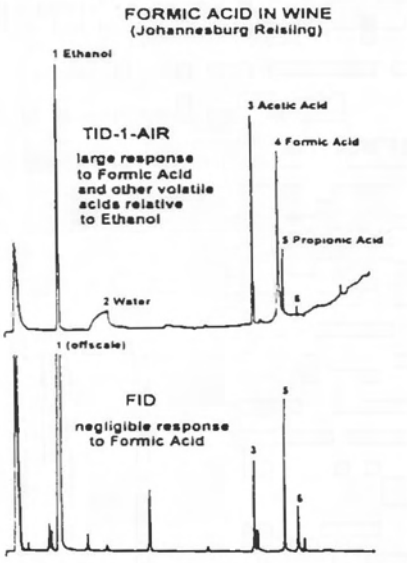
Negative ionization on a ceramic TID-1 surface detects Oxygenates with good selectivity vs. Hydrocarbons.

TID-1 detection provides a simple analysis for the Ethanol additive in gasoline. Only a single gas supply (Nitrogen) suffices for both GC carrier and detector gases. Short analysis times can be used because Ethanol is easily detected amidst many overlapping Hydrocarbon components. TID-1 also detects **Phenols, Glycols,** and other Oxygenated compounds.



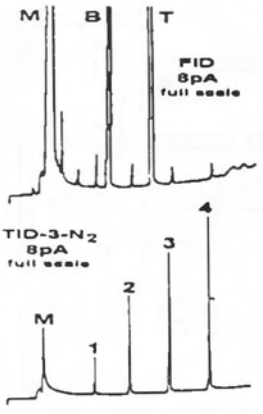
Oxygenate Selective Detection for GC
CARBOXYLIC ACIDS

TID-1 surface ionization with an Air detector gas gives big signals for **Carboxylic Acids** relative to other Oxygenates like Alcohols. TID-1 detection includes **Formic Acid** which is not detected by an FID. TID-1 detection is also **non-destructive** so component aromas can be sensed at the detector exit. H_2O is also detectable to ppm levels



Selective Detection for GC
TRIHALOMETHANES

TID-3 surface catalyzed negative ionization process

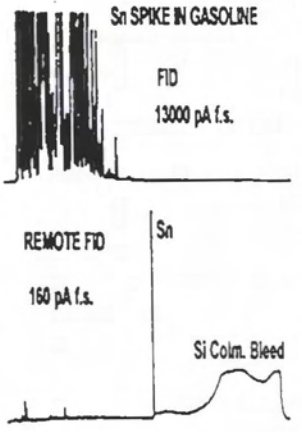


Volatile HALOGENATES detected with a sensitivity of 1 pg/sec, selectivity of 100,000:1 vs. hydrocarbons, and linear response exceeding a range of 10,000 in sample weight.

Unlike other halogen detectors, TID-3 response to Br is significantly more than Cl. Detector gas may be Nitrogen or Air with no requirement for ultra high purity. This detector is much easier and less costly to operate and maintain than an Electrolytic Conductivity Detector.

Sample analyzed:
640 pg each: 1=$CHCl_3$ 2=$CHCl_2Br$ 3=$CHClBr_2$ 4=$CHBr_3$
47,000 pg each: B=benzene T=toluene
2,500,000 pg: M=methanol Solvent: water

Pb – Sn – P – Si
(Lead, Tin, Phosphorus, Silicon)
selective detection with a DET innovation
Organically-Fueled Remote FID



A polarizer and ion collector located several centimeters downstream of a flame jet detect long-lived ion species that originate in a flame fueled by H_2 - CH_4 - Air. Ionization from Hydrocarbon combustion at the jet dissipates before reaching the downstream collector.

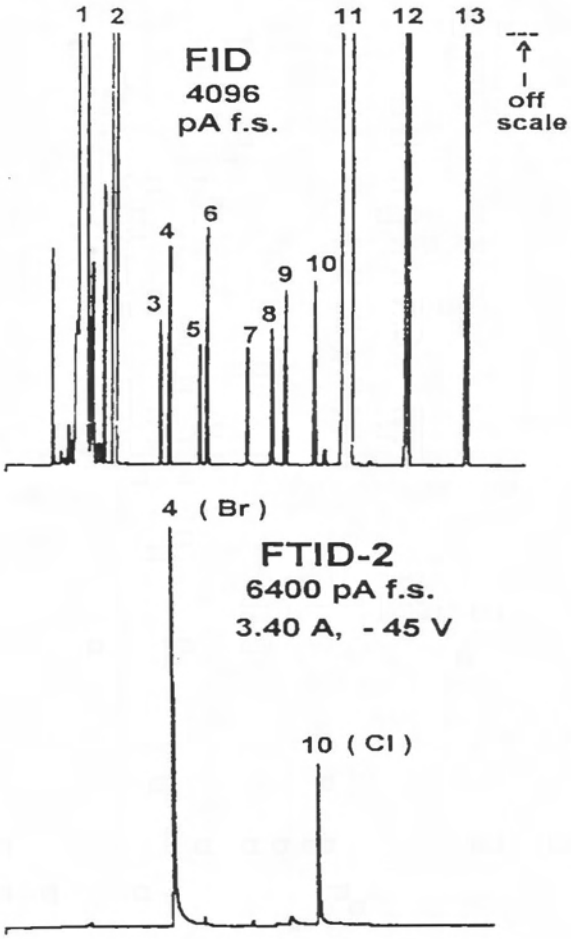
Detectivity of 1 pg/sec for Pb, Sn, P with a selectivity of 500,000:1 versus Carbon.

Sample:
12 ppm tetrabutyltin in gasoline

FTID-2

(Flame Thermionic Ionization)

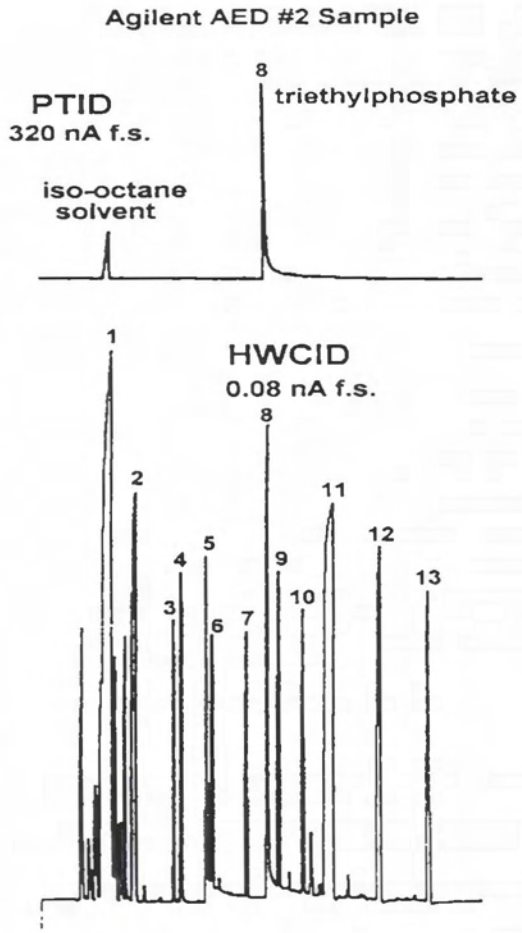
Halogen Selective



PTID

(Phosphorus Thermionic Ionization)

Phosphorus Selective



Agilent AED test sample #2 components: 1=iso-octane solvent; 2=4.04% n–octane; 3=0.07% 4-fluoroanisole; 4=0.07% 1-bromohexane; 5=0.05% tetraethyl orthosilicate; 6=0.05% n–decane (perdeuterated); 7=0.07% nitrobenzene; 8=0.06% triethyl phosphate; 9=0.05% tert-butyl disulfide; 10=0.08% 1,2,4-trichlorobenzene; 11=4.3% n–dodecane; 12=0.43% n–tridecane; 13=0.13% n-tetradecane.

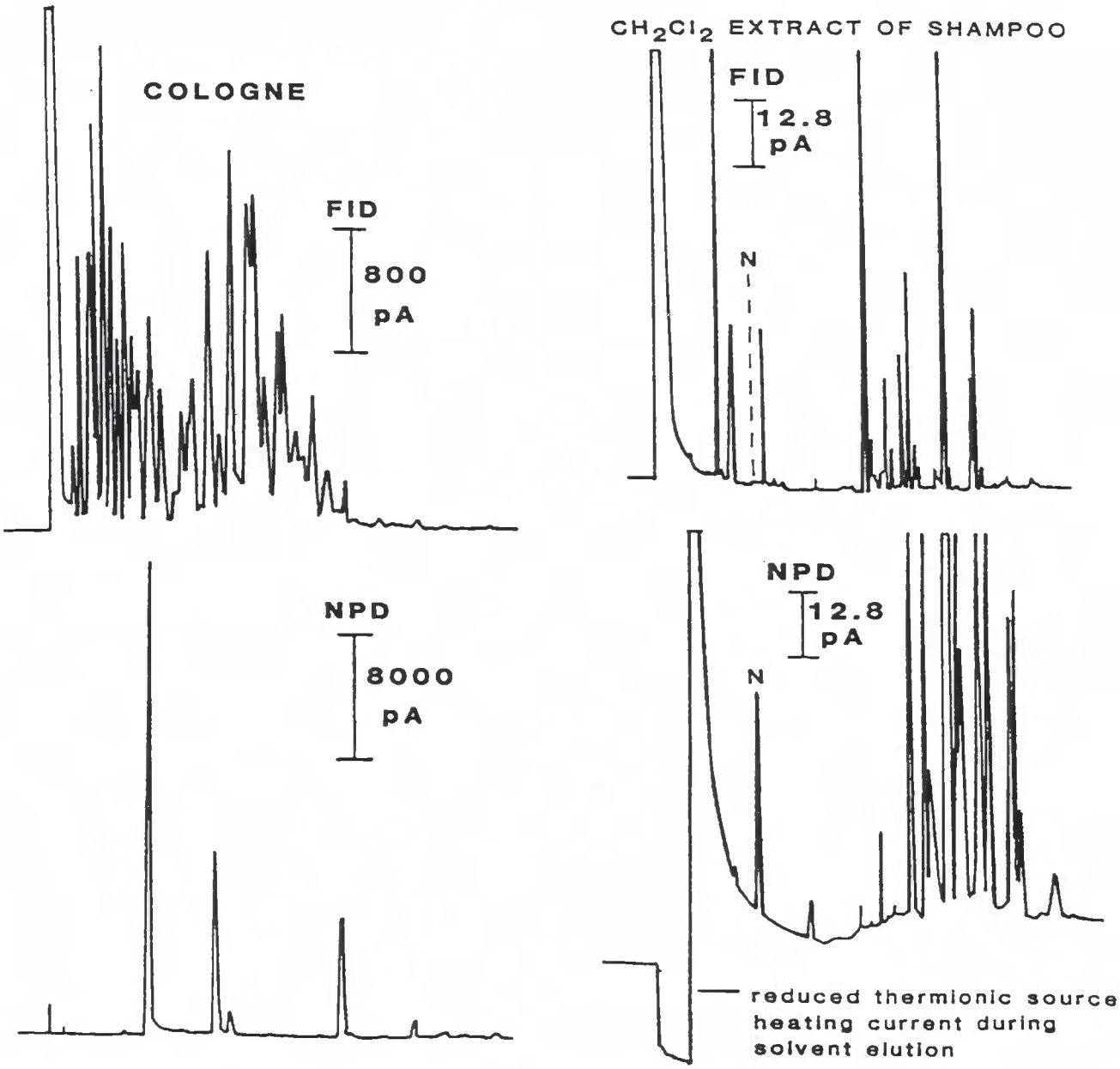
FTID Principle of Detection: Samples combusted in a H_2-CH_4-Air flame. Electronegative combustion products re-ionized by thermionic surface ionization downstream of the flame.

PTID Principle of Detection: Samples decompose in an ignited H_2-Air chemical boundary layer around a hot thermionic surface. High H_2 and Air flows suppress N response and provide very large P signals.

DET
innovations in chemical detection

CHROMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

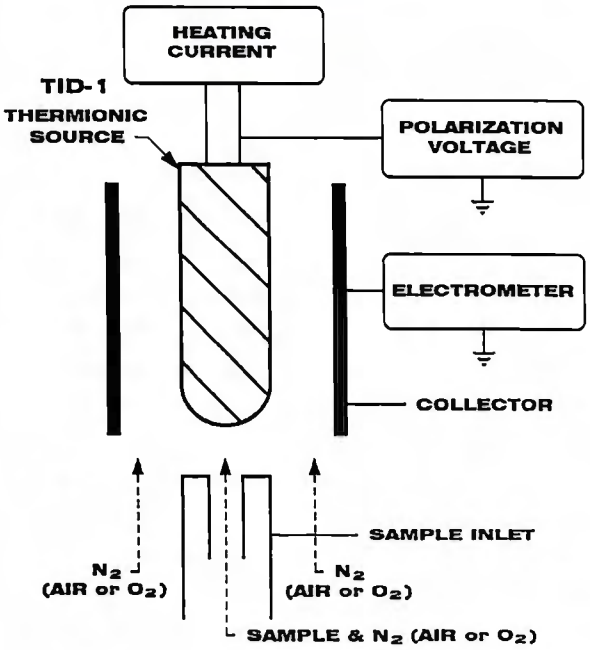
NITROGEN-PHOSPHORUS SELECTIVE DETECTION from DET



Compared to FID analyses of complex samples, an NPD provides both selectivity and detectivity advantages for trace N and P constituents. Selectivity allows shorter analysis times because undetected sample matrix components do not need to be well resolved chromatographically.

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

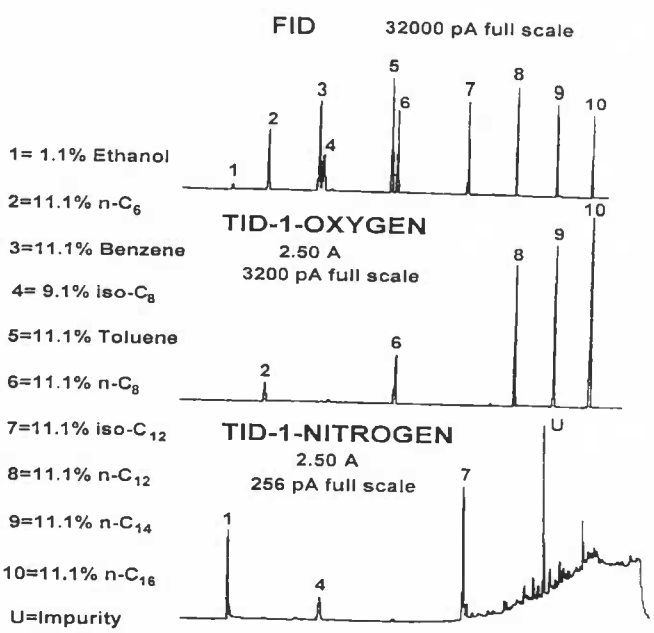
TID-1 Thermionic Surface Ionization is a relatively simple Gas Chromatography detection method that provides selective responses and chromatographic peak patterns quite different than any other type GC detector. A TID-1 detector is comprised of a 1/16 inch diameter ceramic coated ionization source optimally 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 NO_2 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.

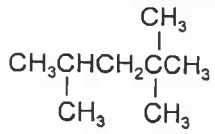
TID-1 detection has also been implemented on both Thermo Scientific and SRI Instruments GC models, again by substituting a TID-1 ion source into NPD equipment and supplying the appropriate detector gases. However, the original detector hardware structures on both the Thermo and SRI GC models are not 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

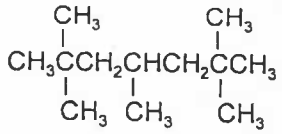
n –OCTANE
$CH_3(CH_2)_6CH_3$

iso-OCTANE
(2,2,4-TRIMETHYLPENTANE)

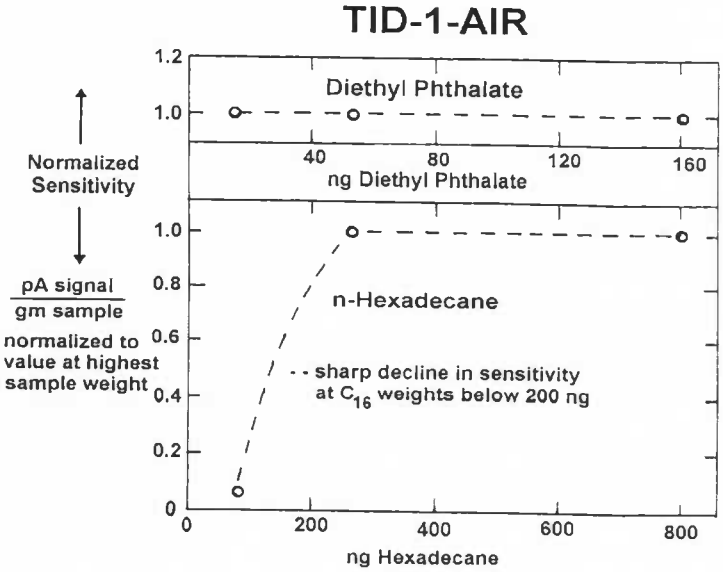


n–DODECANE
$CH_3(CH_2)_{10}CH_3$

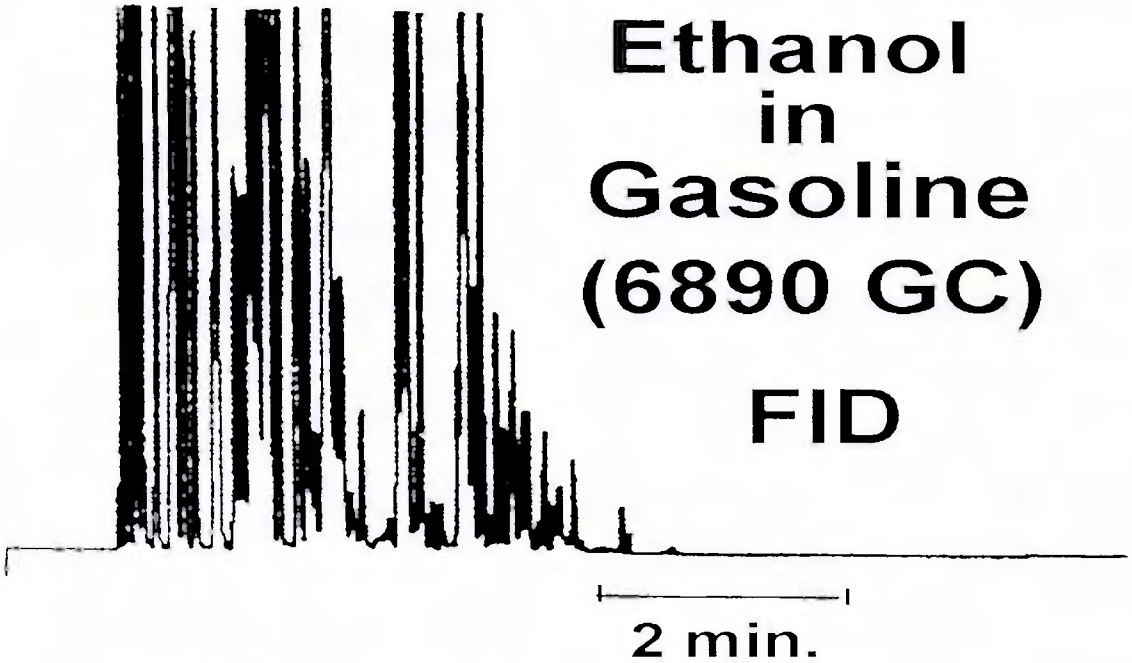
iso-DODECANE
(2,2,4,6,6-PENTAMETHYLHEPTANE)

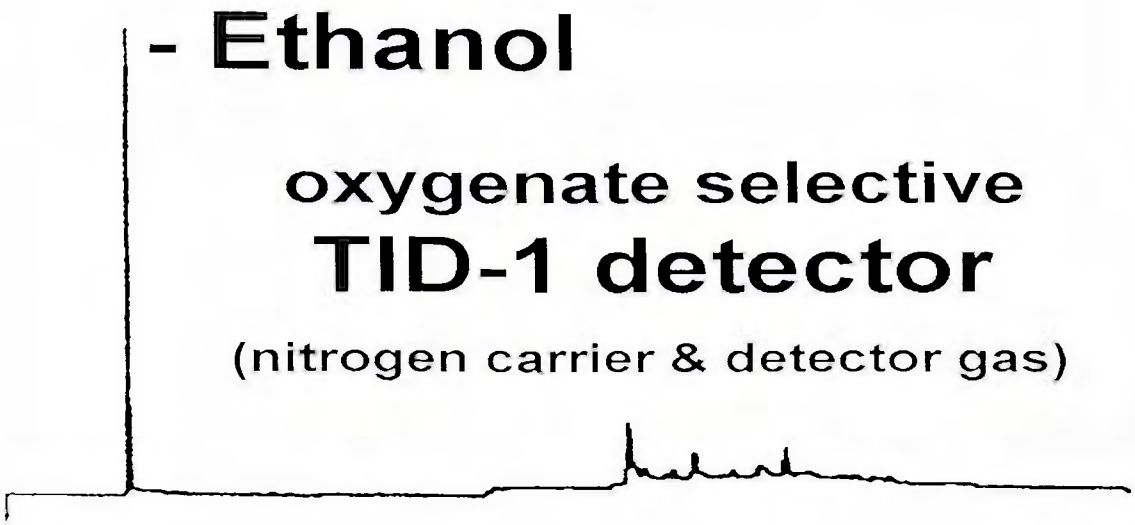


This sample illustrates the basic TID-1 response to high concentrations of Hydrocarbons. In a detector gas environment containing Oxygen, TID-1 response increased in magnitude correlated with the number of Methylene (CH_2) functional groups in linear chain Alkanes. In an inert detector gas of Nitrogen, TID-1 response correlated with the number of branched Methyl (CH_3) 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 m agnified 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 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.

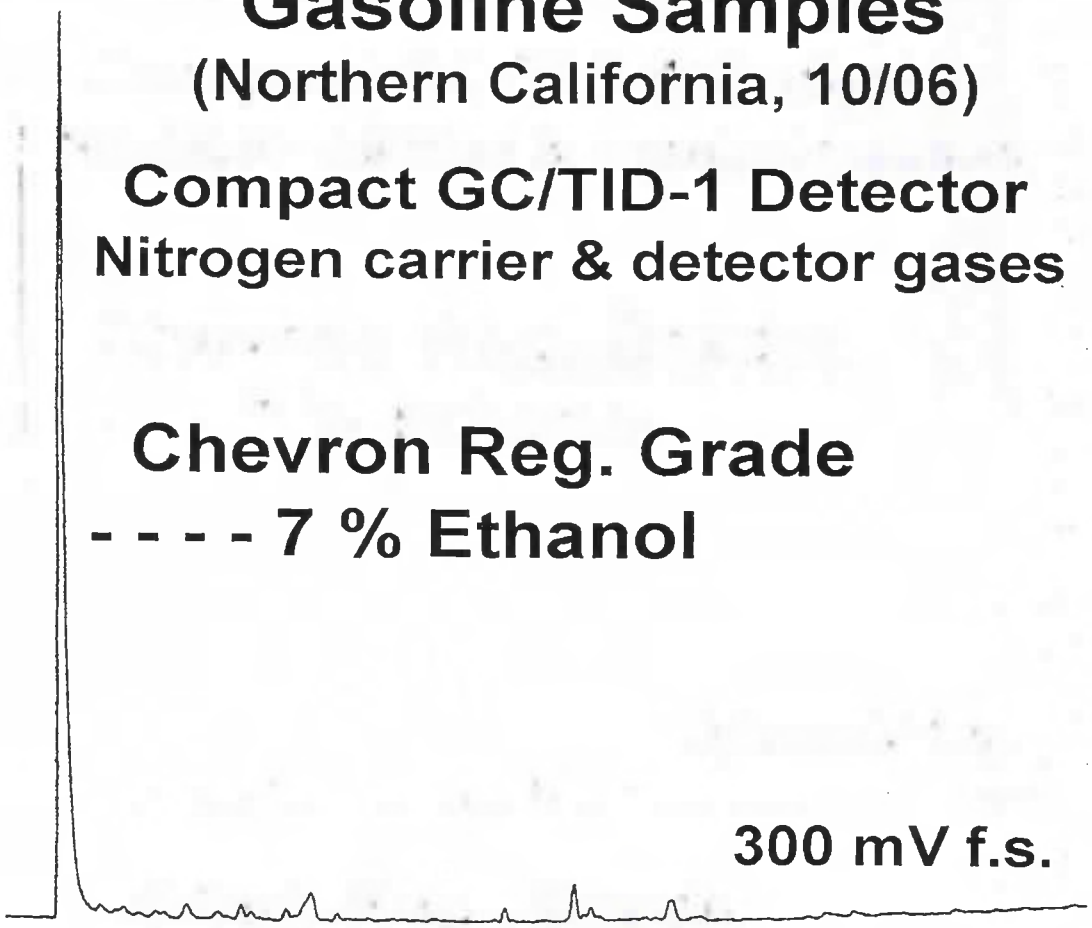


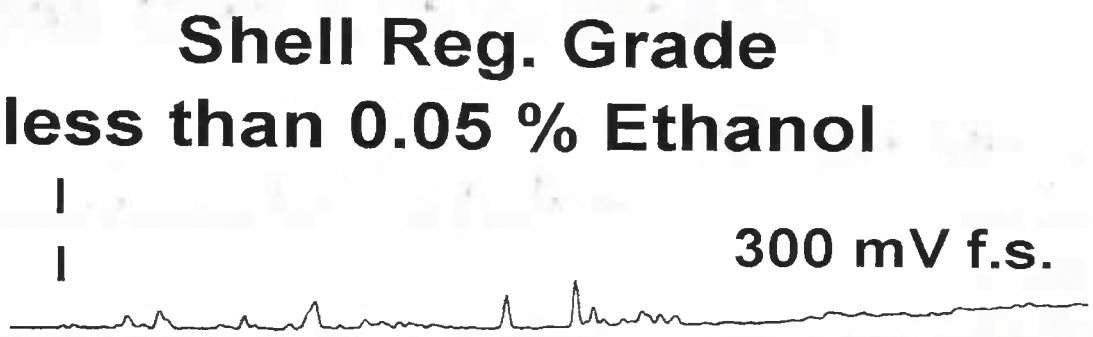


Selective detection of Ethanol in Gasoline using TID-1 surface ionization in a detector gas environment of Nitrogen. This is a signature chromatogram demonstrating how a selective detector can greatly simplify a chemical analysis. Only a single Nitrogen gas is required for both GC carrier and detector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

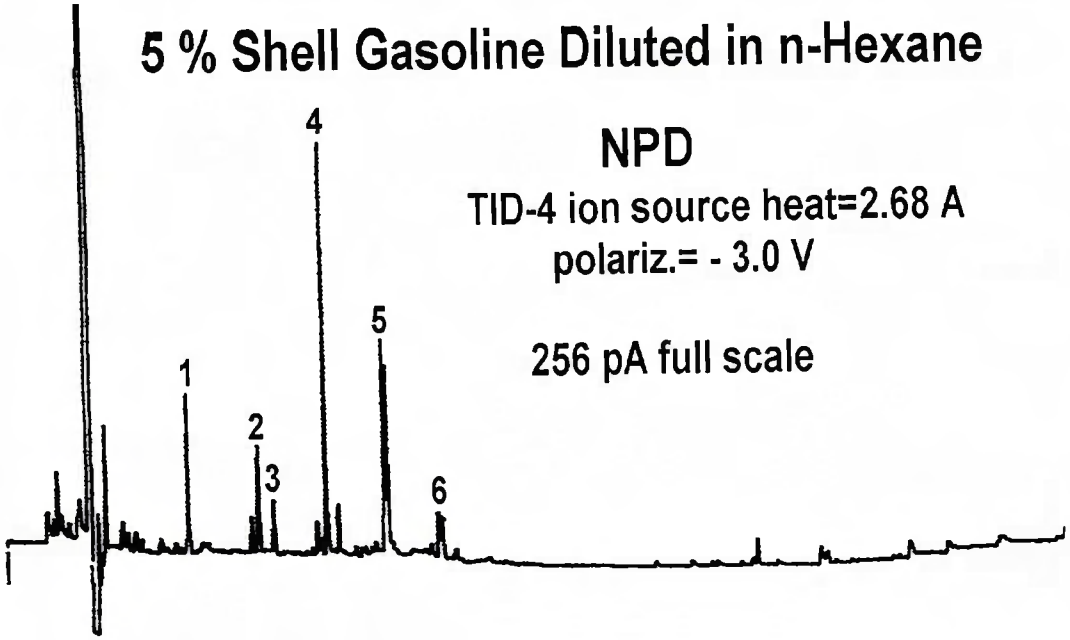
Gasoline Samples
(Northern California, 10/06)

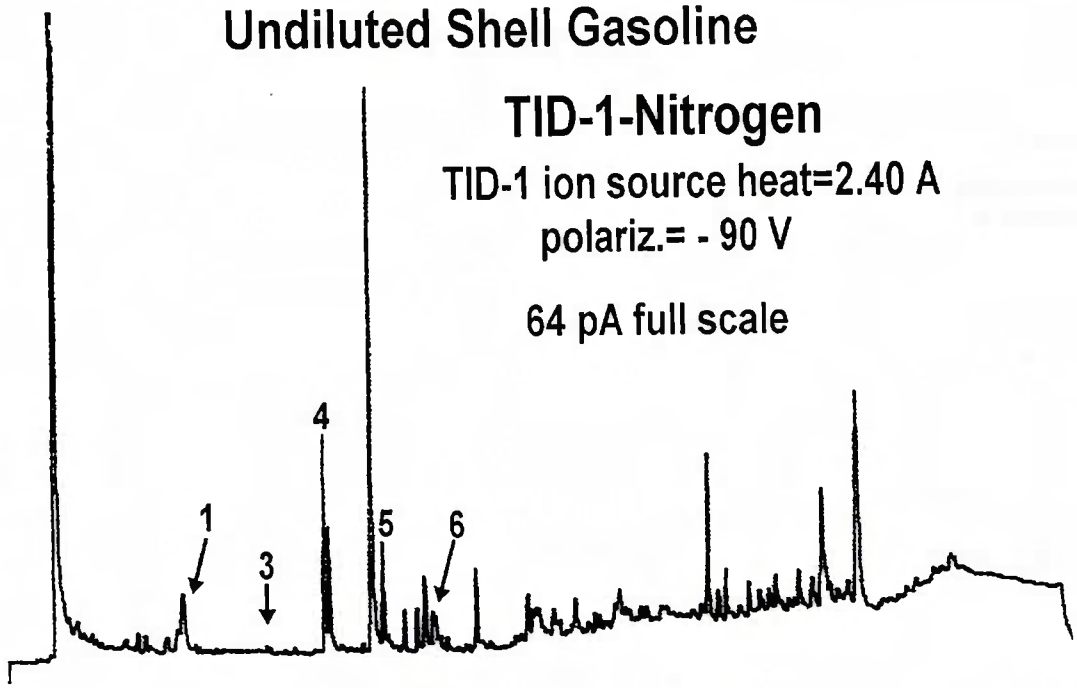
Compact GC/TID-1 Detector
Nitrogen carrier & detector gases





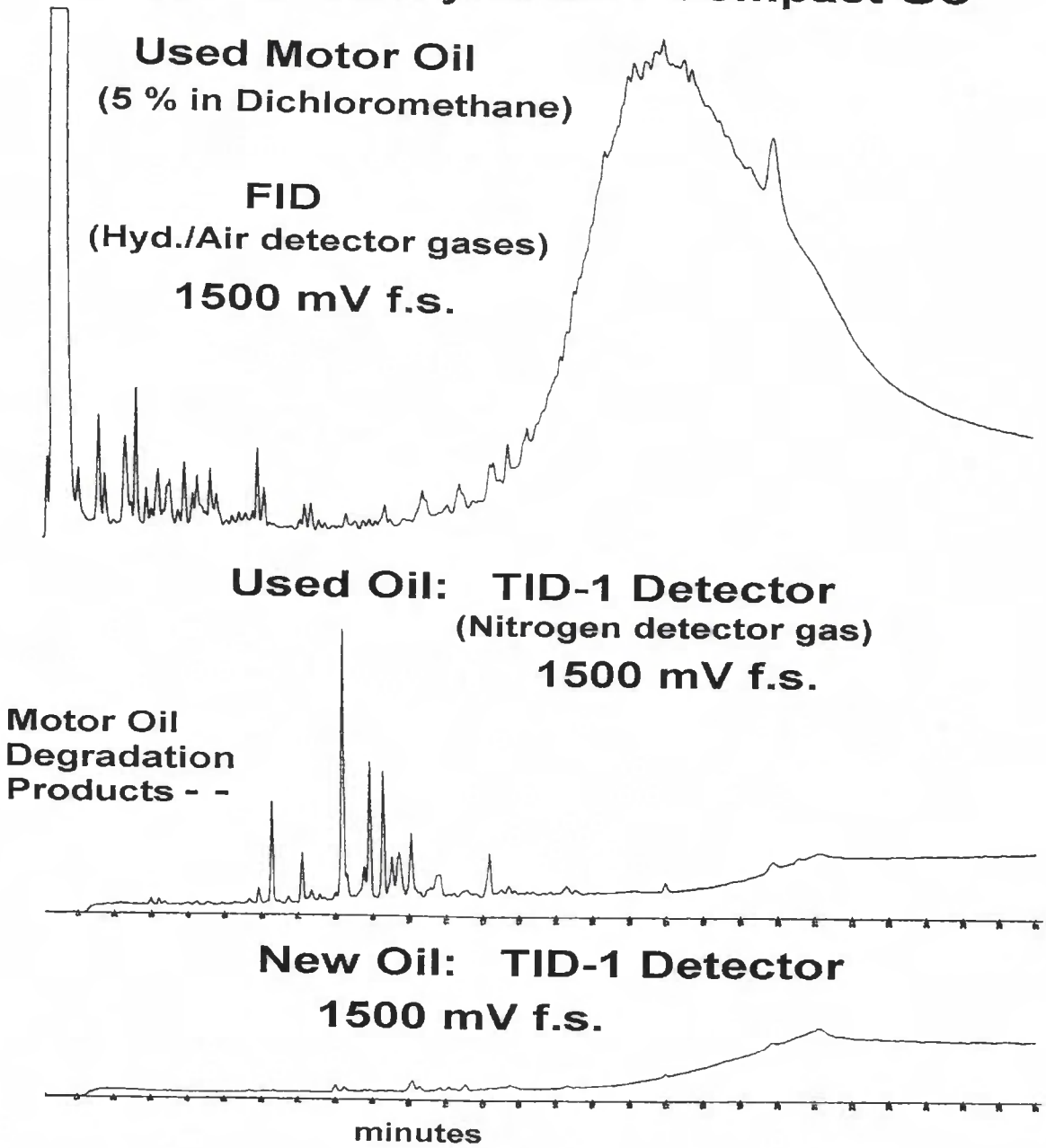
2006 Gasoline samples. Chevron had Ethanol additive, while Shell did not. Hydrocarbon discrimination was sufficient to determine that there was no peak at Ethanol retention time corresponding to 0.05 % or larger Ethanol.





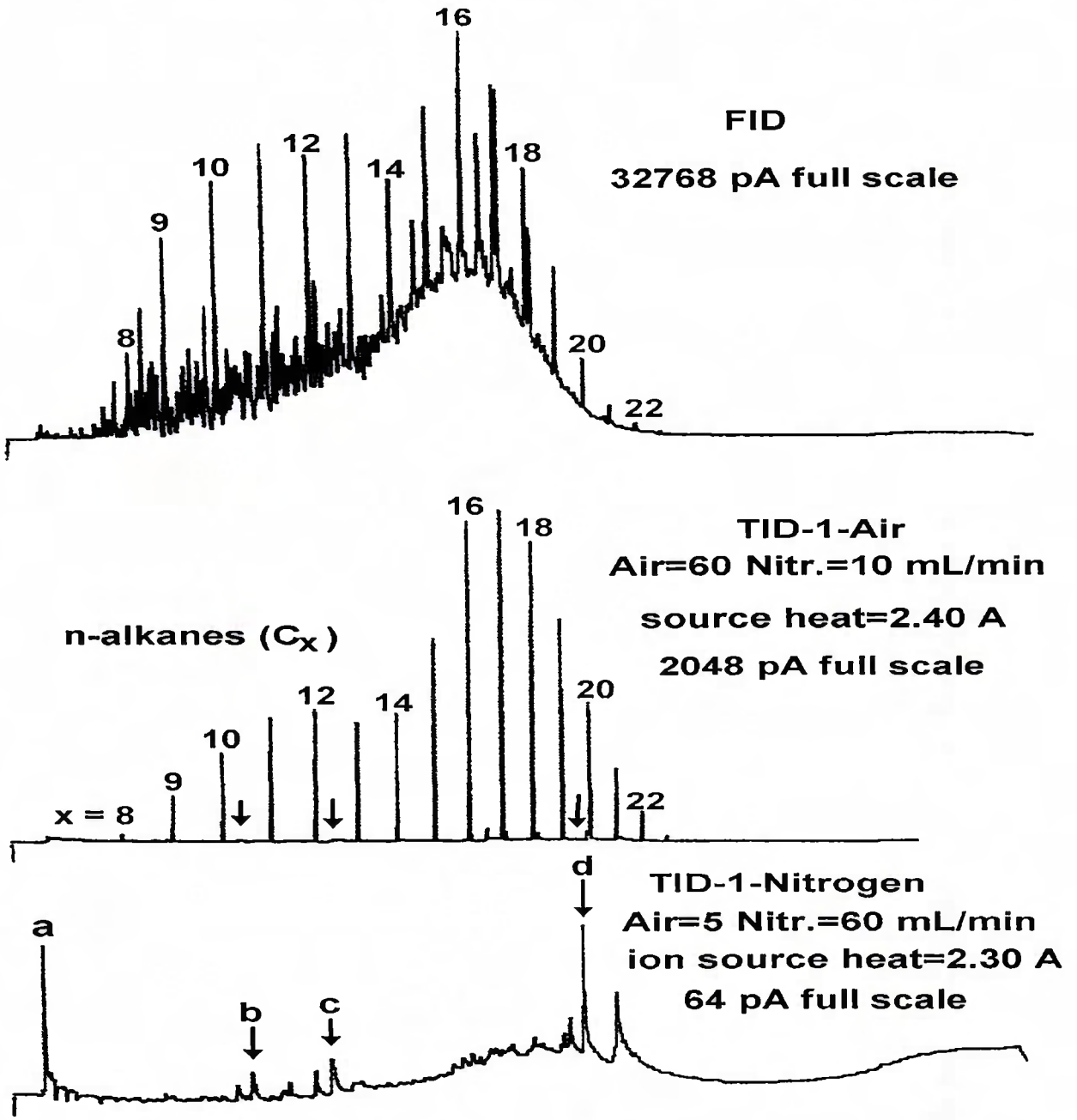
NPD detection of Nitrogen containing detergents added to gasoline - dilution of sample minimizes interferences from gasoline Hydrocarbons. TID-1 detection provides a different gasoline fingerprint. Thermo GC.

Motor Oil Analysis on a Compact GC

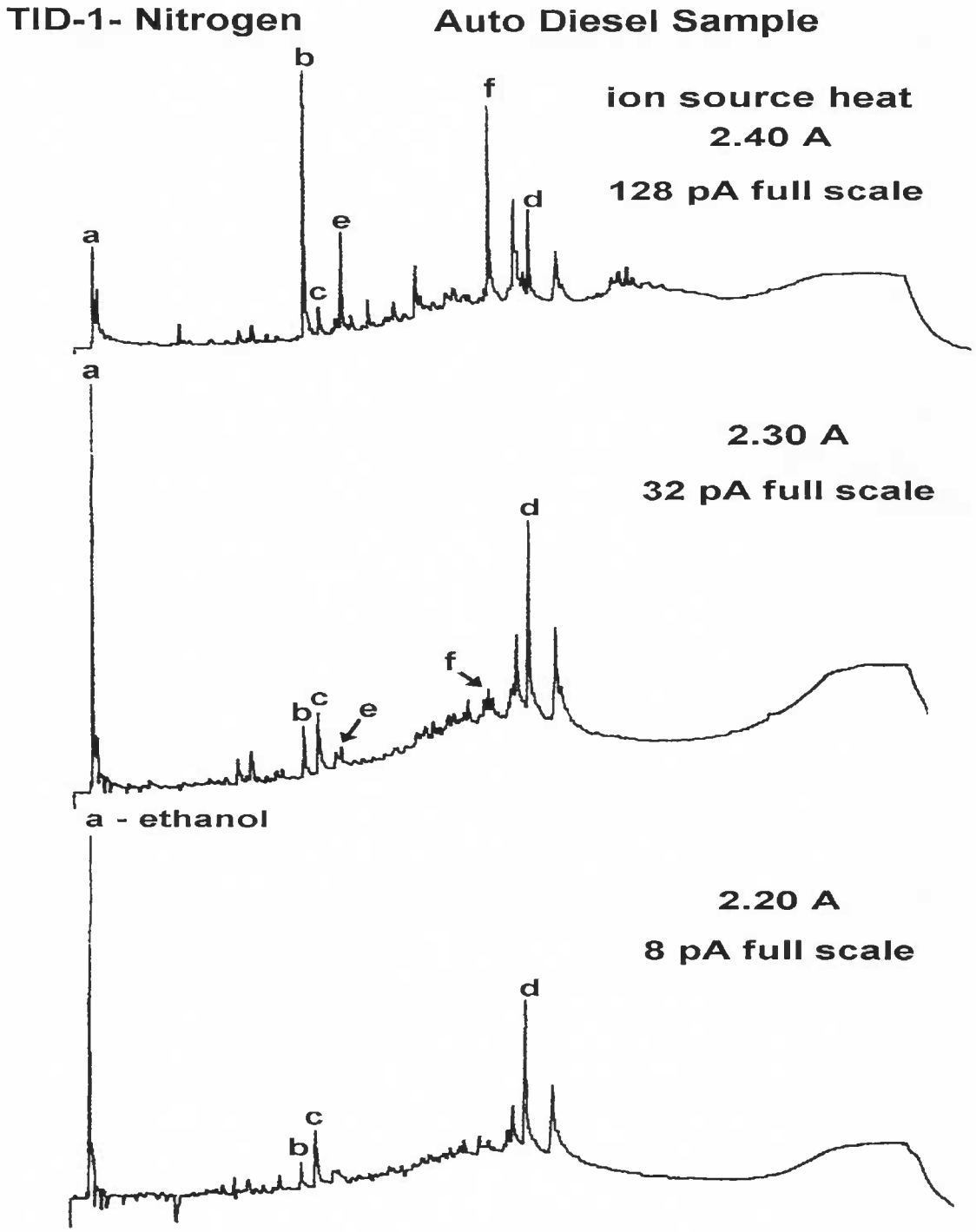


Selective TID-1 ionization in a Nitrogen detector gas environment reveals motor oil degradation products that build up with time as the oil is used. TID-1 monitoring of car oil vs. use can be very simple - take oil drop from car dipstick, dilute 1:3 in n–Hexane, and inject into GC. These data were obtained 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.)

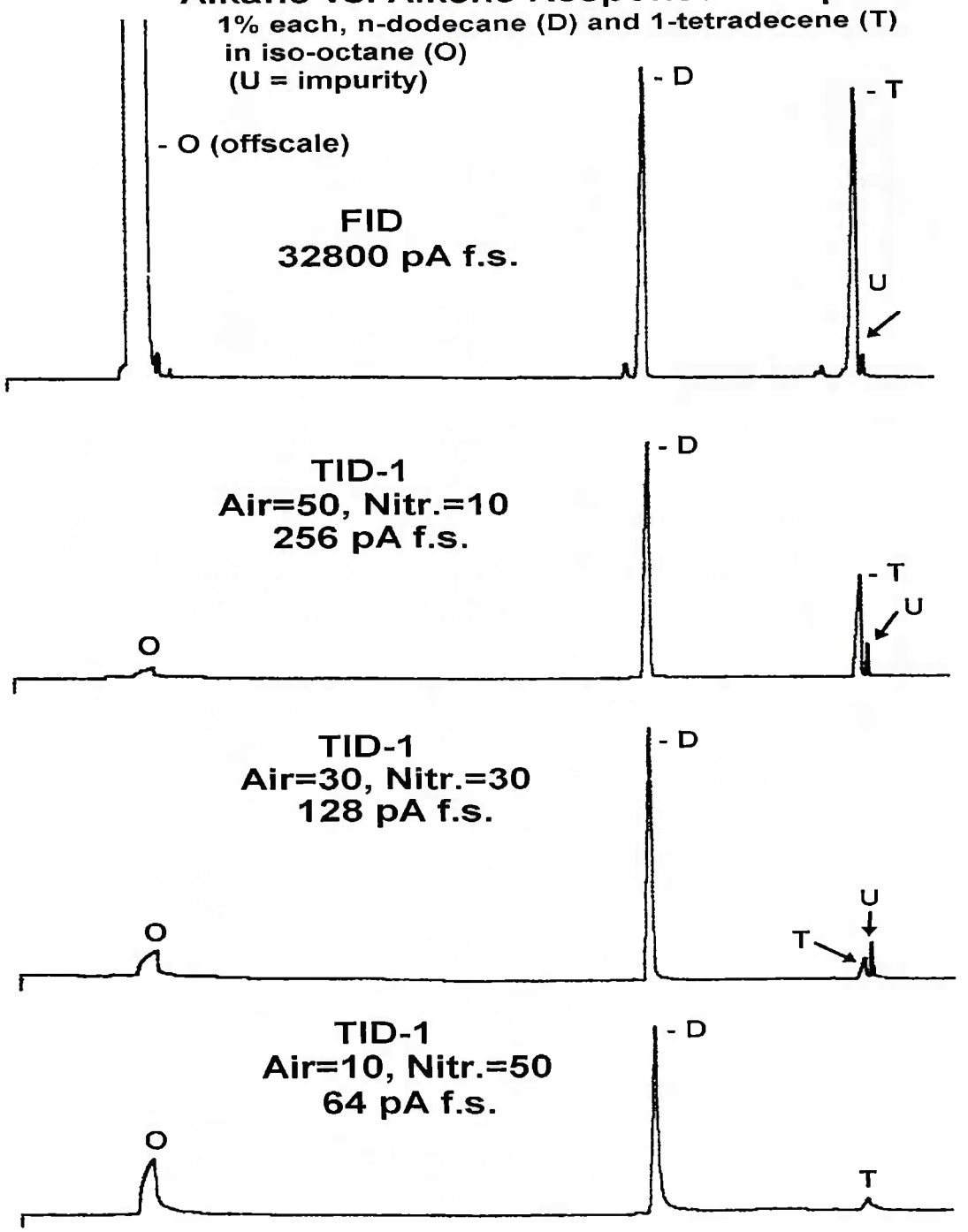


TID-1-Air selectively detected the linear Alkanes. Peak "a" in the TID-1-Nitrogen chromatogram was Ethanol, but other peaks not yet identified.
Agilent 6890 GC. TID data from 6890 NPD equipment modified with DET TID-1 Ion Source and stand-alone DET Current Supply.



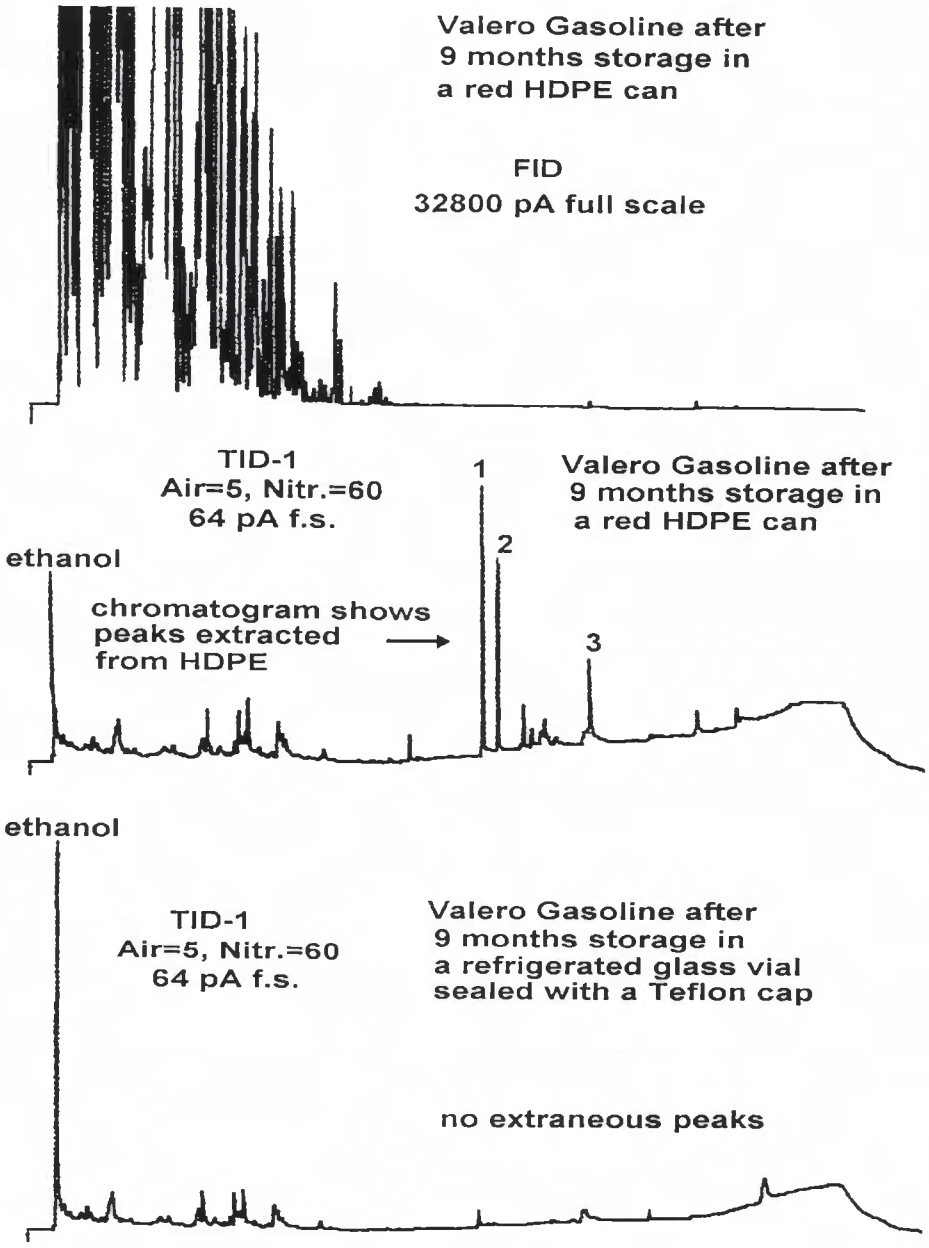
Undiluted Auto Diesel Sample (Valero, 04/09, N. Calif.). Agilent 6890 NPD with DET TID-1 Ion Source and DET Current Supply and Nitrogen detector gas. Data show how chromatogram peak patterns change with increasing ion source temperature.

Alkane vs. Alkene Response Comparison

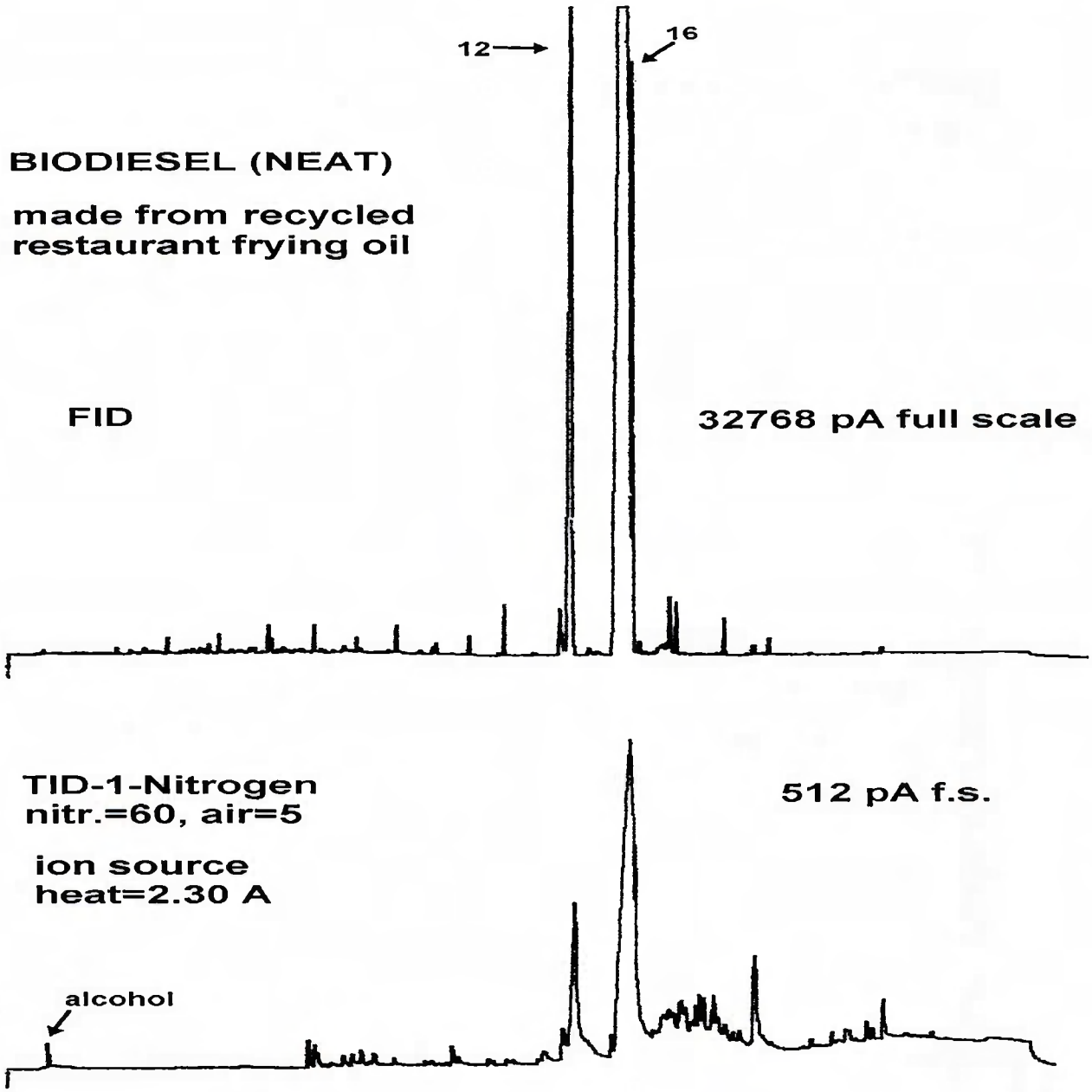


In a detector gas environment containing Oxygen, TID-1 ionization responds to CH_2 functional groups in high concentrations of linear Alkanes, but has significantly lower response to linear Alkenes which have a carbon double bond in addition to CH_2 groups.

Gasoline Extraction of Storage Container Constituents

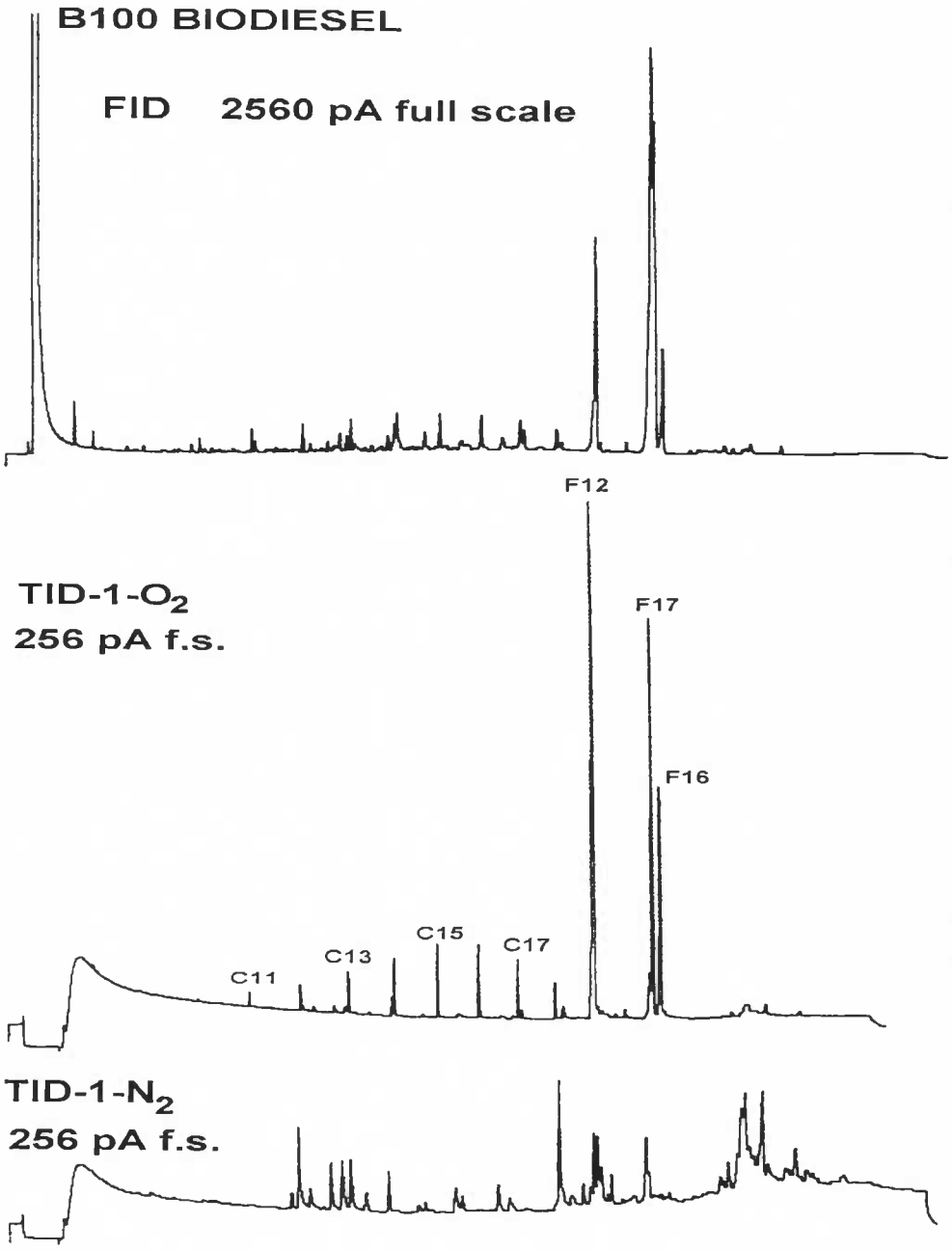


In a detector gas environment of predominantly Nitrogen, excellent Hydrocarbon discrimination of TID-1 ionization allows Gasoline to be used as an extracting solvent. TID-1 chromatogram of Gasoline stored in a commonly used HDPE can exhibits peaks extracted from the container. Retention time of peak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

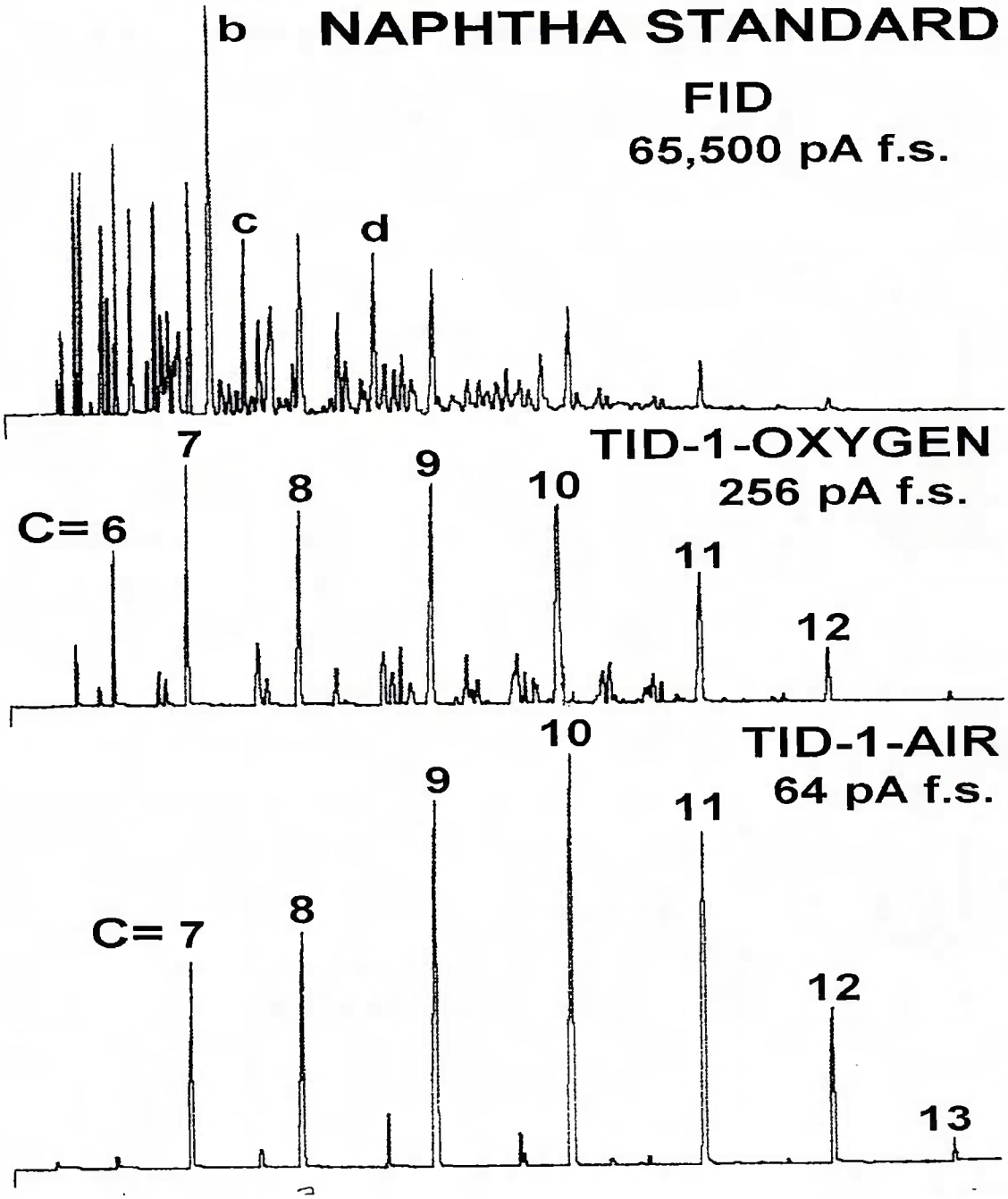


UNDILUTED (NEAT) BIODIESEL SAMPLE

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.

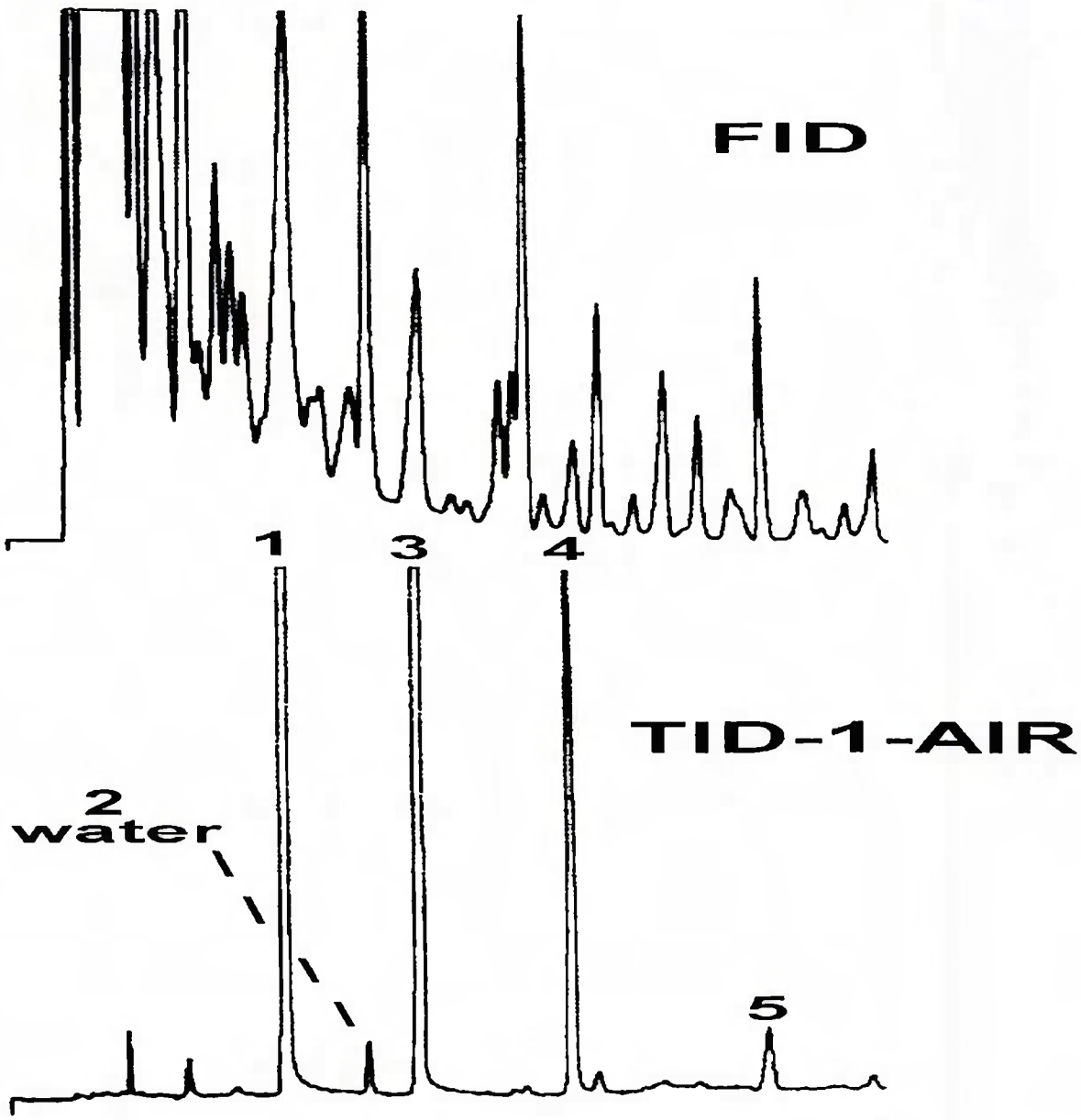


Comparison of FID and TID chromatograms of a 20mg/mL sample of B100 Biodiesel in a Methylene Chloride solvent. Cx nomenclature refers to linear Alkanes, F12, F16, and F17 refer to Palmitic, Stearic, and Oleic FAMes, respectively. TID-1-N_2 peaks are not yet identified.



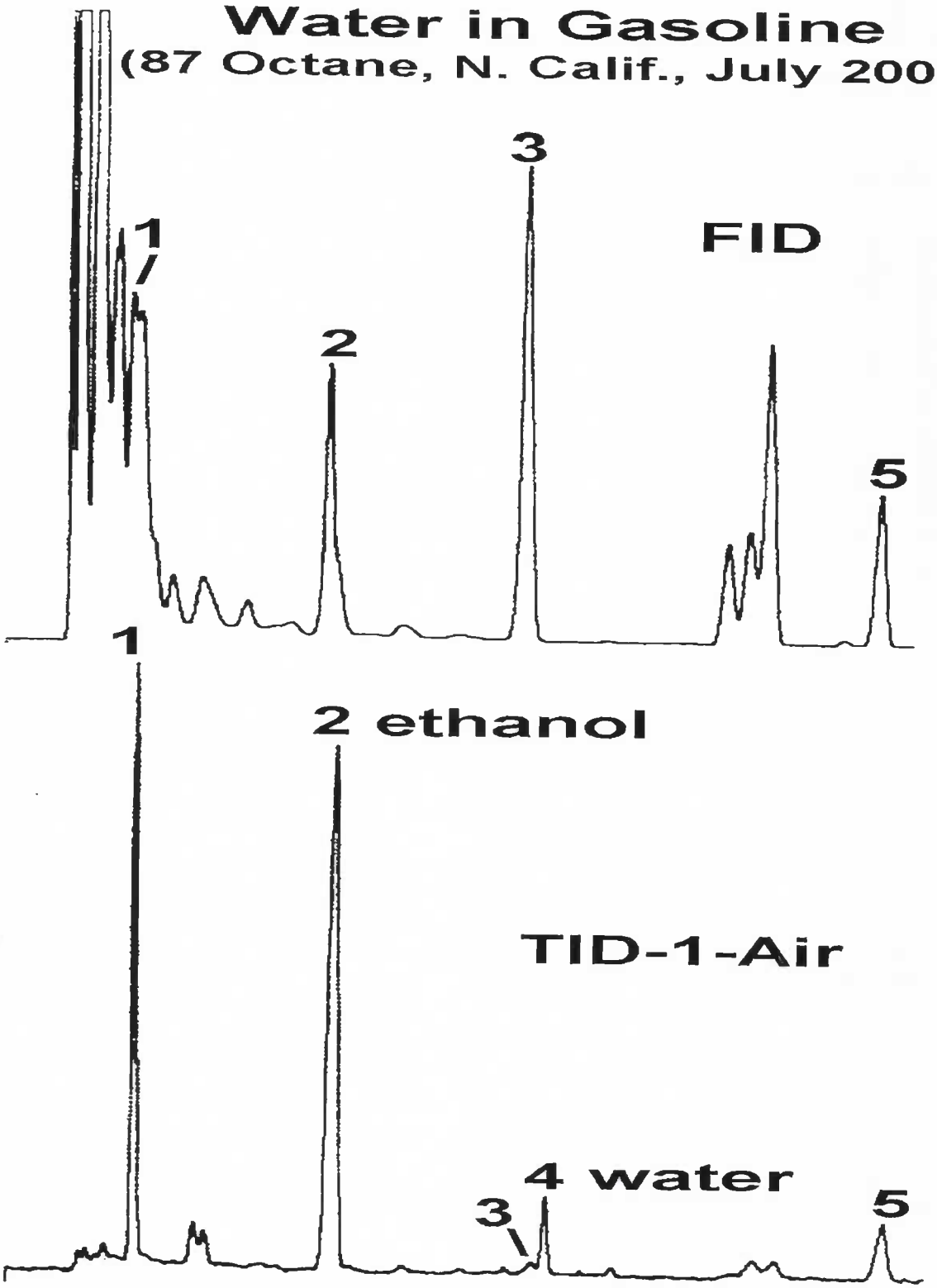
Agilent 6890 GC. TID-1 ion source in 6890 NPD hardware with DET Current Supply for ion source power. C=x indicates Carbon number in linear Alkanes; b = Methyl-cyclohexane & cis-1,2-Dimethylcyclopentane; c = Toluene; d = m-Xylene & p-Xylene.

NAPHTHA STANDARD

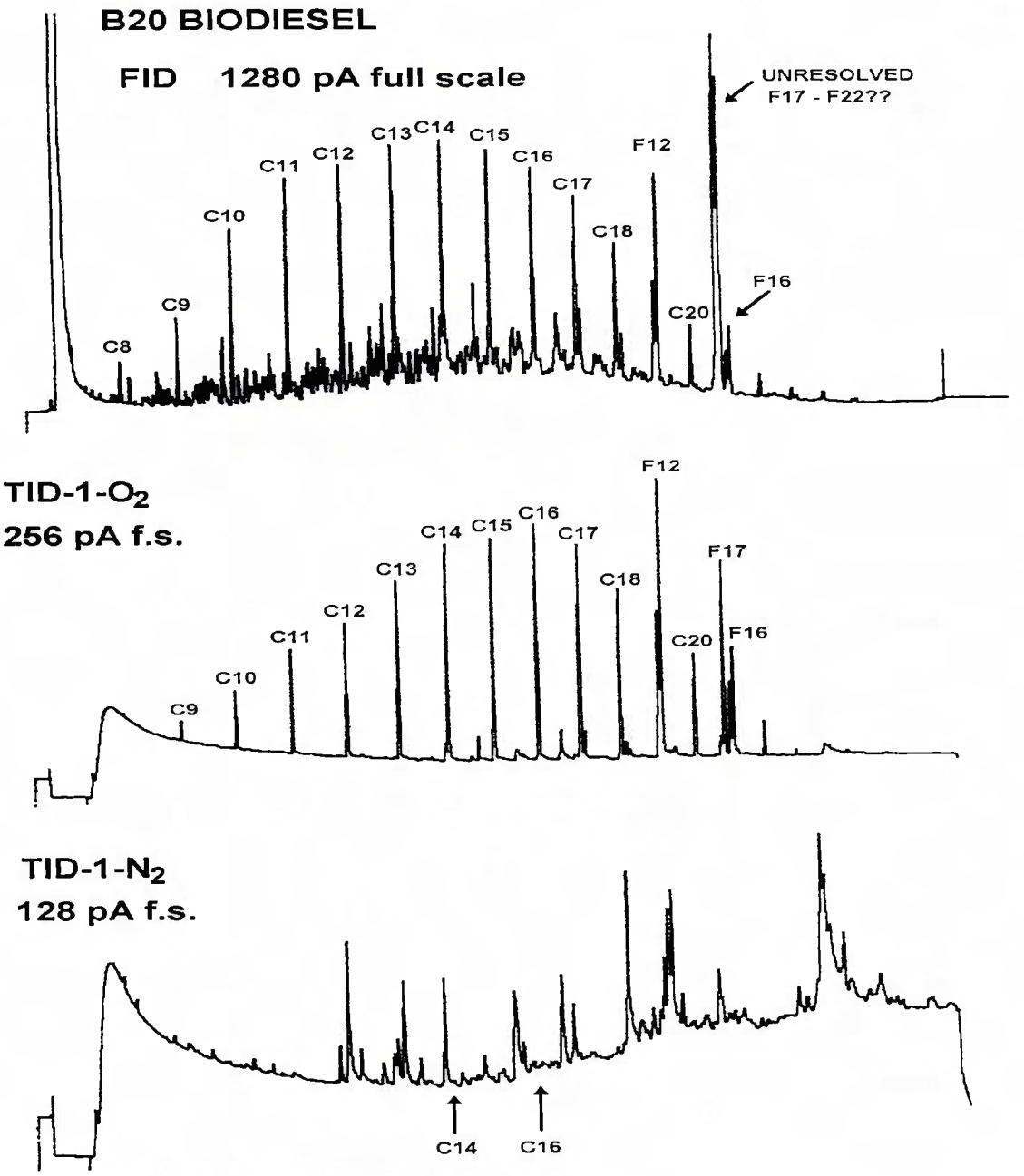


TID-1-Air DETECTION OF WATER IN A NAPHTHA STANDARD

Peaks labeled 1, 3, an 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.

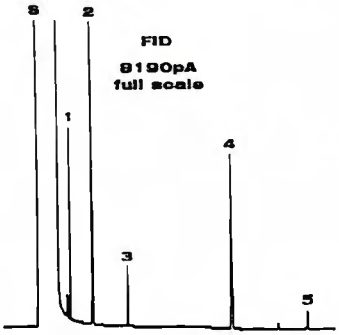


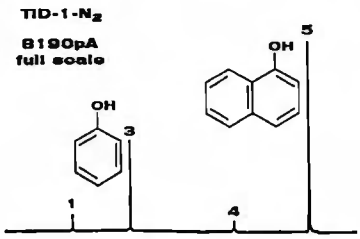
Unique TID-1 selectivity allows detection of Water in a complex Hydrocarbon matrix like Gasoline.



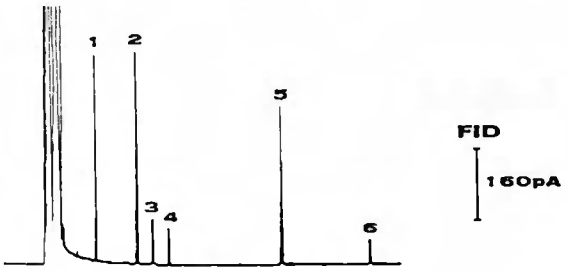
Comparison of FID and TID chromatograms of a 20mg/mL sample of B20 Biodiesel in a Methylene Chloride solvent. Cx nomenclature refers to linear Alkanes, Fx nomenclature refers to FAMEs. F12, F16, and F17 are Palmitic, Stearic, and Oleic FAMEs, respectively. TID-1-N_2 peaks are not yet identified.

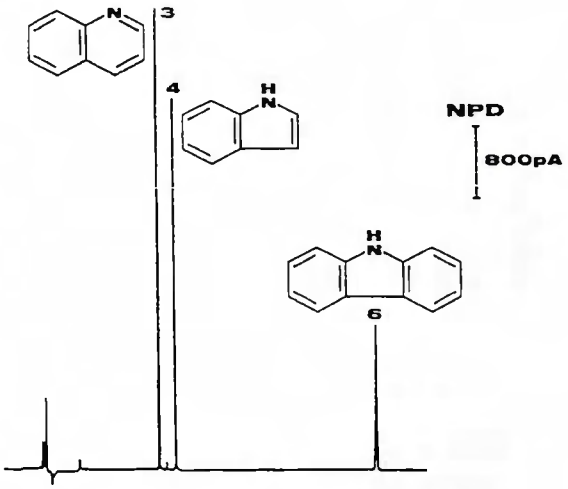
OTHER TID-1 RESPONSES OF RELEVANCE TO PETROLEUM ANALYSES

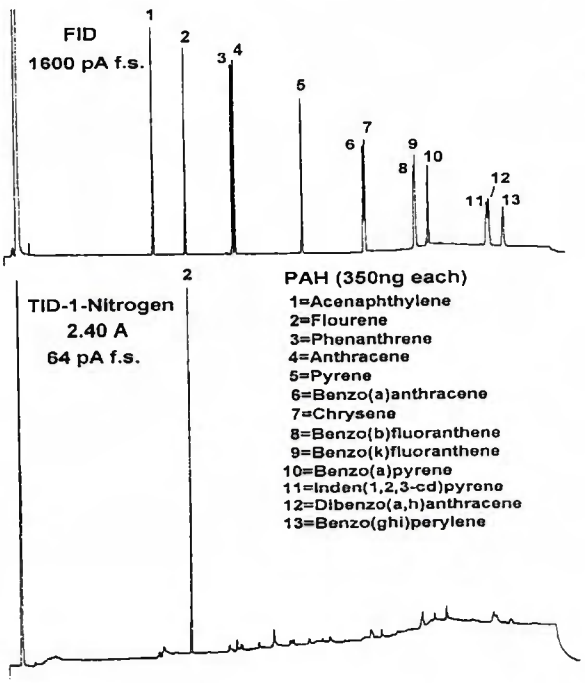




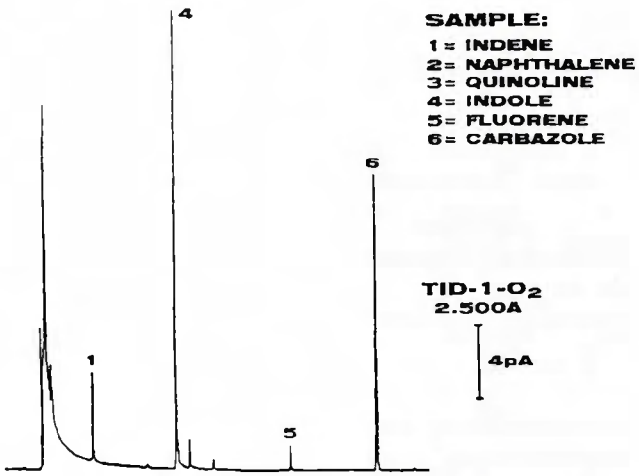
LARGE RESPONSE OF PHENOLS VS. ALCOHOLS
S=Benzene solvent, 1=260ppm Cyclopentanol, 2=990ppm p-Xylene, 3=51ppm Phenol, 4=350ppm n-Decanol, 5=51ppm 1-Naphthol



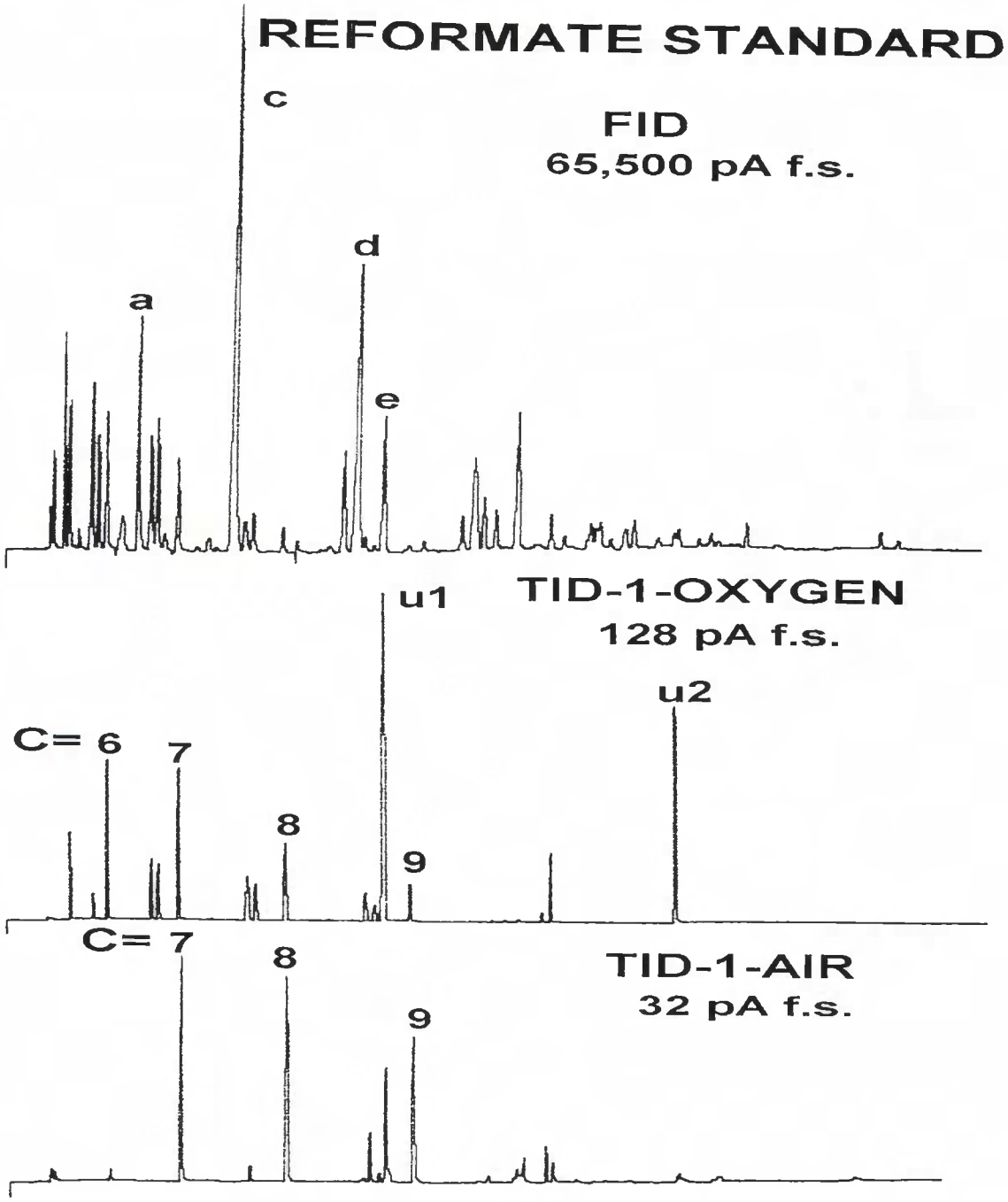




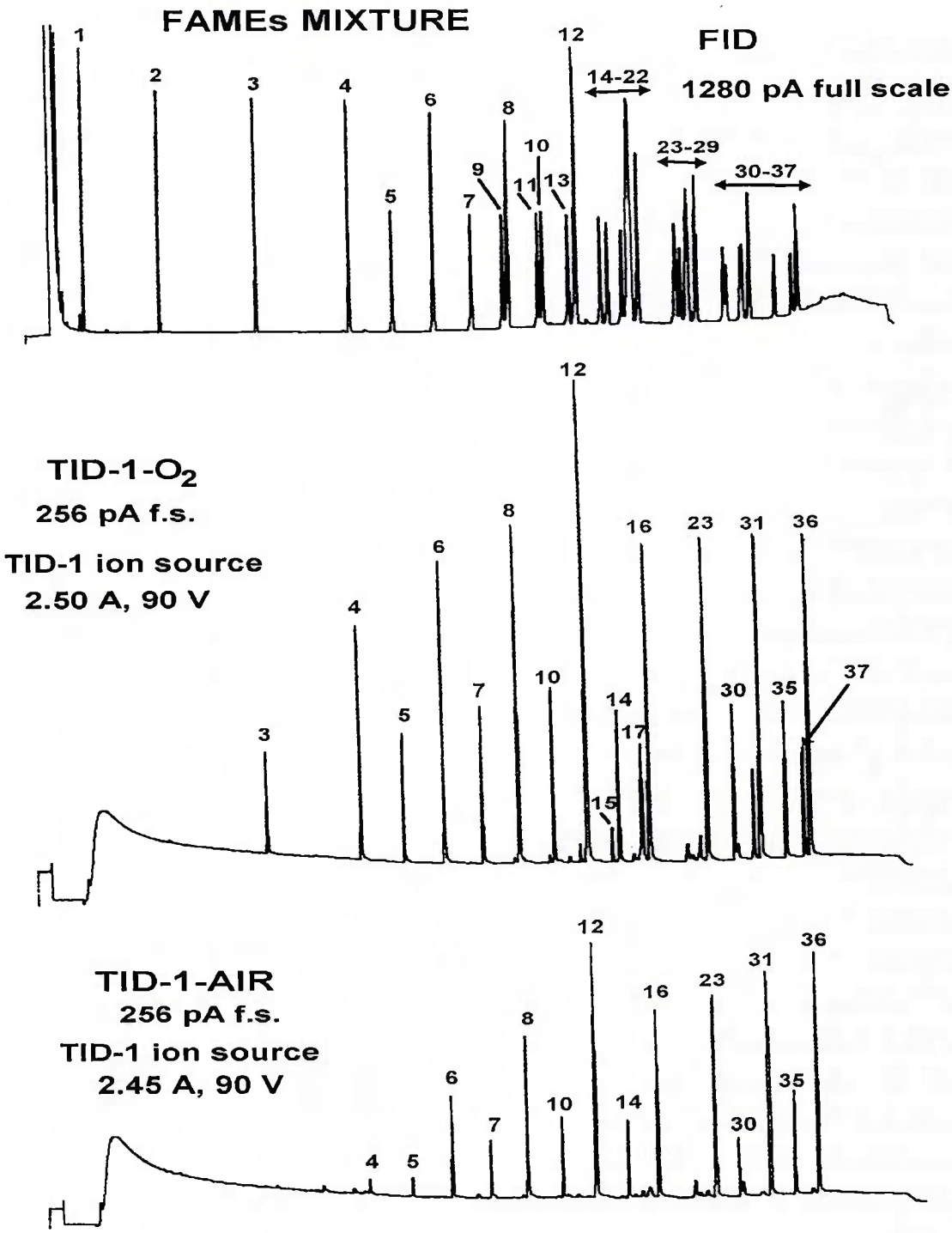
SELECTIVE DETECTION OF THE 5 MEMBER HYDROCARBON RING STRUCTURE IN FLUORENE



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.

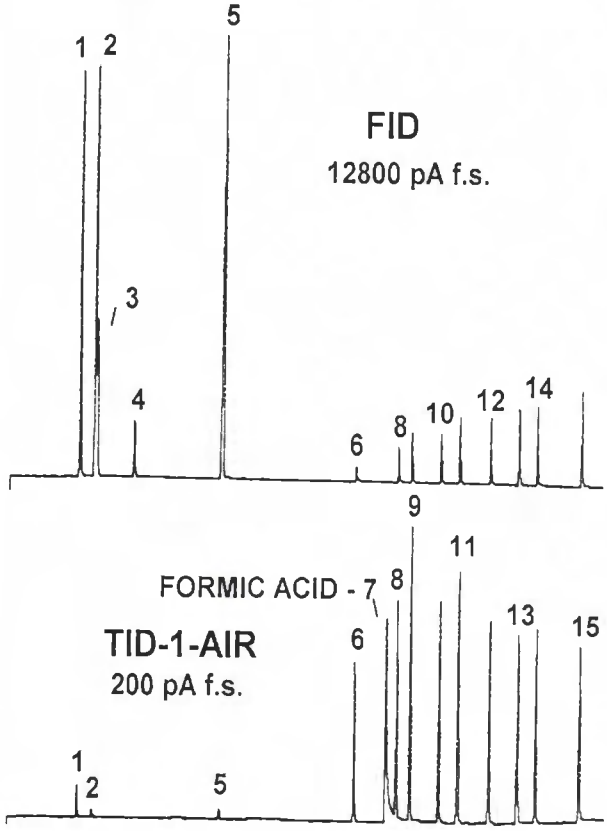


Agilent 6890 GC. TID-1 ion source in 6890 NPD hardware with DET Current Supply for ion source power. C=x indicates Carbon number in Linear Alkanes; a = Benzene; c = Toluene; d = m-Xylene & p-Xylene; e = o-Xylene; u1 & u2 = unidentified components (likely heteroatoms).



TID-1 detection of long chains of CH_2 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.

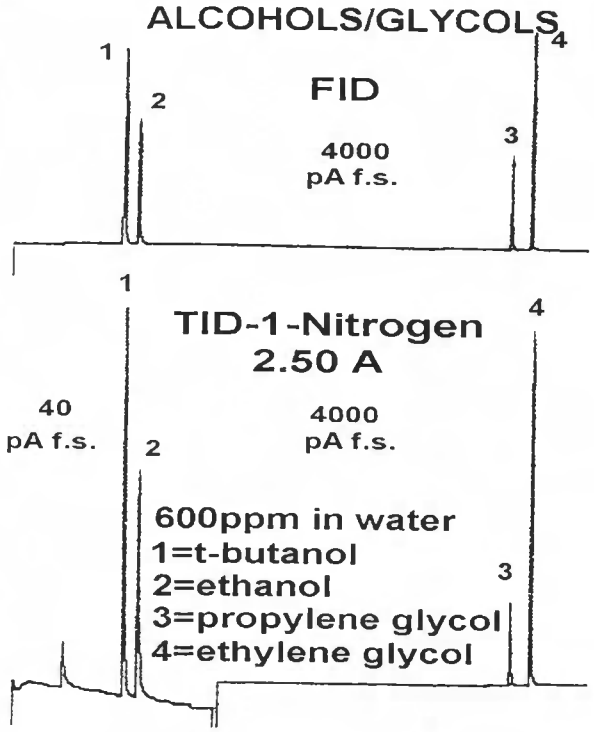
CARBOXYLIC ACID SELECTIVITY



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.

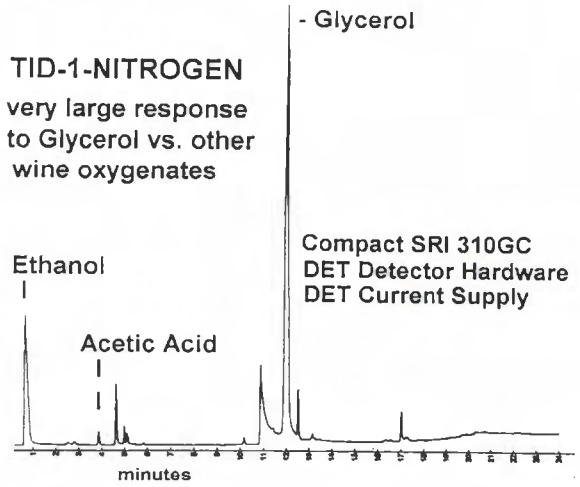
Sample in Water solution:
1=Ethanol (1%), 2=Ethyl Acetate (1%),
3=Benzene (0.15%), 4=Toluene (0.1%),
5=iso-Pentanol (1%), 6=Acetic Acid (0.1%),
7=Formic Acid (0.1%), 8=Propionic Acid (0.1%),
9=iso-Butyric Acid (0.1%), 10=Butyric Acid (0.1%),
11=iso-Valeric Acid (0.1%), 12=n-Valeric Acid (0.1%)
13=iso-Caproic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

ALCOHOLS/GLYCOLS

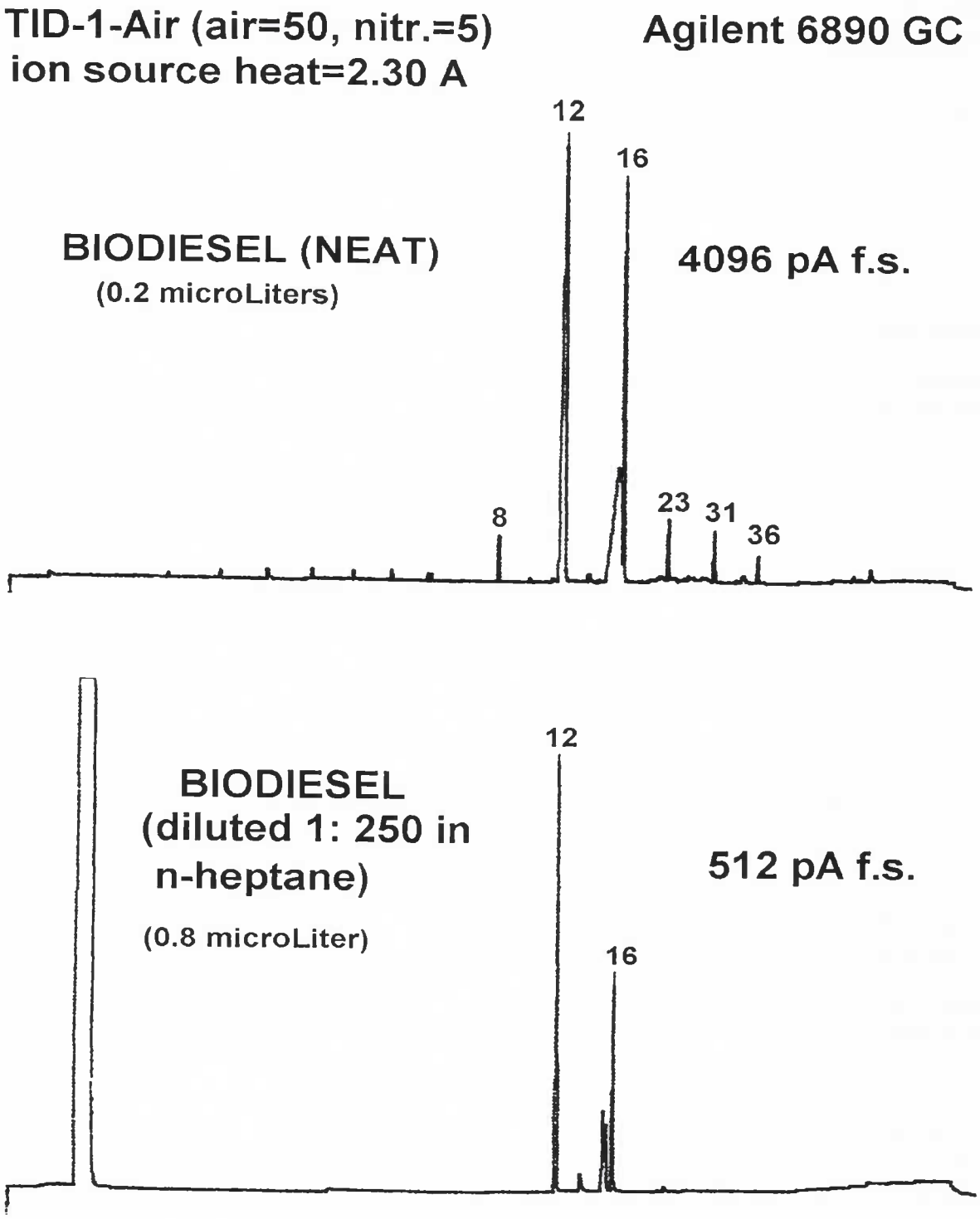


LARGE TID-1 RESPONSE TO GLYCOLS VS. ALCOHOLS.

SHIRAZ WINE SAMPLE



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



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%.

DET

innovations in chemical detection

Ceramic Coated NPD Ion Sources from DET

(new prices effective 1 December 2009)

DET ion sources are compatible with the Agilent 6890/7890 NPD, as well as DET NPD/TID hardware retrofits for Thermo, Varian, SRI Instruments, and HP 5890 GC models.

BEST PERFORMANCE - 2 NPD CERAMIC COATINGS ARE AVAILABLE:

TID-2 (Black Ceramic) - for applications requiring P or both P and N detection (e.g., pesticides); **P DETECTIVITY = 70 fg P/sec** with **MINIMAL PEAK TAILING;**

TID-4 (White Ceramic) - for applications requiring only N detection (e.g., drugs); this is our best N response - **N DETECTIVITY = 70 fg N/sec.**

LOWEST COST: new source , recycled* source

***recycling** - return depleted sources to DET; we can salvage the electrical connector and Aluminum connector holder and attach them to new source wiring with a new TID-2 , TID-4, or any other DET ceramic coating; recycled sources are tested for performance comparable to a new source, and are available at a lower cost.

compare DET prices vs. other type NP ion sources - Agilent "Blos" glass (susceptible to melting), Agilent white ceramic (reportedly now sensitive to ambient moisture), ; Varian ceramic (badly tailing Phosphorus peaks),
(why pay more for less quality?)

HIGHEST QUALITY (30 years experience in ceramic ion source technology):

- unlike glass NPD beads, DET ceramics are robust rigid structures that will not soften or melt at the 600- 800°C temperatures required for NP detection, and are tolerant of a wide variety of operating conditions;

- DET ceramics have long operating life, and unlimited shelf life with no special requirement for protection from ambient moisture.

- DET ion sources are backed by operating/troubleshooting advice from the leading experts in NP detection.

VISA, MASTER CARD, cards accepted.

Contact DET for advice on simple conversions from NPD to other modes of thermionic ionization detection such as selectivity to **Nitro compounds, Oxygenates, Halogenates, CH_2 functional groups** , and other compounds.

DET

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USED GC DEALERS - CONSIDER THE VALUE ADDED ADVANTAGES OF THERMIONIC SURFACE IONIZATION DETECTION TECHNOLOGY

unprecedented capability for interchange between multiple modes of selective chemical detection using low cost, uncomplicated detector equipment

1. Simple, inexpensive detector components feature an electrically heated, cylindrically shaped ceramic ion source element positioned on the axis of an ion collector cylinder for stream-lined gas flow and optimum ion collection.

2. Detector hardware structures designed for easy custom mounting onto an existing FID or NPD type detector base to provide access to 2 or 3 detector gases – variable orientations of signal probe arm to avoid adjacent structures – easy self-aligning top access installation of ion source elements.

3. Multiple modes of selective detection achieved with the same basic equipment by easy changes of the ion source element and detector gases – 9 different choices for the ionizing element are currently available.

4. Selectivity modes include compounds containing N and P atoms (NPD), O, Cl, Br, I, Pb, Sn, or Si atoms, as well as selectivity for NO_2, CH_2, or Pyrrole vs. Pyridine functional groups, among others.

5. Unlike other GC detectors, Thermionic Ionization Detectors (TID) do not require ultra high purity gases – ambient Air is acceptable for some modes.

6. Unlike glass NPD ion sources, rigid ceramic coated surfaces withstand NPD operating temperatures of 600 to 800°C without softening or melting, and have unlimited shelf life when not in use.

7. Stainless steel/ceramic detector hardware structures capable of operation at wall temperatures in excess of 400°C.

8. Unique sensitivities and selectivities often reveal trace level sample impurities not seen by other types of GC detectors.

9. Only a few loose parts for simple, inexpensive service and maintenance.

(versatile detector capability helps sell the entire GC instrument)

CATALYTIC COMBUSTION IONIZATION

DET introduces a GC detection method that selectively ionizes Methylene (CH_2) groups in Petroleum, Biofuel, and FAME samples

Principle of Detection

Fuel compounds elute sequentially from a GC column into a detector gas environment containing Oxygen. Compounds containing a sufficiently high concentration of CH_2 groups ignite a momentary burst of flame ionization as they impact a heated, catalytically active ceramic surface.

Important Consequences of this Chemical Detection

1. Demonstrates that high temperature oxidation of CH_2 groups is a primary process contributing to combustion ignition of Petroleum, Biofuel, and FAME constituents.

2. The temperature required for ignition of fuel combustion is lowered with increased catalytic activity of the ceramic.

3. GC chromatograms of different fuel samples provide fingerprint patterns showing the most combustible components of each sample.

4. Compounds with saturated Carbon bonds ignite in combustion more easily than compounds with Carbon double bonds.

5. Aromatic Hydrocarbon compounds are NOT easily ignited in combustion by this technique.

DET
innovations in chemical detection

DETector Engineering & Technology, inc.
486 N. Wiget Lane, Walnut Creek, CA 94598 USA
telephone: (925) 937-4203 fax: (925) 937-7581
e-mail: DETplp@aol.com www.det-gc.com

AN EXTENSIVE LIBRARY OF SELECTIVE DETECTION APPLICATIONS:

- sub-picogram detection of NP pesticides and drugs (NPD);
- exceptional femtogram sensitivity for Nitro explosives like 2,4-Dinitrotoluene and TNT, as well as Nitro pesticides like Methyl Parathion (TID-1 mode);
- sub-picogram detection for some Halogenated pesticides like Heptachlor, Dieldrin, Chlordane, Pentachlorophenol, Atrazine, etc (TID-1 mode);
- low picogram detection of Trihalomethane purification byproducts in drinking water (TID-3 mode);
- selective detection of Ethanol and other Alcohols in Petroleum and Biofuels (TID-1-Nitrogen mode);
- selective detection of Acetic, Formic, and other Carboxylic Acids in Wine and other food and flavor analyses (TID-1 mode);
- selective detection of linear chain Hydrocarbons and Fatty Acid Methyl Esters (FAMEs) in petroleum and biofuels with discrimination between saturated and unsaturated Carbon bonds (Catalytic Combustion Ionization);
- picogram detection of BisPhenol A (BPA) and Phthalates in food packaging products (TID-1 mode);
- detection of Glycerol and Glycols in wine and food products (TID-1-Nitrogen);
- detection of Poly Brominated Diphenyl Ether (PBDE) flame retardants used on packaging for computers and other commercial products (TID-3 mode);
- selective detection of Lead and Tin in environmental samples (Remote FID);
- low picogram detection of Phenols in environmental samples (TID-1);
- low picogram detection of Vanillin and Salicylates in food flavorings (TID-1);
- detection of trace Water in solvents and petroleum samples (TID-1-Air mode);
- simple detection of the buildup of decomposition products in motor oil versus automobile usage miles of the oil (TID-1-Nitrogen mode);
- selective detection of Acrylamide in processed food products (NPD).

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ATTENTION - users of the Agilent, Thermo, or SRI NPD

RECYCLE USED BEADS

Instead of disposing of depleted ion sources (i.e., beads) as common trash, send them back to DET for an **ENVIRONMENTAL FRIENDLY** salvage of component parts. The Twinex connector and Aluminum connector holder on all types of Agilent or DET ion sources can be re-used with otherwise all new parts. DET ion source assemblies made with these recycled parts have the same performance as a new ion source, and are less expensive (i.e., $315 vs. $350 for a new source, these prices effective Dec. 1, 2009).

Recycled ion source types available for N or P detection:
TID-2 (black ceramic) provides the sharpest P peaks;
TID-4 (white ceramic) provides best possible N response;
TID-6 (gray ceramic) for P selectivity with suppressed N.

Also available with new or recycled parts - for simple, inexpensive extended uses of NPD equipment:
TID-1 (very white ceramic) for selective detection of Nitro compounds, Oxygenates, and some Halogenates;
TID-3 (white ceramic) for selective detection of volatile Halogenates with sharp peaks;
TID-5 (black ceramic) for selective detection of Br and I with suppressed response to other Halogen atoms.

Contact DET for expert advice on using NP and other types of thermionic detection on various GC models.

DET

innovations in chemical detection

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TID-4 (White Ceramic) - for applications requiring only N detection (e.g., drugs); this is our best N response - **N DETECTIVITY = 70 fg N/sec.**

LOWEST COST: new source $350, recycled* source $315. (prices in US dollars).

***recycling** - return depleted sources to DET; we can salvage the electrical connector and Aluminum connector holder and attach them to new source wiring with a new TID-2 , TID-4, or any other DET ceramic coating; recycled sources are tested for performance comparable to a new source, and are available at a lower cost.

compare DET prices vs. other type NP ion sources - Agilent "Blos" glass (susceptible to melting), $639; Agilent white ceramic (reportedly now sensitive to ambient moisture), $415; Varian ceramic (badly tailing Phosphorus peaks), $1090. **(why pay more for less quality?)**

HIGHEST QUALITY (30 years experience in ceramic ion source technology):
- unlike glass NPD beads, DET ceramics are robust rigid structures that will not soften or melt at the 600- 800°C temperatures required for NP detection, and are tolerant of a wide variety of operating conditions;

- DET ceramics have long operating life, and unlimited shelf life with no special requirement for protection from ambient moisture.

- DET ion sources are backed by operating/troubleshooting advice from the leading experts in NP detection.

VISA, MASTER CARD, AMERICAN EXPRESS cards accepted.

Contact DET for advice on simple conversions from NPD to other modes of thermionic ionization detection such as selectivity to **Nitro compounds, Oxygenates, Halogenates, CH_2 functional groups** , and other compounds.

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.

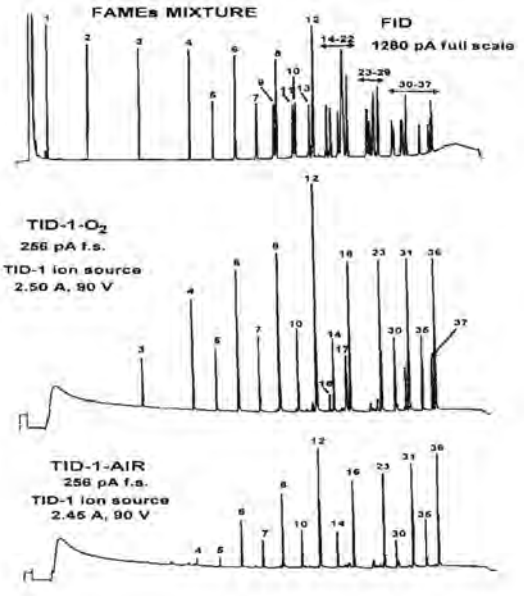


Figure 1. FAME Unsaturates in TID chromatograms: **15**=cis-10-Heptadecenoic (C17:1), 2wt%; **17**=Oleic (C18:1n9c), 4wt%; **37**=Nervonic (C24:1n9), 2wt%. Some of the **FAME Saturates**: **12**=Palmitic (C16:0), 6wt%; **14**=Heptadecanoic (C17:0), 2wt%; **16**=Stearic (C18:0), 4wt%; **23**=Arachidic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

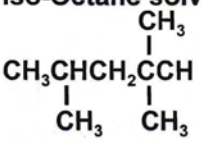
Given the observation that a Carbon double bond can significantly reduce the magnitude of response produced by Catalytic Combustion Ionization of CH_2 groups in FAME compounds, a related examination of Alkanes versus Alkenes was undertaken. Figure 2 compares FID and TID-1 chromatograms for a mixture 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)



n–Dodecane (D)

$CH_3(CH_2)_{10}CH_3$

1-Tetradecene (T)

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

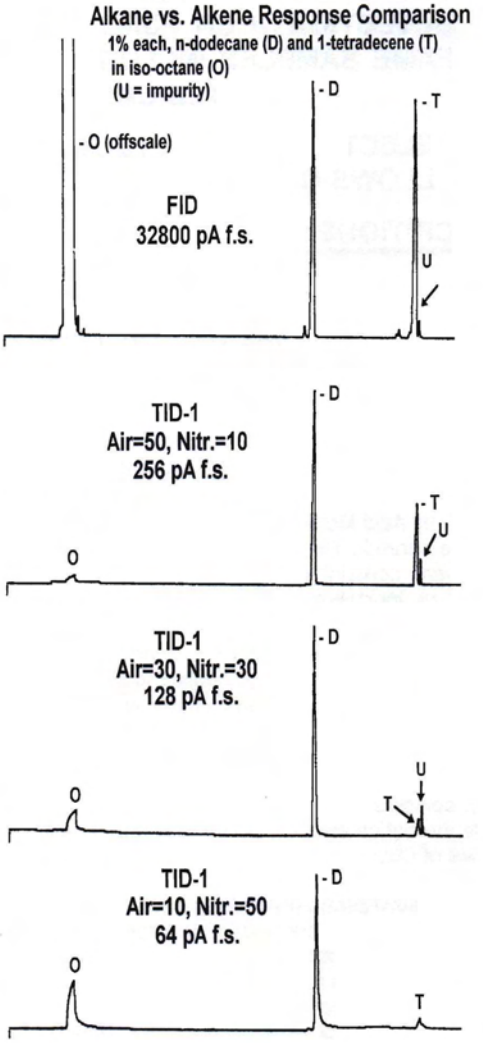


Figure 2. 0.6µL injected. Agilent 6890 GC.
30m x 0.53mm HP-1ms, He=6 mL/min, 50 -160°C at 6°C/min.
TID data from Agilent NPD equipment modified with TID-1 ion source powered by a DET Current Supply, and Air/N_2 detector gases (i.e., no H_2). Detector = 320°C.
TID-1 ion source heat =2.30 A, polarization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

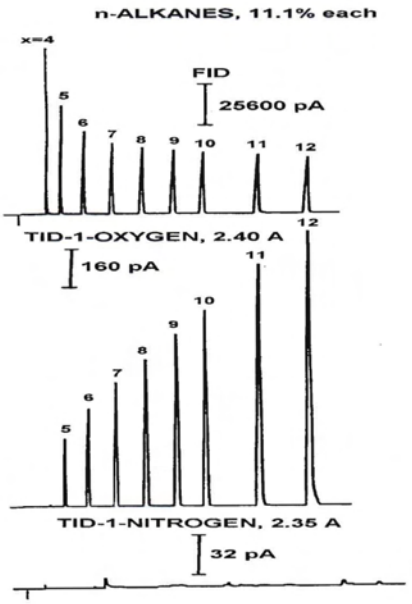


Figure 3. n–ALKANES, $CH_3(CH_2)_xCH_3$
Varian GC with DET retrofit NPD/TID hardware and stand-alone DET Current Supply.

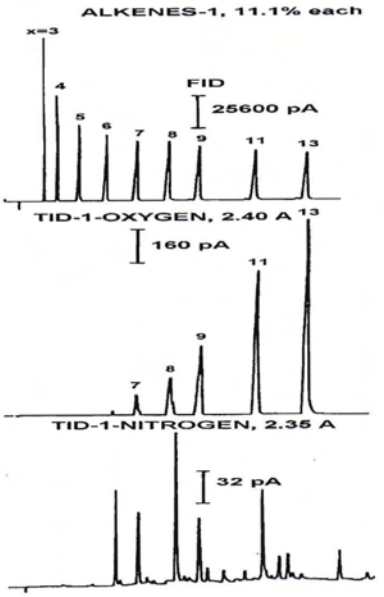


Figure 4. 1-ALKENES, $CH_2{=}CH(CH_2)_xCH_3$

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.

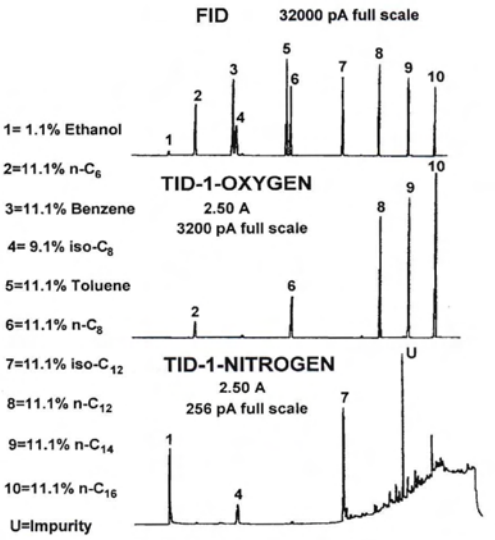


Figure 5. 0.1µL injection of sample mixture. Varian GC, DET retrofit hardware and DET Current Supply.

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.

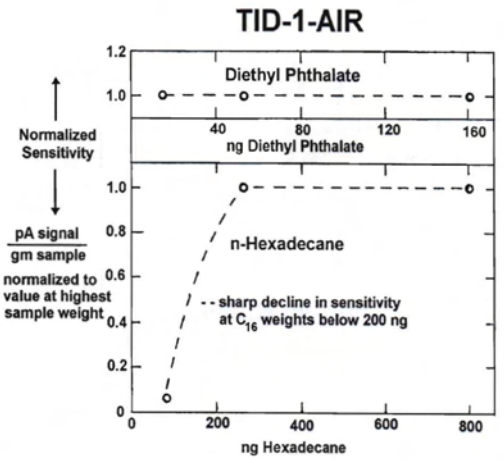


Figure 6. Graph of normalized sensitivity vs. sample weight. Sensitivity=pA of peak height divided by gm of sample weight. Sensitivity data normalized by dividing by the sensitivity corresponding to the highest sample weight.

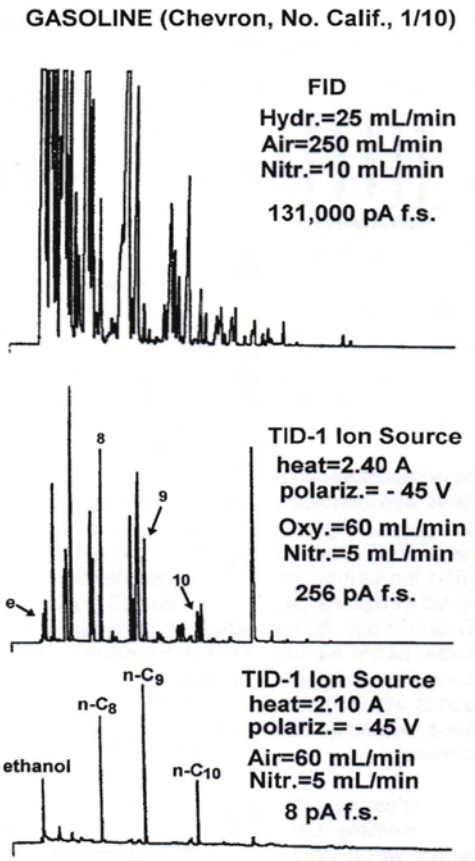


Figure 7. 0.6µL Gasoline injected neat. Agilent 6890 NPD equipment modified with DET TID-1 ion source and DET stand-alone Current Supply.

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.

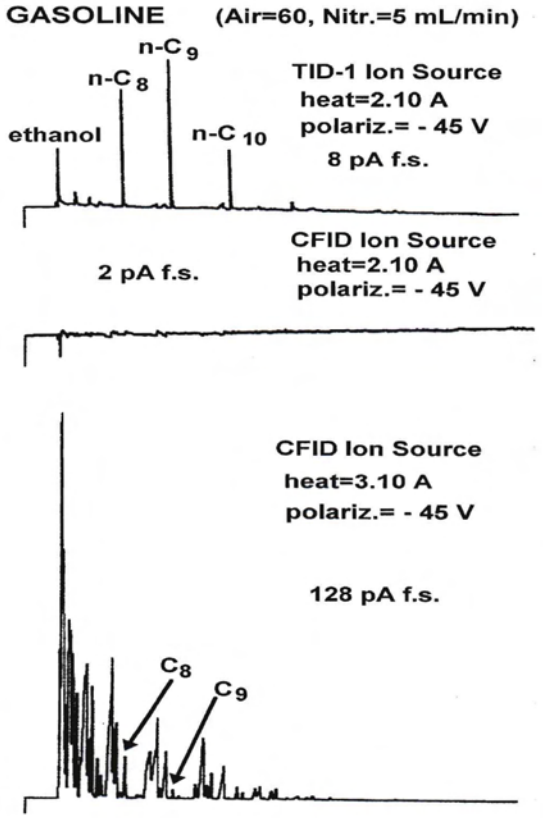


Figure 8. Same Gasoline sample and equipment as Figure 7, except interchange of TID-1 and CFID type ceramic ion sources.

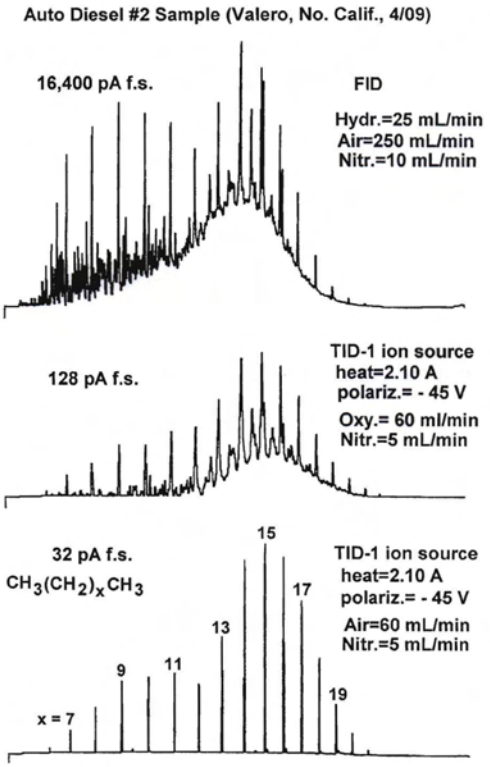


Figure 9. 0.2µL Diesel Fuel injected neat. Same Agilent and DET equipment as Figure 7.

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.

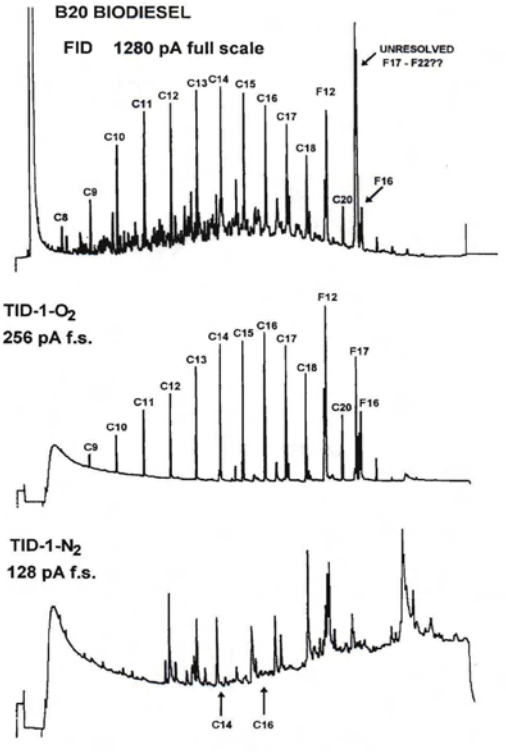


Figure 10. 0.7µL injected. 20mg/mL B20 in Methylene Chloride. Thermo Scientific Trace GC with DET NPD/TID detector hardware and Thermo's NPD electronics.
To minimize upset from the Chlorinated solvent, TID-1 heat was turned OFF during first 2 minutes of the run.

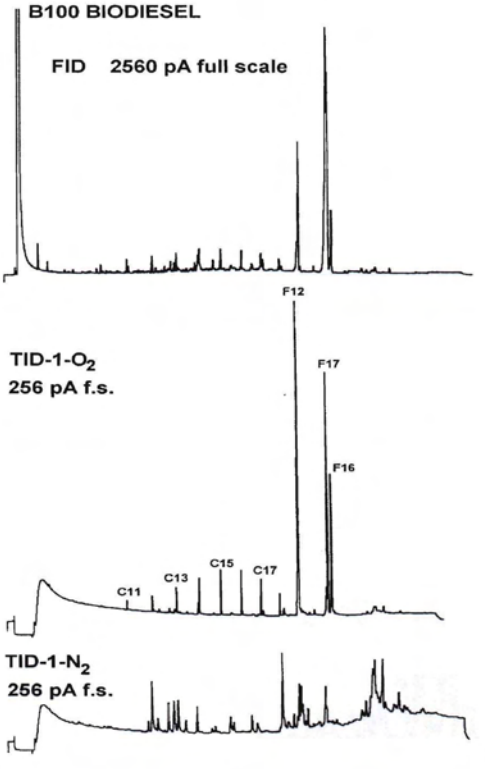


Figure 11. 0.7µL injected. 20mg/mL B100 in Methylene Chloride. Same equipment as Figure 10.

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 B20 and B100 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.

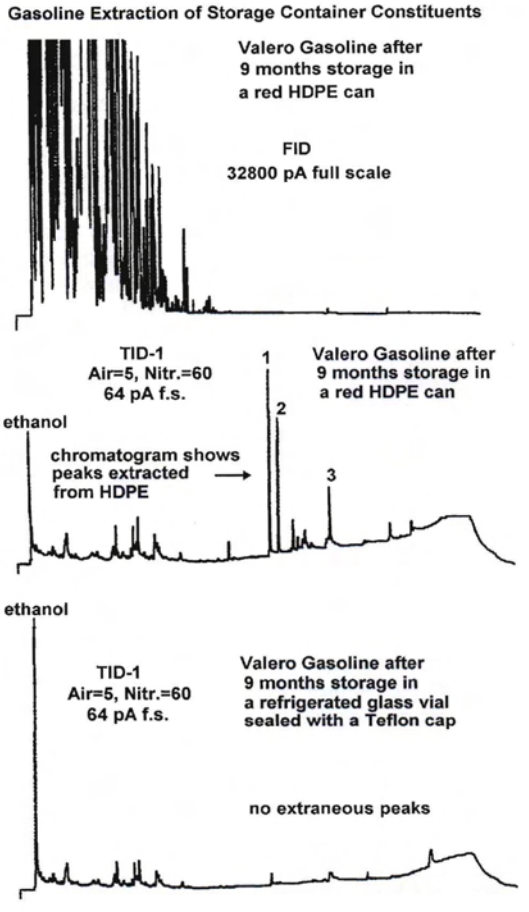


Figure 12. Agilent 6890 NPD equipment modified with a DET TID-1 ion source powered by a stand-alone DET Current Supply.

DET REPORT

NO.62 MAY 2010

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.

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DET NPD/TID/FID RETROFITS FOR DIFFERENT GC MODELS

DET retrofits consist of a stainless steel/ceramic tower that custom mounts onto the existing FID/NPD base on the GC. The tower can accommodate DET hex flanged ion sources such that the ion source is positioned on the axis of a collector electrode cylinder. This concentric cylinder geometry provides a streamlined gas flow through the detector , and an optimum electric field for ion collection. For a complete detector, add an Ion Source to the following assemblies.

THERMO TRACE GC:

NPD/TID/FID Tower Assembly, part #010-860-55,

DET hardware and ion sources are compatible with Thermo's NPD electronics which provides Constant Current ion source heating and a wide range of polarization voltage selections. This combination of DET hardware and Thermo NPD electronics provides the most versatile NPD/TID detection currently available. Different modes of detection are achieved by simple changes in the type of ion source, and in the type of detector gases.

VARIAN GC MODELS:

NPD/TID/FID Tower Assembly, part #010-860-20,

DET hardware and ion sources are compatible with Varian's TSD electronics which provides Constant Current ion source heating at a fixed polarization of - 4 V. For modes of detection other than NPD, a stand-alone DET Constant Current Supply provides a selection of higher polarization voltages which provide more sensitive detection than the Varian supply.

optional DET Current Supply, part #001-901-01 (115Vac),

SRI INSTRUMENTS:

NPD/TID/FID Tower Assembly, part #050-864-98,

DET hardware is compatible with signal measurement using SRI's FID/NPD amplifier. DET ion sources with a bare wire termination can be powered with SRI's NPD electronics, but setting power levels is not very user friendly. An improvement is to use the stand-alone DET Current Supply described above, and ion sources with a Twinex connector as is standard on Agilent, Thermo, and Varian instruments.

HP 5890 (same equipment fits the FID base on an Agilent 6890):

NPD/TID/Remote FID/FTID Tower Assembly, part #040-862-12,

DET hardware is not compatible with the 5890 detector electronics, so the stand-alone DET Current Supply and a stand-alone Electrometer (Keithley 6480 Picoammeter recommended) are required. In addition to NPD and TID modes, this equipment can be used for a Remote FID mode for selective detection of P, Sn, Pb, and Si, or an FTID mode for selectivity to N and Cl.

DET Current Supply as above, Keithley Picoammeter,

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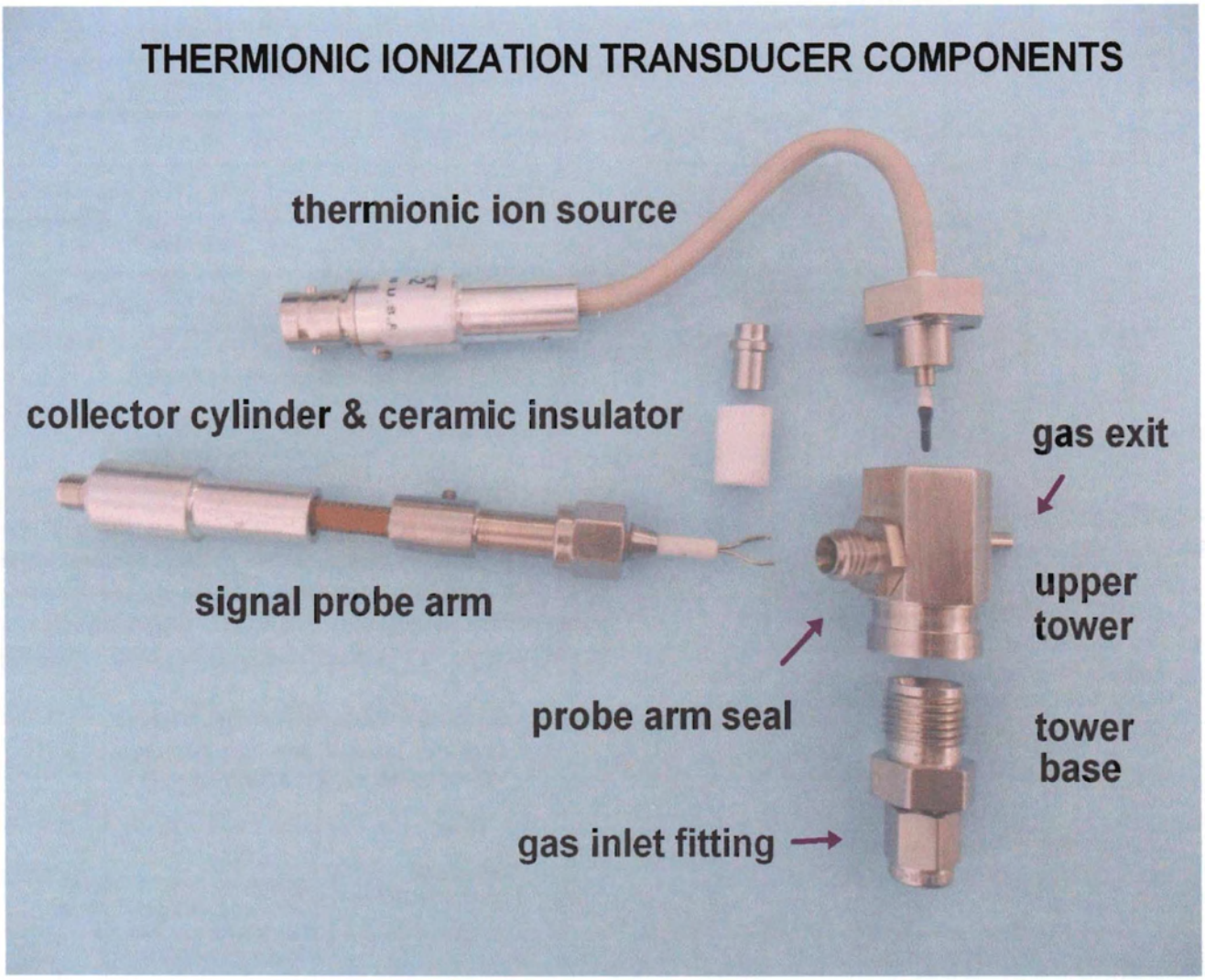
DET Thermionic Detectors & Transducers

a simple design with only a few loose parts for easy, inexpensive maintenance



All DET structures have a common upper tower which contains the collector cylinder and ceramic insulator, a signal probe arm, and the ion source. The tower base can be custom designed to retrofit onto an FID base already existing on a GC, or it can be provided with a choice of Swage or Tube inlet/outlet fittings for use as a stand-alone transducer. In the illustration above, the inlet is a 1/8 inch Swage fitting and the outlet is a 1/8 inch tube. The tower base shown above as a separate part is normally permanently attached to the upper tower. A selection of different ceramic ion source coatings is available for simple changes of the mode of selective detection using the same basic detector structure.

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CHROMalytic +61(0)3 9762 2034

ECHnology Pty Ltd

Australian Distributors; Importers & Manufacturers

COMPACT GC ANALYZER
for selective detection of
OXYGENATES & NITRO COMPOUNDS
or
NITROGEN-PHOSPHORUS COMPOUNDS
(NPD)

GC SPECIFICS

- SRI Instruments model 310 is an easily portable small size & weight.
- heated flash vaporization injector with a deactivated glass liner.
- accommodates one 15m or 30 m x 0.53mm metal capillary column.
- heated detector base.
- electronic pressure control of carrier & 2 detector gases.
- built-in data system provides signal measurement plus capability for programmed column temperature & carrier gas pressure when coupled to a laptop computer.

SELECTIVE DETECTION SPECIFICS

- DET Thermionic Ionization Detector hardware features concentric cylinder geometry for streamlined gas flow and most efficient ion collection.

- ceramic coated Thermionic Ion Sources are mounted on a self-aligning flange for easy interchangeability.

- TID-1 type ion source provides selectivity for Oxygenates and Nitro-compounds with just Nitrogen or Air as the detector gas; also non-destructive so sample aromas can be sensed at the detector exit.

- Nitrogen-Phosphorus selectivity (NPD) provided by TID-2 type ion source for sharpest P peaks, or by TID-4 ion source for best possible N response.

- stand-alone DET Current Supply provides precision thumbwheel control of ion source heating power plus switch selection of different polarizations for optimum response in all modes of detection.

NEW PRODUCT ANNOUNCEMENT
JUNE 2006

COMPACT GC ANALYZER FOR SELECTIVE DETECTION OF OXYGENATES OR NITROGEN-PHOSPHORUS COMPOUNDS

DETector Engineering & Technology has combined its Thermionic Ionization Detector equipment with an SRI Instruments Model 310 GC to provide a compact GC analyzer for the selective detection of either Oxygenates and Nitro-compounds, or for the selective detection of Nitrogen-Phosphorus compounds (i.e., NPD). Selectivity is determined by the type of ceramic coated Thermionic Ion Source installed in the detector, and the composition of detector gases supplied. One type of selective detection can be easily and inexpensively adapted to the other type by changing the ion source and reconfiguring the detector gases. A stand-alone DET electronics module provides precision controlled power for the Ion Source, while SRI's NPD type amplifier provides signal measurement. SRI's built-in PeakSimple™ software in the GC allows operational control and signal processing to be accomplished by connection to a laptop computer. The equipment is small in physical size and weight, and is easily transported on the seat of a small sedan.

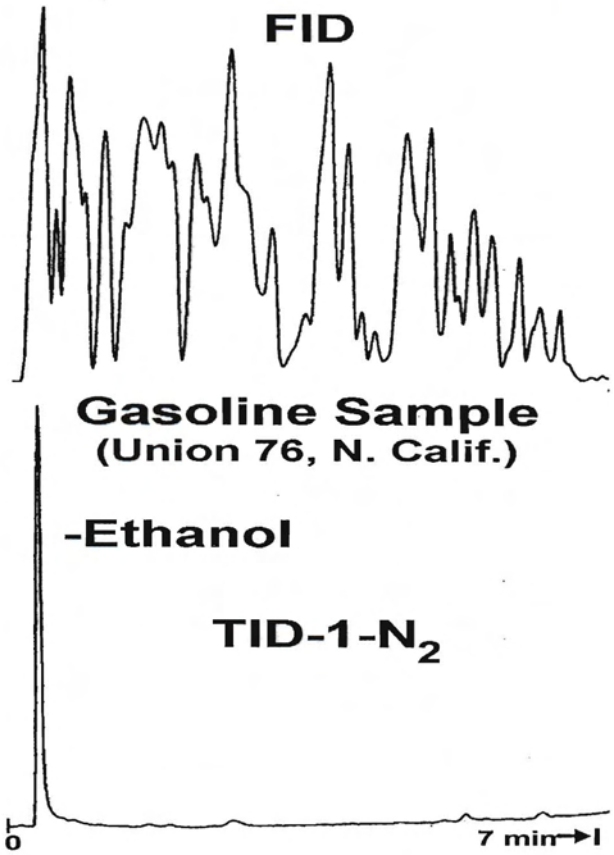
GC Specifics. Dimensions of the SRI 310 GC are 12.75 inches wide, 14.75 inches deep,12.75 inches tall, and the weight is 32.5 pounds. The column oven accommodates 15m or 30m long, 0.53mm diameter metal capillary columns (MXT® type from Restek, or Ultra-ALLOY™ type from Quadrex) formed in 3.0 inch diameter coils. The GC is equipped with a heated Flash Vaporization Injector: a heated detector base; and electronic pressure control of the column carrier gas and two detector gases. The detector gas lines are configured with restriction tubing normally used for supplying Hydrogen and Air to the SRI NPD, and signals are measured with the SRI NPD amplifier. In the case of Oxygenates detection, either Nitrogen or Air are supplied through the two detector gas lines. SRI's built-in PeakSimple™ data system provides data acquisition, as well as capability for programmed control of both column temperature and carrier gas pressure.

DET Modifications to the SRI GC. A Twinex chassis connector is mounted on the right side external wall of the GC, and a cable is routed internally to the detector vicinity to allow control of ion source power with a stand-alone DET module. The Flash Injector is modified by insertion of a 72 cm long direct injection glass liner (Restek part # 20345). A 4 inch length of uncoated, deactivated 0.53mm fuzed silica tubing is press-tight sealed into the injector liner, and extends into the column oven where it connects to the metal capillary column with a low volume stainless steel adaptor fitting which has been deactivated by Restek's Siltek® process. SRI's original 1/8 inch to 0.8mm Graphite seals for the injector and detector ends of the column have also been replaced by 1/8 inch tube to 1/16 inch Swagelok® reducer fittings and smaller diameter 1/16 inch x 0.8 mm Graphite ferrule seals. The smaller Graphite ferrules provide a more reliable seal and are less likely to stick in the fitting upon removal.

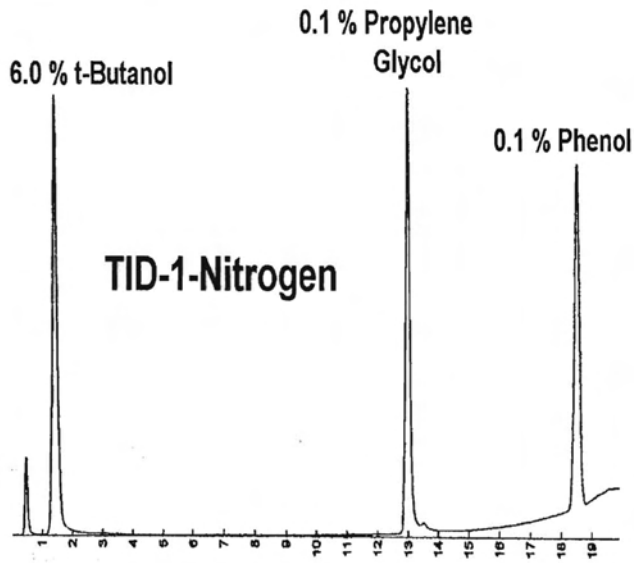
DET Detector Hardware. The Thermionic Ionization hardware includes a ceramic tipped jet structure that guides the end of the metal capillary column into the heated detector base. The detector structure provides a preferred ionization geometry with the cylindrically shaped ion source located on the axis of a collector electrode cylinder. This configuration provides a streamlined flow of gases through the detection volume, and an optimum electric field for collection of ions. Ion sources used in this equipment attach to the detector structure with 3 screws, and are self-aligning without any additional positioning. These ion sources are identical in structure, and are interchangeable with those used in the Agilent Technologies model 6890 NPD.

DET Electronic Module.
A DET Detector Current Supply module provides precision control of the heating current for the ion source, plus a selection of several different polarization voltages for optimizing detector response in all modes of detection. The DET supply is a stand-alone module that is 6 inches wide, 10 inches deep, 5.5 inches tall, and weighs 7.5 pounds. It couples to the SRI GC via a 4 foot long cable. Precision controlled constant heating currents in the range of 0 to 4000 mA are provided to the ion source via a thumbwheel control. A selection of -5, -15, or -45 Volts polarization between the ion source and collector electrode is also provided. -5 V polarization is used for NP detection, whereas - 45 V is used for best response to Oxygenates.

EXAMPLES OF SELECTIVE DETECTION WITH A COMPACT GC

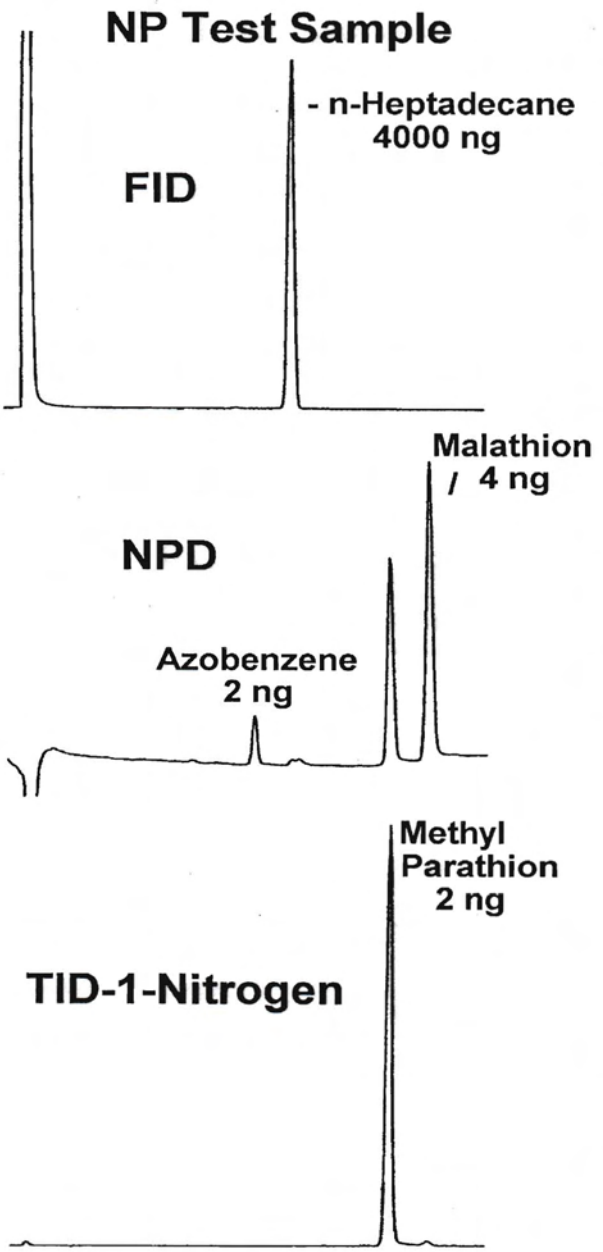


ETHANOL IN GASOLINE. Ionization on a TID-1 ceramic surface provides excellent selectivity for detection of Ethanol amidst the many Hydrocarbon components of gasoline. A single Nitrogen gas suffices as both carrier and detector gas. For these data, a 0.3 µL sample of a commercial gasoline was injected into the 185°C glass insert of the flash vaporization injector. The column was a 15 m x 0.53 mm x 5.0 µm MXT-1 type. Column temperature program was 45°C - 1.5 min, 45 - 205°C at 20°C/min, 205°C - 2 min. The carrier gas was also pressure programmed at 9.0 psi - 1.5 min, 9.0 - 11.1 psi at 0.267 psi/min, 11.1 psi - 2 min. Due to the excellent selectivity of TID-1 ionization, there was no need to chromatographically separate overlapping Hydrocarbon peaks. However, to prevent buildup of sample components on the column, the total analysis time of 11.5 minutes was used, although the Ethanol peak eluted within the first minute. Detector temperature was 270°C. For the TID-1 data, N_2 was supplied at 8 psi through the "H_2" labeled detector gas line, and at 2 psi through the "Air" labeled detector gas line. Heating current to the TID-1 ion source was 2.50 A, and the polarization was - 45 V. FID data were obtained by replacing the TID-1 ion source with an FID Ignitor/Polarizer Probe element, and by supplying H_2 at 35 psi and Air at 5 psi to the detector. The FID flame was ignited by raising the heating current to 3.10 A. Once flame ignition occurred, the heating current through the FID probe was reduced to zero. FID polarization was - 45 V.



LARGE RESPONSES TO GLYCOLS AND PHENOLS. TID-1 ionization responses to some Oxygenate classes are substantially bigger than others, although all have good selectivity versus Hydrocarbons. Two classes with especially large responses are Glycols and Phenols. These data demonstrate that a sample containing 0.1 % concentrations of Propylene Glycol and Phenol in an iso-Octane solvent, produced TID-1 responses for those compounds which were similar in magnitude to a much higher 6 % concentration of t-Butanol. Carboxylic Acids, Vanillin, and Methyl Salicylate are examples of other Oxygenates having large TID-1 responses, while Aldehydes, Ketones, Esters, and Phthalates have responses comparable to that of Alcohols. Column was a 30 m x 0.53 mm x 2.0 µm MXT-Wax, temperature programmed at 50°C - 2 min, 50 - 190°C at 8°C/min, 190°C - 1 min. Helium was the carrier gas programmed at 20 psi - 2min, 20 - 34 psi at 0.8 psi/min, 34 psi - 1 min. Detector gas was Nitrogen supplied at 2 psi and 8 psi through the "Air" and "H_2" detector lines. Injector = 190°C, detector = 250°C, and TID-1 source heat = 2.60 A.

EXAMPLES OF SELECTIVE DETECTION WITH A COMPACT GC



NP PESTICIDES. One of the main applications of an NPD is the detection of trace level pesticides. The present equipment provides that NP selective capability in a compact GC package. The sample analyzed here was Varian's TSD (i.e., NPD) test sample (Varian part 82-005048-04). This is the standard used at DET for final testing all ceramic coated NP and TID-1 ion sources. It contains 2 ng/µL of Azobenzene as a representative N compound; 2 ng/µL of Methyl Parathion and 4 ng/µL of Malathion as representative Organophosphorus pesticides; and 4000 ng/µL of n–Heptadecane as a representative high concentration Hydrocarbon. At the sensitivities displayed in the 3 chromatograms, an FID showed a response only for the Hydrocarbon; an NPD showed responses to the N and P components with only minimal response to the Hydrocarbon; and the TID-1 detector responded to only the Methyl Parathion component.

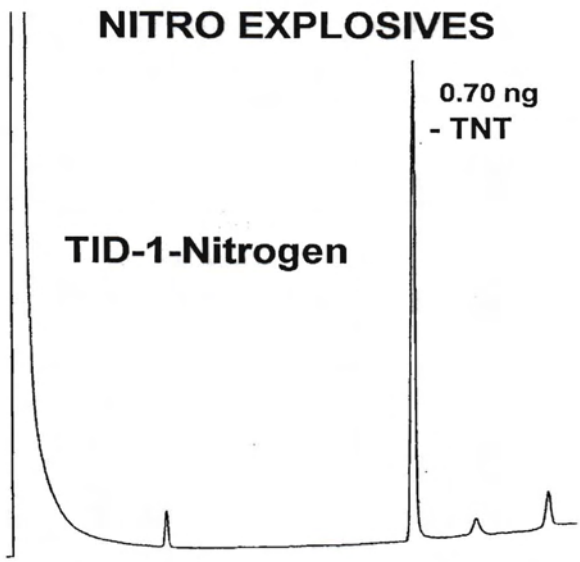
GC Conditions. 15m x 0.53mm x 5.0µm MXT-1 column. Temperature program = 170 - 230°C at 10°C/min, 230°C - 1 min. Helium carrier gas program = 8 - 10 psi at 0.333 psi/min, 10 psi - 1 min. Injector = 220°C, detector = 275°C.

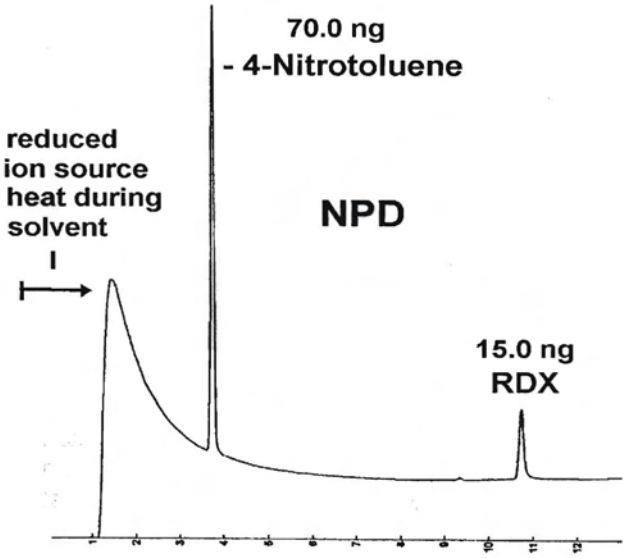
FID Data. Hydrogen = 35psi, Air = 5 psi. FID Ignitor/Polarizer Probe heated to 3.100 Amps to ignite flame, then reduced to 0 A. Polarization = - 45V.

NPD Data. Hydrogen = 7psi, Air = 2 psi. Ceramic TID-2 type ion source used. Source heat = 3.080 A supplied continuously to maintain ignited Hydrogen-Air boundary layer chemistry around the ion source surface. Source polarization = - 5 V.

TID-1 Data. Nitrogen through "H_2" line = 7 psi, Nitrogen through "Air" line = 2 psi. Ceramic TID-1 ion source used at 2.500 A heating current and - 45 V polarization. Large selective response to Methyl Parathion is due to the presence of a strong electronegative NO_2 functional group in a para location relative to other functionalities in that molecule. For similar type compounds, TID-1 ionization provides better selectivity and detectivity than an NPD.

EXAMPLES OF SELECTIVE DETECTION WITH A COMPACT GC





NITRO EXPLOSIVES. Both the NPD and TID-1 modes of detection can be applied to the detection of trace levels of Nitro Explosives in environmental samples. The sample analyzed here was a mixture of 70.0 ng of 4-Nitrotoluene, 0.70 ng of TNT, and 15.0 ng of RDX in a solvent consisting of 93 % Methanol and 7 % Acetonitrile. The data demonstrate the exceptional sensitivity of TID-1 detection for the molecular structure of TNT versus the other two Nitro compounds. In contrast, the NPD provides a more uniform response to all three Nitro compounds, but its detectivity for TNT is not nearly as good as the TID-1 mode.

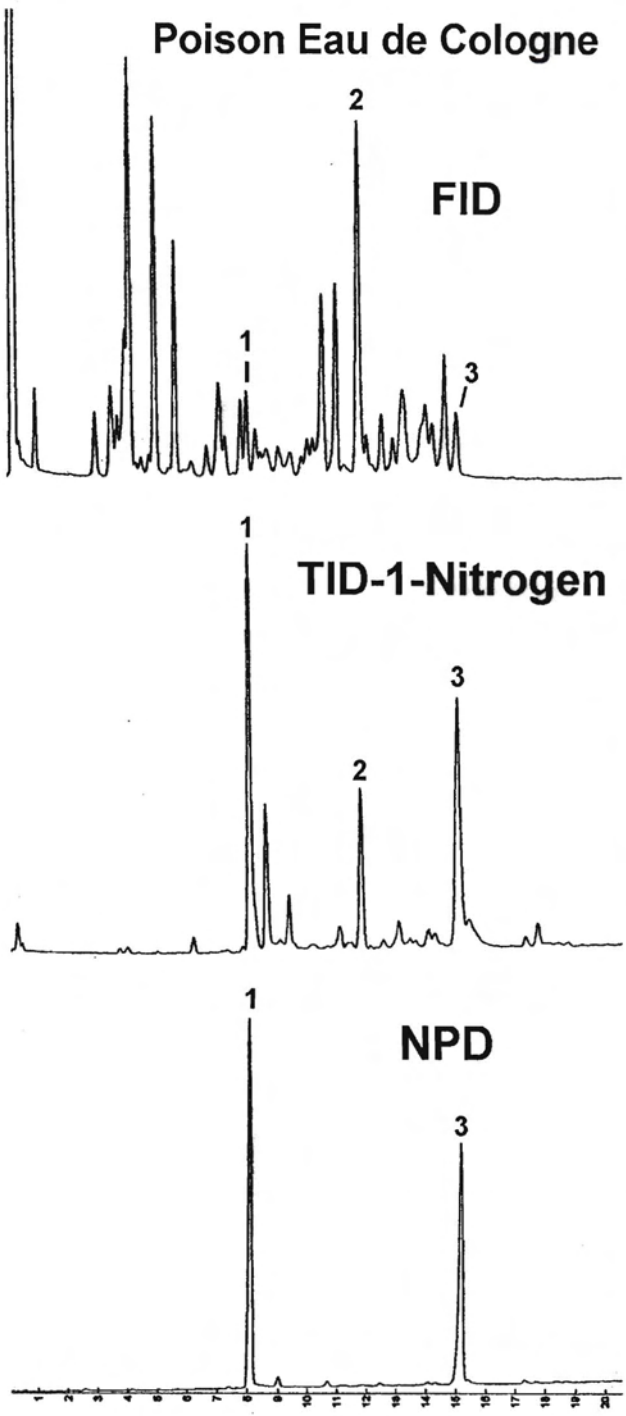
GC Conditions. 15m x 0.53mm x 5.0µm MXT- 1 column. Temperature program = 120 - 220°C at 8°C/min, 220°C - 2min. Helium carrier gas pressure program = 7 - 10.2 psi at 0.26 psi/min, 10.2psi - 2 min. Injector = 220°C, detector = 270°C.

TID-1 Data. Nitrogen through "H_2" line = 8 psi, Nitrogen through "Air" line = 2 psi. TID-1 source heat = 2.550 A, polarization = - 45 V.

NPD Data. Hydrogen = 8 psi, Air = 2 psi. TID-4 type ion source heat = 3.050 A, polarization = - 5 V.

The large Acetonitrile component of the solvent presented an added complication for this sample since both the NPD and TID-1 respond to the Acetonitrile. The NPD chromatogram illustrates a method of dealing with an overly responsive solvent component. This involved extinguishing the H_2 - Air chemistry just prior to injection by reducing the ion source heating current from 3.050 A to 2.050 A, and resetting to 3.050 A at 1 minute into the chromatogram after most of the Acetonitrile had eluted through the detector. This reduction of source heating current during solvent elution is easily accomplished with the thumbwheel adjustment of source heating current on the stand-alone DET Current Supply module.

EXAMPLES OF SELECTIVE DETECTION WITH A COMPACT GC



FRAGRANCES. This analysis provides a good example of the selectivity provided by TID-1 and NPD detection versus an FID detector. The sample analyzed was the commercial fragrance, Poison Eau de Cologne (Christian Dior, Paris). Amongst the numerous peaks exhibited in the FID chromatogram, both the TID-1 and NPD detectors selectively responded to just a few of the sample components.

Unlike the FID and NPD where the sample is consumed in the detector's reactive gas phase H_2 - Air chemistry, the TID-1 detector is non-destructive to sample components. Consequently, aromas of the different fragrance components of this sample could be sensed at the exit of the TID-1 detector, even at retention times when the detector itself was not producing any measurable signal for the component eluting from the column. Hence, during the evolution of the TID-1 chromatogram, it was possible to associate specific aromas with many of the peaks known to be present from the FID chromatogram.

With the present GC system configured originally for either TID-1 or NPD detection, it is easy and inexpensive to convert to the other mode of thermionic detection. In addition, conversion to an FID mode is possible for comparison versus the selective thermionic modes of detection. For users who are interested solely in FID detection with a compact GC, the present system is not very economical. A better choice for those users would be to simply buy the GC and FID from SRI Instruments.

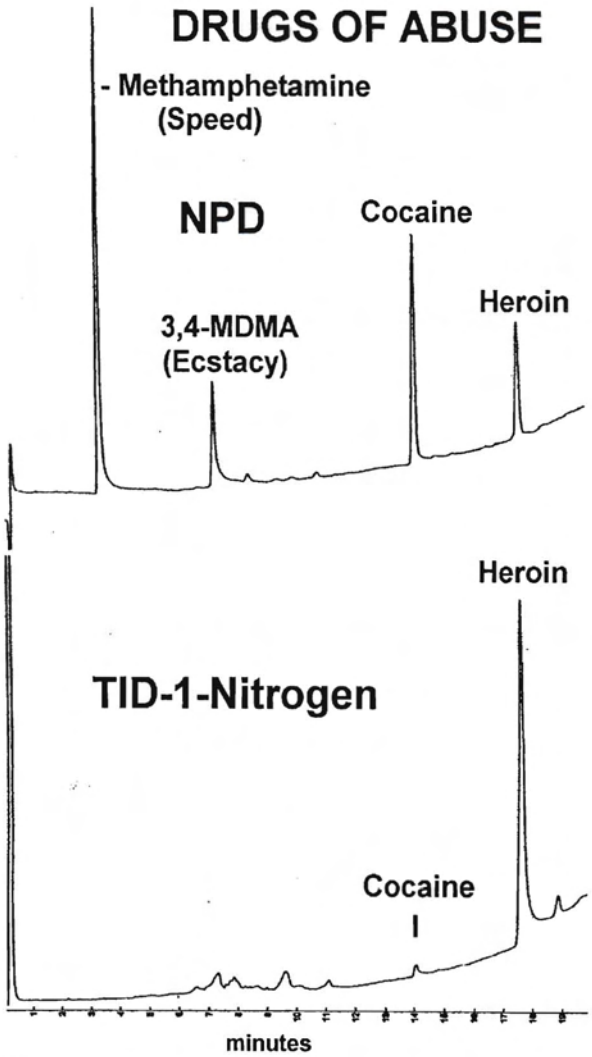
GC Conditions. 15m x 0.53mm x 5.0µm MXT-1 column. Temperature program = 60 - 260°C at 10°C/min, 260°C - 3 min. Helium carrier gas program = 13 - 21 psi at 0.4 psi/min, 21 psi - 3 min. Injector = 250°C, detector = 285°C.

FID Data. Hydrogen=35psi, Air=5psi. Flame ignition at 3.400 Amps, then FID Probe reduced to 0 Amps, polarization = - 45 V.

TID-1 Data. Nitrogen through "H_2" line - 8psi, Nitrogen through "Air" line=2psi. TID-1 ion source heat = 2.600 A, polarization = - 45 V.

NPD Data. Hydrogen=8psi, Air=2psi. TID-4 ion source heat=3.160 A, polarization = - 5 V.

EXAMPLES OF SELECTIVE DETECTION WITH A COMPACT GC



DRUGS OF ABUSE. Another important application of NPD equipment is the detection of drugs of abuse. For applications like this where only compounds containing N atoms are of interest, DET provides an exclusive TID-4 type ceramic ion source which is formulated to provide the best possible N response. This ion source produces more tailing of Phosphorus peaks than a TID-2 type source, so it is not recommended for applications where both N and P detection are required. These data compare the responses of NPD (TID-4) and TID-1 ionization for a sample containing 12 ng each of Methamphetamine, Ecstacy, Cocaine, and Heroin in a Methanol solvent. The NPD detected all four drug compounds, while TID-1 detection provided selectivity for just the Heroin.

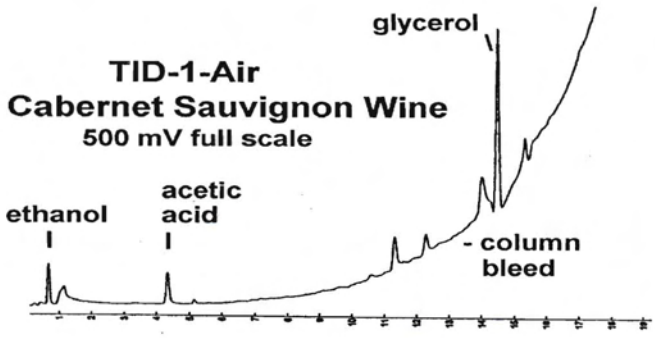
GC Conditions. 15m x 0.53mm x 5.0µm MXT-1 column. Temperature program = 100 - 290°C at 10°C/min, 290°C -1min. Helium carrier gas program = 13 - 20 psi at 0.37 psi/mi, 20 psi - 1 min. Injector = 280°C, detector = 300°C.

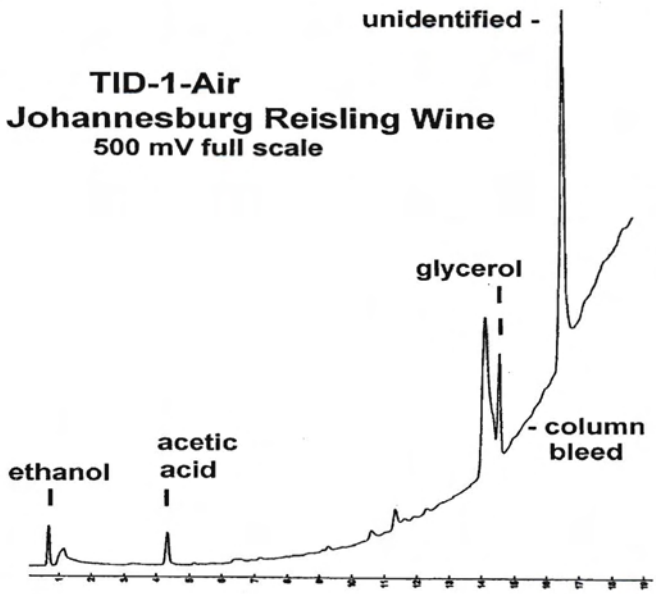
NPD Data. Hydrogen = 8 psi, Air = 2 psi. Ceramic TID-4 type ion source used. TID-4 source heat = 3.050 A, polarization = - 5 V.

TID-1 Data. Nitrogen through "H_2" line = 8 psi, Nitrogen through "Air" line = 2 psi. TID-1 source heat = 2.60 A, polarization = - 45 V.

Aside from the different ceramic coating formulations for the ion sources, a major difference between the NPD and TID-1 modes of detection is the existence of the ignited H_2 and Air chemistry in the NPD. This gas phase boundary layer of highly reactive species causes decomposition of sample compounds into products which ultimately extract electrons from the hot surface to form the detected negative ion current. As a result of this decomposition chemistry, the NPD provides general response to most organic compounds containing N or P atoms, irrespective of the original molecular structure of the compound. In contrast, in TID-1 detection, there is only direct ionization by impact of the sample on the ion source surface with no intervening gas phase chemistry. Hence, TID-1 detection is much more dependent on the detailed molecular structure of the sample molecule, and especially on the existence of electronegative functionalities within that structure.

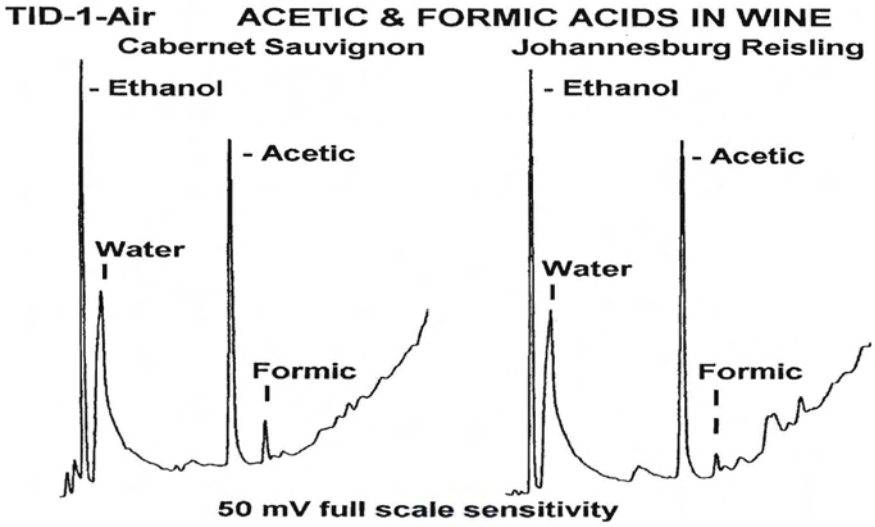
EXAMPLES OF SELECTIVE DETECTION WITH A COMPACT GC





GLYCEROL IN WINE. TID-1 response to Alcohols is largest when Nitrogen is supplied as the detector gas. When Air or Oxygen are supplied as the detector gas, Alcohol responses are diminished even more relative to high responding oxygenates like Glycols, Phenols, and Carboxylic Acids. This characteristic is especially useful in analyses of alcoholic beverages like wine. These data illustrate the detection of Glycerol in two different wine varietals. 1.6µL of each wine was injected into a 240°C glass liner of the injector. The column used was a 30m x 0.53mm x 2.0µm MXT-Wax, with a temperature program of 100 - 240°C at 8°C/min, 240°C - 1 min. He carrier was pressure programmed at 21 - 35 psi at 0.8 psi/min, 35 psi - 1 min.TID-1 ion source heat = 2.65 A. The column temperature program pushed the upper limit of the Carbowax® polyethylene glycol column coating, and there was a significant column bleed contribution at the end of the chromatograms. This was undoubtedly enhanced by the fact that TID-1 ionization provides excellent detection for Glycols.

ACETIC AND FORMIC ACIDS IN WINE. When the early segments of the Cabernet Sauvignon and Johannesburg Reisling chromatograms are amplified as shown below, peaks for Acetic and Formic Acids are clearly indicated. One of the attributes of TID-1 detection is that it detects Formic Acid, whereas an FID detector does not. Another attribute is that TID-1 detection is not destructive, so aromas of sample constituents can be sensed by a sniffing tube extending from the detector exit port out the top of the GC package.



This is a universal thermionic detector power supply that can also be used in conjunction with NPD equipment on the Agilent Technologies 6890 GC to provide better response stability with time, plus the capability of easily changing the 6890 NPD to other modes of thermionic detection.

Selective Detection of Oxygenates and Nitro-Compounds. For this detection, DET's TID-1 type ceramic ion source is used in the detector structure, and either Nitrogen or Air are supplied via a gas tee to the "H_2" and "Air" detector gas inlets on the GC. A Nitrogen detector gas environment normally provides the best discrimination versus Hydrocarbon compounds, while an Air environment can be used to suppress responses from certain classes of Oxygenated compounds relative to others. Phenols, Carboxylic Acids, Glycols, Vanillin, and Methyl Salicylate are known to provide especially large TID-1 ion signals in comparison to Alcohols, Aldehydes, Ketones, and Phthalates. All these Oxygenates are detected with good selectivity versus Hydrocarbons. In comparison to other Oxygenates, Ethers (e.g., MTBE) are known to have very small TID-1 responses. Very, very large TID-1 responses are obtained for Nitro compounds like TNT, Methyl Parathion, and 4-Nitrophenol which have a strong electronegative NO_2 functional group located in a para location relative to other functionalities on a Benzene ring.

TID-1 detection is compatible with either He or N_2 as the GC carrier gas. In applications where N_2 carrier provides adequate chromatographic separation, there is the advantage that both carrier and detector gases can be the same single gas supply. One notable feature of TID-1 detection is that it is nondestructive, so aromas of different chemical compounds can be sensed at detector exit tubing extending out the top of the GC package. Possible applications of this compact GC with TID-1 detection include the selective detection of Ethanol in Gasoline; high sensitivity to TNT and 2,4-Dinitrotoluene versus other explosives; high sensitivity and selectivity to nitro pesticides like Methyl Parathion; excellent selectivity for detecting Heroin amongst other drugs of abuse; and detection of Acetic and Formic Acids in Wine.

Selective Detection of Nitrogen-Phosphorus Compounds. NP detection requires supplies of Hydrogen and Air to be connected to the GC in addition to the column carrier gas. DET manufactures 2 types of ceramic ion sources for use in NP detection. One is a Black Ceramic, TID-2 type ion source, which has a surface formulated to provide sharp Phosphorus peaks. TID-2 is recommended for user's requiring P or both P and N detection (e.g., pesticides). A second White Ceramic, TID-4 type ion source, is formulated to provide the best possible N response at the sacrifice of some tailing of P peaks. TID-4 is recommended for users requiring only N detection (e.g., drugs of abuse). Both of these NP ion source types are identical to ion sources used widely on the Agilent Technologies 6890 NPD.

Easy and Inexpensive Conversion from One Detection Mode to Another. A GC system originally configured for either Oxygenate or NP detection, can be adapted to the other mode of selective detection by simply replacing the ion source (cost $285), and by plumbing in the appropriate detector gases. Some of the accompanying application illustrations also demonstrate that universal FID detection is possible by replacing the ceramic ion source with a bare wire FID i gnitor/polarizer element. Selective detection of volatile Halogenates is also a possibility with a ceramic coated TID-3 type ion source.

Part Numbers/Prices:

001-931-11, Oxygenates/Nitro Analyzer, $13,200. includes TID-1 ion source, gas fittings for same gas through 2 detector gas lines as well as carrier gas; 15m x 0.53mm MXT-1 column or equivalent; power strip for 115 Vac.

101-931-11, NPD (TID-2) Analyzer, $13,200. includes TID-2 ion source for P and/or both N and P; 15m x 0.53mm MXT-1 column or equivalent; 115 Vac power strip

501-931-11, NPD (TID-4) Analyzer, $13,200. Same as above except includes TID-4 ion source for best N signal.

Interchangeable Ion Sources:

010-901-00, TID-1 Ceramic Ion Source, $285.
use with N_2 or Air detector gases, provides selective response to Oxygenates and Nitro compounds.

010-902-00, TID-2 Ceramic Ion Source (NPD), $285.
requires H_2 and Air detector gases, provides selective response to N or P compounds with very sharp P peaks.

010-904-00, TID-4 Ceramic Ion Source (NPD), $285.
requires H_2 and Air detector gases, provides NP selectivity with best possible N response.

020-902-00, FID Ignitor/Polarizer Probe, $195.
requires H_2 and Air detector gases, provides universal Hydrocarbon response.

010-903-00, TID-3 Ceramic Ion Source, $285.
use with N_2 or Air detector gases, provides selective detection of volatile Halogenates such as Trihalomethanes.