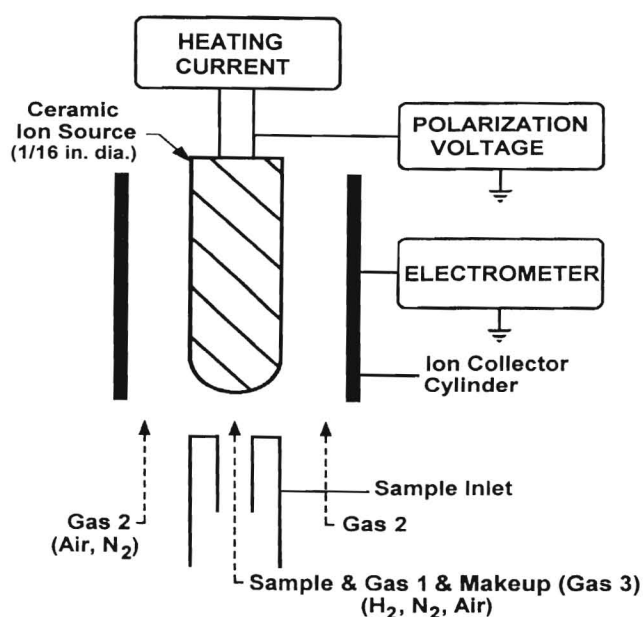


# Thermionic Surface Ionization

Unique GC detection technology converts selected chemical compounds into measurable ion currents using a family of electrically-heated, catalytically-active ionizing surfaces made of proprietary ceramic materials.

Optimum concentric cylinder detector geometry used on the Agilent 6890/7890 NPD and all DET hardware features a cylindrically-shaped ion source positioned on the axis of an ion collector cylinder, with top access for easy interchange of ion source types.

THERMIONIC IONIZATION DETECTOR DESIGN  
(CONCENTRIC CYLINDER GEOMETRY)



4 parameters determine selectivity and sensitivity:

1. catalytic ionizing activity of the ion source as determined by the composition of its ceramic coating (an unlimited number of ceramic formulations are possible);
2. temperature of the ion source (typically in the range 300 - 900°C);
3. composition of the gases flowing past the ion source (e.g., N<sub>2</sub>, Air, O<sub>2</sub>, N<sub>2</sub>O, H<sub>2</sub>, and combinations thereof);
4. the magnitude of the polarizing voltage between the ion source and collector (typical range - 4 to - 100 V).

Multiple modes of detection are achieved using the same basic equipment, a choice of different ion source ceramics, and various permutations of the 4 operating parameters - detector selectivity choices include compounds containing N, P, O, Cl, Br, I, Pb, Sn, or Si atoms, or NO<sub>2</sub>, Pyrrole, CH<sub>2</sub>, and certain other functional groups - new compound selectivities continue to be identified, as well as many tandem combinations of different detection modes.

Inexpensive equipment based on Thermionic Surface Ionization principles provides detection capabilities unmatched by any other type of GC detector.

# DET

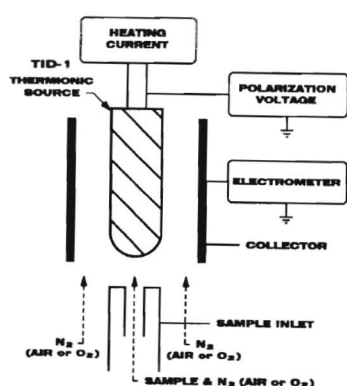
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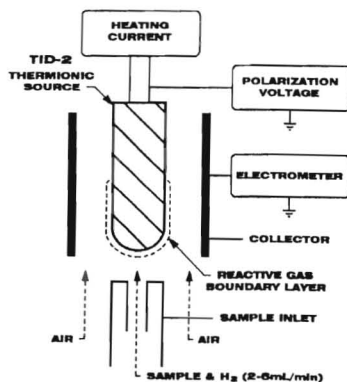
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## GC DETECTOR INNOVATIONS by DET (different implementations of the same basic detector geometry)

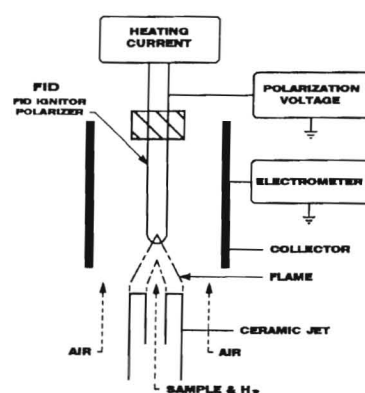
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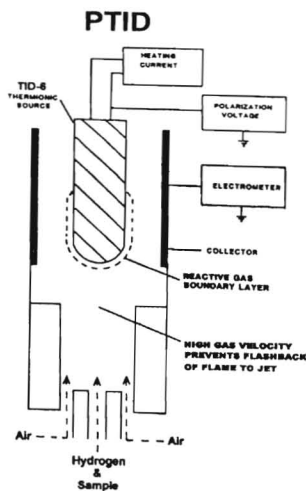
**NPD**



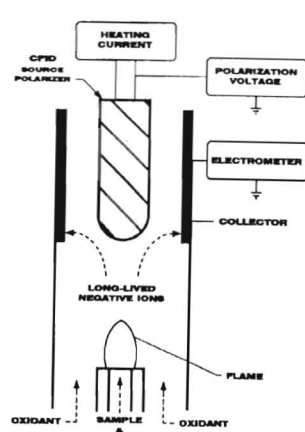
**FID**



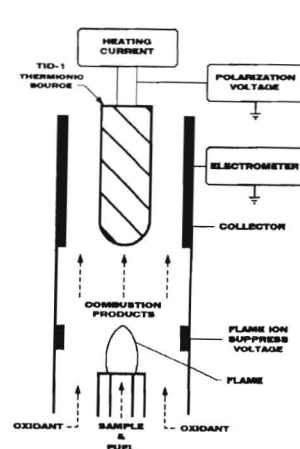
**PTID**



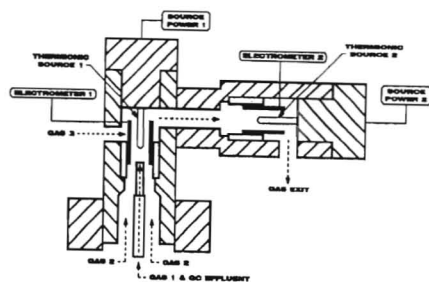
**REMOTE FID**



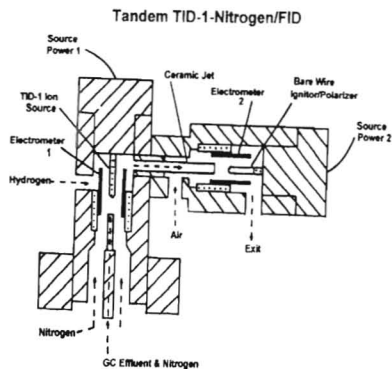
**FTID**



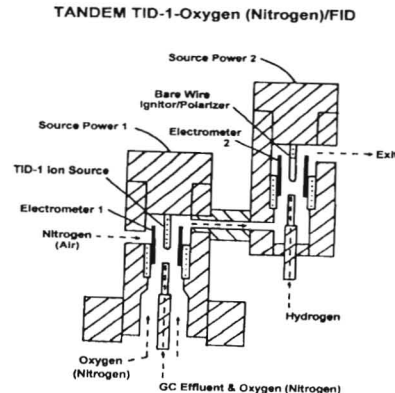
**TANDEM TID**



**TANDEM TID-Nitrogen/FID**



**TANDEM TID-Oxygen/FID**



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## **DET Chemical Detection Products based on Scientific Principles of THERMIONIC SURFACE IONIZATION and FLAME IONIZATION featuring Electrically Heated Ion Sources made of Proprietary Ceramics**

**multiple modes of selective detection using common detector components**

**COMMON COMPONENTS** - inexpensive detection equipment features a concentric cylinder geometry in which interchangeable ion source elements are positioned on the axis of a collector electrode, with the ion sources heated by an electrical current and polarized at a negative voltage with respect to the collector - ion sources are small cylindrical rods formed from multiple layers of ceramic coatings molded over a wire core and mounted on a stainless steel flange.

**THERMIONIC IONIZATION DETECTION (TID)** - sample compounds directly impact the ion source and form gas phase ions by extracting negative charge from the ceramic surface - selectivity and sensitivity of detection depends on the catalytic ionizing activity of the ceramic, and on whether the detector gas environment is inert (e.g., Nitrogen) or oxidizing (e.g., Air or Oxygen) - available types of ceramic ion sources are as follows:

**TID-1** - selective for some Nitro and Halogenated compounds at Femtogram and Picogram levels; many Oxygenates at Picogram and Nanogram levels with especially large responses for Phenols, Carboxylic Acids, Glycols, Glycerol, Vanillin, and Methyl Salicylate; Pyrrole vs. Pyridine functional groups; Water vapor at ppm levels with Air detector gas; also used in the Catalytic Combustion Ionization mode for selectivity to Methylene ( $\text{CH}_2$ ) functional groups.

**TID-10** - similar selectivity as TID-1, but with enhanced sensitivity to high concentrations of compounds with branched Methyl ( $\text{CH}_3$ ) functional groups; also can be used in the Catalytic Combustion Ionization mode.

**TID-3** - selective for volatile Halogenates such as Trihalomethanes.

**TID-5** - selective for Br and I compounds with suppressed Cl response.

**TID-7** - selective for Halogenates such as PCBs

**NITROGEN PHOSPHORUS DETECTION (NPD)** - NP selectivity turns on when the ion source is heated sufficiently (i.e., 600 - 800°C) to ignite a dilute mix of Hydrogen in Air to form a chemically reactive gaseous boundary layer around the hot ion source surface - samples are decomposed in the ignited boundary layer, and electronegative N and P decomposition products extract negative charge from the hot ion source to form detectable gas phase ions - DET has developed 2 types of ceramic ion sources for NP detection as follows:

**TID-2 (Black Ceramic)** - NP detection with negligible tailing of P peaks - 70fg P/sec detectivity;

**TID-4 (White Ceramic)** - NP detection with the largest possible N response - 70fg N/sec detectivity;

**PHOSPHORUS THERMIONIC IONIZATION DETECTION (PTID)** - a TID-6 ion source is located downstream of a small diameter flow restrictor such that when the ion source is heated sufficiently to ignite a pre-mixed stream of high concentration Hydrogen in Air, the high total gas flow prevents flame flash back from the source to the original mixing point of the Hydrogen and Air - like an NPD, the ignited chemistry remains as a boundary layer about the hot source - this mode provides selective detection for P compounds with very large signals and suppressed N response.

**REMOTE FID DETECTION (RFID)** - a CFID ion source & collector electrode are located several centimeters downstream of a self-sustained Hydrogen/Methane/Air flame - ions produced by Hydrocarbon combustion dissipate rapidly downstream of the flame, but combustion of Lead (Pb), Tin (Sn), Phosphorus (P), or Silicon (Si) compounds produces long-lived ions that persist to be selectively detected at the downstream collector - an organic fueled flame improves selectivity.

**FLAME THERMIONIC IONIZATION DETECTION (FTID)** - an electrically heated TID-1 or TID-2 ion source located several centimeters downstream of a self-sustained Hydrogen/Methane/Air flame re-ionizes the electronegative neutral products of the flame combustion of samples - a TID-2 source provides selectivity for Halogenates, while a TID-1 source provides selectivity for Halogenates and Nitrogen compounds.

**FLAME IONIZATION DETECTION (FID)** - an FID Probe consisting of an uncoated bare wire loop, and a collector electrode are located adjacent a self-sustained Hydrogen/Air flame burning at an unpolarized ceramic tipped jet - the FID Probe serves as flame ignitor and polarizer, and the flame ionization provides Universal detection of organic compounds.

**HOT WIRE COMBUSTION IONIZATION DETECTION (HWCID)** - similar to a PTID configuration except a heated bare wire FID Probe is used to maintain an ignited Hydrogen/Air boundary layer - Universal detection like an FID, but sensitivity about 100 times less than an FID - does not require a jet structure - provides about a factor of 2 enhancement for Aromatics vs. Alkane Hydrocarbons.

**CATALYTIC FLAME IONIZATION DETECTION (CFID)** - uses a self-sustained flame similar to an FID except includes an electrically heated ceramic CFID ion source to augment the gaseous flame ionization with surface ionization from the hot catalytic ion source - Universal detection with similar response factors for Halogenates and Hydrocarbons.

**CATALYTIC COMBUSTION IONIZATION DETECTION (CCID)** - uses a catalytic TID-1 or TID-10 ion source heated to 300 - 400°C in an oxidizing detector gas environment to ignite a momentary burst of flame ionization as individual peaks of high concentration sample compounds elute from the GC column and impact the ion source - provides selective ionization of Methylene ( $\text{CH}_2$ ) functional groups in linear chain Alkane, FAME, and Triglyceride compounds with discrimination vs. compounds with unsaturated Carbon double bonds.

**TANDEM DETECTION (TID/NPD, NPD/TID, FID/FTID, TID/FID, etc.)** - 2 simultaneous detector signals with many different possible combinations of ion sources and detector gas environments.

**REACTOR THERMIONIC IONIZATION ANALYSIS (RTIA)** - stand-alone TID or NPD transducer attached to a heated inlet reactor with a sample pump pulling ambient Air through both transducer and reactor - provides selective screening of vapors generated by Thermal Desorption and Thermal Oxidation of non-volatile constituents of liquid or solid samples - TID-1 or TID-10, TID-3, TID-7, and NPD (TID-2 or TID-4) ion sources can be used in the transducer for different selectivities.

**STAND-ALONE TID, NPD, OR FID TRANSDUCERS** - transducer exit connected to a sampling pump provides real time monitoring of selective or universal organic vapors in incoming ambient Air stream - selectivity determined by type of ion source element installed.



## DET Retrofit Equipment for Different Brand GC Instruments

**GENERAL CONSIDERATIONS** - DET ion sources are available mounted in either a 3/4 inch hexagonal shaped flange or in a 1/4 inch tube. The hex mounting is used in all DET hardware structures as well as in Agilent 6890/7890 NPD equipment, whereas the tube mounting is used in NPD hardware structures designed by Thermo Scientific and SRI Instruments.

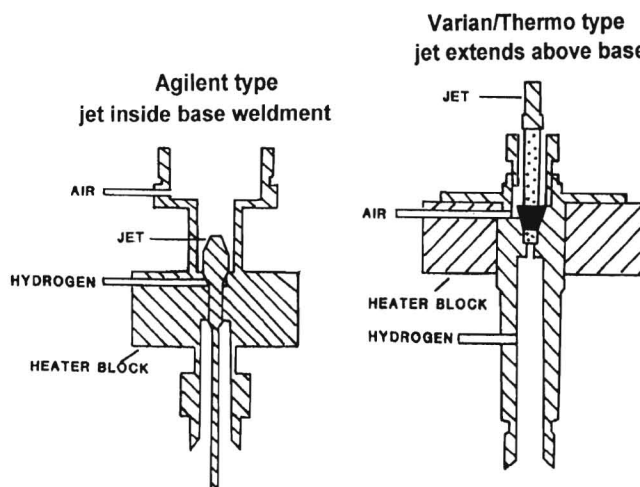
Retrofit DET hardware structures are designed to custom fit onto an FID/NPD detector base already on the GC, so that the existing detector heater block and pneumatics lines can be used.

Generally, GC FID bases have one of the 2 basic styles illustrated in the figure. For the Varian/Thermo type base, the jet extends above the detector base, and a DET retrofit includes a ceramic tipped jet and a tower structure that fits down over the jet. An ion source mounts into the top of the tower such that it is positioned in close proximity to the top of the jet. A DET retrofit tower in this case is identified as an NPD/TID/FID assembly because all variations of those modes of detection can be achieved with the appropriate choice of ion source type and detector gases.

For the Agilent type FID base, the jet is located down inside a stainless steel weldment, and a DET retrofit tower extends down into and on top of the weldment. With this retrofit configuration, the ion source and surrounding collector electrode are constrained to a location several centimeters downstream of the top of the jet. Unlike an FID, the jet in an NPD is not required to support a self-sustaining flame, so DET recommends using a wide bore jet that allows capillary columns of 0.53 mm diameter or less to be inserted clear through the jet to a location closer to the ion source. A DET retrofit tower for this type of detector base is identified as a Remote FID assembly because it can be used for NPD/TID detection modes as well as Remote FID and FTID modes of selectively which use the column pulled down to the jet top and a self-sustaining flame ignited at the jet.

**AGILENT 6890/7890 GC MODELS** - Agilent designed the 6890 NPD hardware to accommodate the hex flanged ion sources manufactured by DET. Consequently, any of the different type ceramic ion sources developed by DET can be mounted into 6890/7890 NPD hardware and used to achieve modes of detection beyond just NPD. A limitation of 6890/7890 NPD equipment is that the associated Agilent NPD electronics is not optimum in providing Constant Voltage heating of the ion source instead of preferred Constant Current heating, as well as being limited to a very low polarization between the ion source and collector electrode. As an alternative to powering ion sources with Agilent's NPD Bead Voltage supply, DET has a stand-alone Current Supply module for more stable Constant Current heating of ion sources plus a selection of both low and high polarizations. Whereas, a low polarization is fine for NP detection, higher polarizations can provide 10 times better signal to noise for other modes of selective TID detection. DET also recommends using a wide bore jet with 6890/7890 NPD equipment so that capillary columns of 0.53mm diameter or less can be inserted clear through the jet to a termination closer to the ion source. This eliminates any possible degrading interaction of samples with the jet metal; it eliminates jet orifice clogging from complex sample matrices; and eliminates the need to ever replace the jet. DET also recommends that 6890/7890 NPD users avoid using the Adjust Offset feature of the electronics as that inevitably operates the ion source hotter than needed, and shortens ion source lifetime.

2 Different Styles of FID Detector Bases and Jet Locations



Varian/Thermo type base is easier to fit with DET NPD/TID detector tower structures.



**THERMO SCIENTIFIC TRACE GC** - DET retrofit hardware consists of an NPD/TID/FID tower assembly and ceramic tipped jet that mount easily onto the Thermo detector base. In contrast to Thermo's NPD hardware structure, the DET retrofit provides a preferred concentric cylinder geometry for the ion source and collector, and provides an easy top access for self-aligning mounting of the ion source. Ion sources used with the DET retrofit are identical to those used with Agilent 6890/7890 equipment, and all DET ion source types are available for use in NPD, TID, or FID modes. Thermo's NPD electronics currently are the best available with regard to providing optimum response in all NPD and TID modes of detection, and the combination with DET retrofit hardware provides easy conversion to many different types of selectivity and applications. In addition to an NPD/TID/FID tower, the Thermo base can also be fit with a Remote FID tower which positions the ion source several centimeters downstream of the jet so a flame can be ignited at the jet for additional Remote FID and FTID modes of selective detection. A Tandem Tower configuration has also been fit onto the Thermo base so that 2 simultaneous detector signals can be obtained from the same GC effluent.

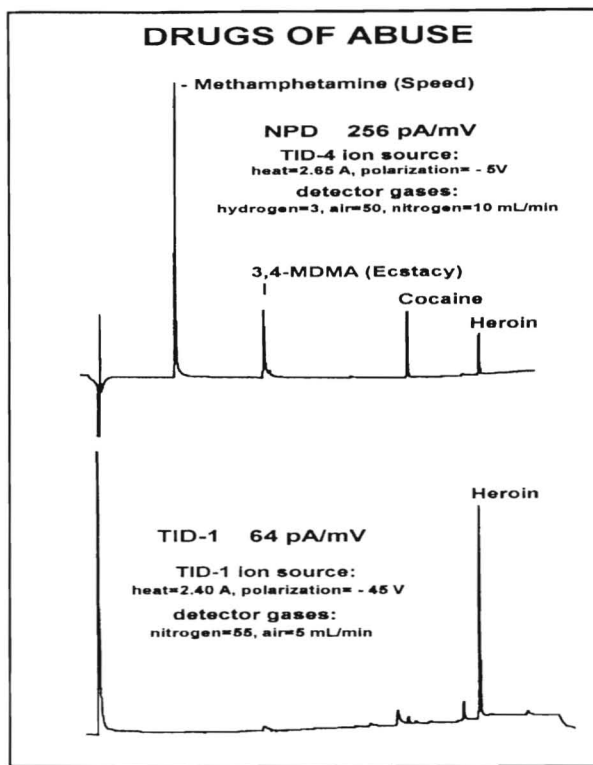
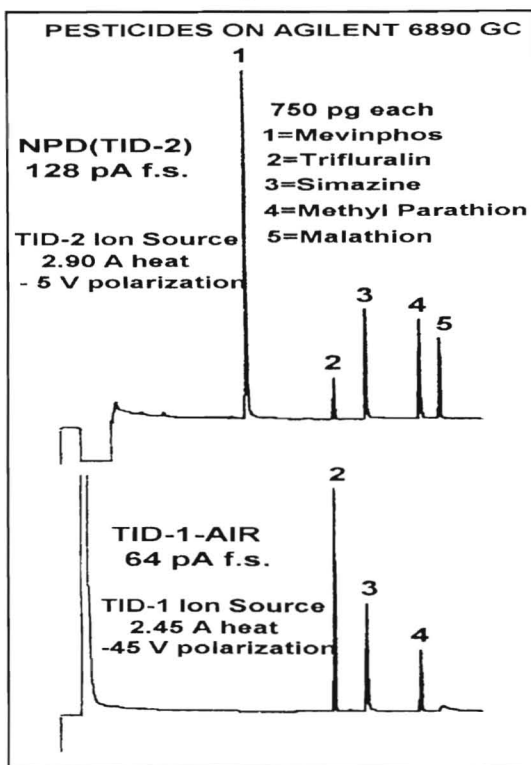
**VARIAN/BRUKER TSD GC MODELS** - Similar to the Thermo retrofit, a DET retrofit NPD/TID/FID tower assembly and ceramic tipped jet are designed to mount easily onto the Varian/Bruker detector base. In contrast to the Varian/Bruker TSD hardware structure, the DET retrofit is about half as large, and provides a preferred concentric cylinder geometry for the ion source and collector. It also provides an easy top access for self-aligning mounting of the ion source into the tower. Ion sources used with the DET retrofit are identical to those used with Agilent 6890/7890 equipment, and all DET ion source types are available for use in NPD, TID, or FID modes. The DET hardware is compatible with the Varian/Bruker TSD electronics which works fine for NP detection. However, for detection modes other than NPD, a stand-alone DET Current Supply is recommended for powering the ion sources in order to achieve a tenfold improvement in signal to noise. Like the Thermo retrofits, alternative Remote FID and Tandem TID tower assemblies are available to provide additional modes of selective detection.

**SRI INSTRUMENTS GC MODELS** - Like the Thermo and Varian/Bruker retrofits, a DET hardware retrofit for SRI GC models consists of an NPD/TID/FID tower assembly and ceramic tipped jet that mount onto a heated FID/NPD base on the SRI GC. As with other DET retrofits, the DET hardware provides an optimum concentric cylinder geometry for stream-lined gas flow and efficient ion collection, and easy end mounting of the ion source. If SRI's NPD electronics are used to power the ion sources, then the ion source structures are identical to those used on Agilent 6890/7890 GC models except there is no Twinex electrical connector attached. An alternative to using SRI's NPD electronics is to substitute a stand-alone DET Current Supply for more stable precision control of ion source heat and polarization, and more user friendly adjustments. When the DET supply is used, then the ion sources include the Twinex connector and are identical to those used on Agilent equipment. SRI's NPD signal amplifier suffices for signal measurement, and their built-in Peak Simple data system provides data analysis capability when coupled to a laptop or desktop computer. The combination of an SRI GC and DET hardware with multiple choices of interchangeable ion sources provides a small portable system applicable to many different types of chemical analyses.

**HP 5890 MODEL** - The FID/NPD base on an HP5890 GC is the "Agilent" configuration described earlier. DET retrofit hardware in this case consists of a Remote FID tower assembly that positions the ion source several centimeters downstream of the jet. In addition, the DET retrofit includes a wide bore jet that allows capillary columns of 0.53 mm diameter or less to be inserted clear through the jet to a termination closer to the ion source. This is the preferred configuration for NPD and TID modes of detection. For Remote FID and FTID modes, the column is pulled down flush with the top of the jet and a flame is ignited at that jet top. DET's 5890 retrofit hardware is not compatible with existing 5890 detector electronics, so a stand-alone DET Current Supply is required, as well as a stand-alone electrometer such as a Keithley 6485 Picoammeter. The DET 5890 retrofit combination of hardware and electronics provides the capability for easy interchange among all available modes of NPD, TID, Remote FID, and FTID selective detection. In addition, the stand-alone electronics can be used to support selective detection with any stand-alone DET transducers.



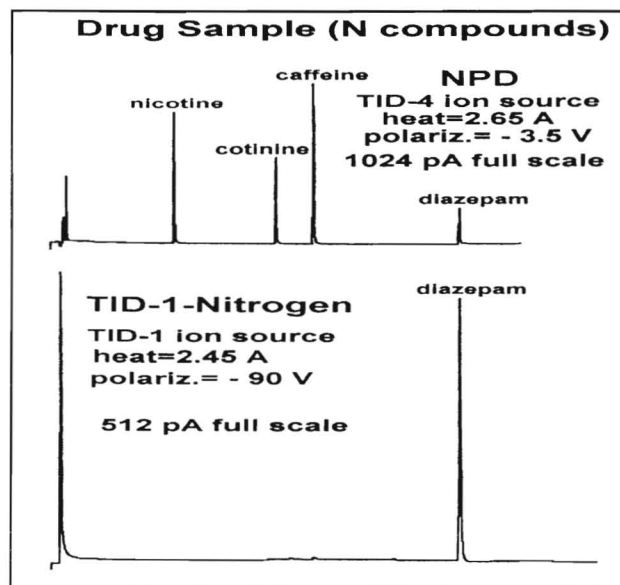
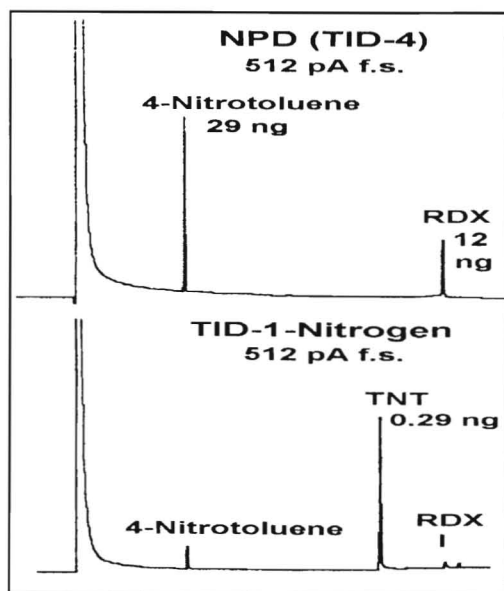
## THERMIONIC SURFACE IONIZATION DETECTION FOR GC selectivity for NITROGEN and PHOSPHORUS compounds (NPD)



TID-2 Black Ceramic designed for sharp P peaks

TID-4 White Ceramic designed for best N response

TID-1 mode is more compound selective than NPD



Nitro Explosives detection – NPD detects all N compounds – TID-1 mode has exceptional sensitivity for TNT

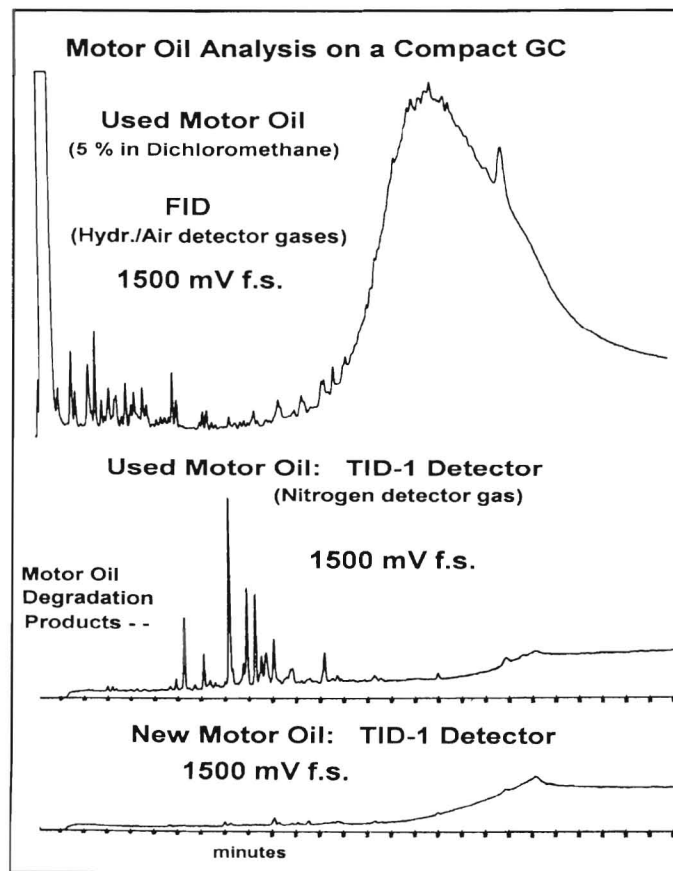
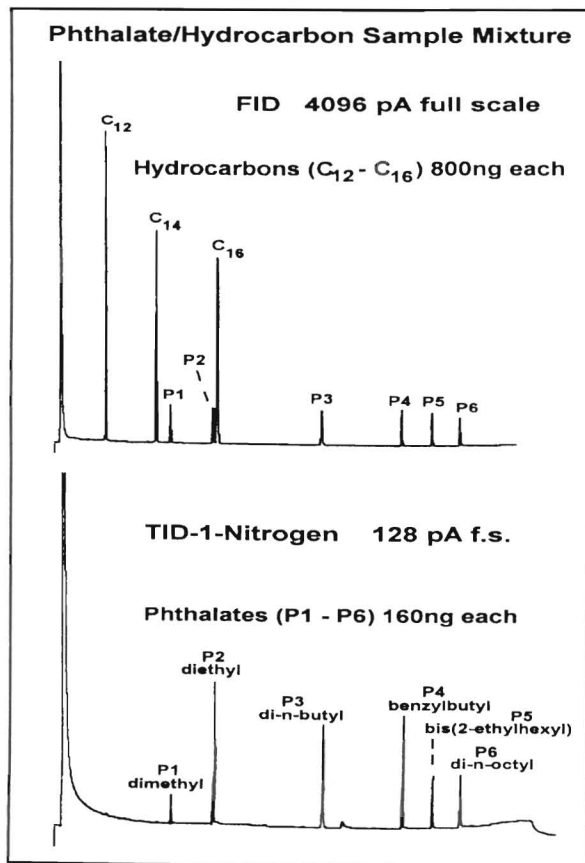
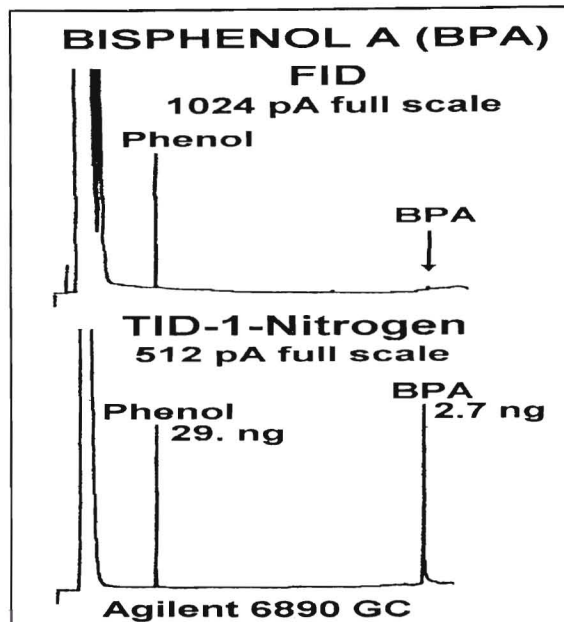
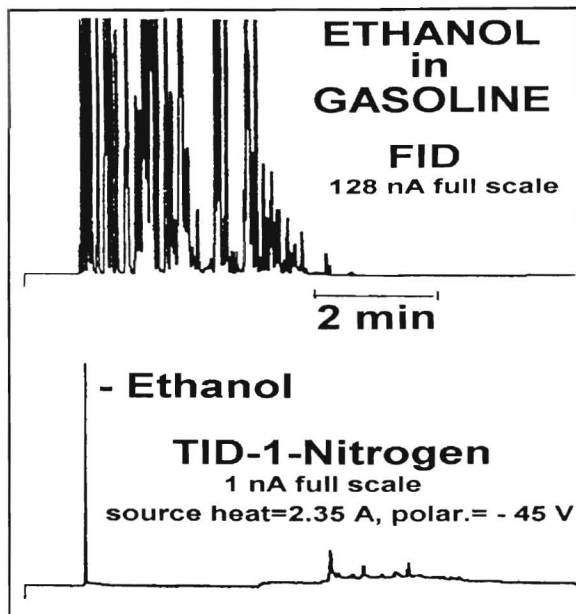
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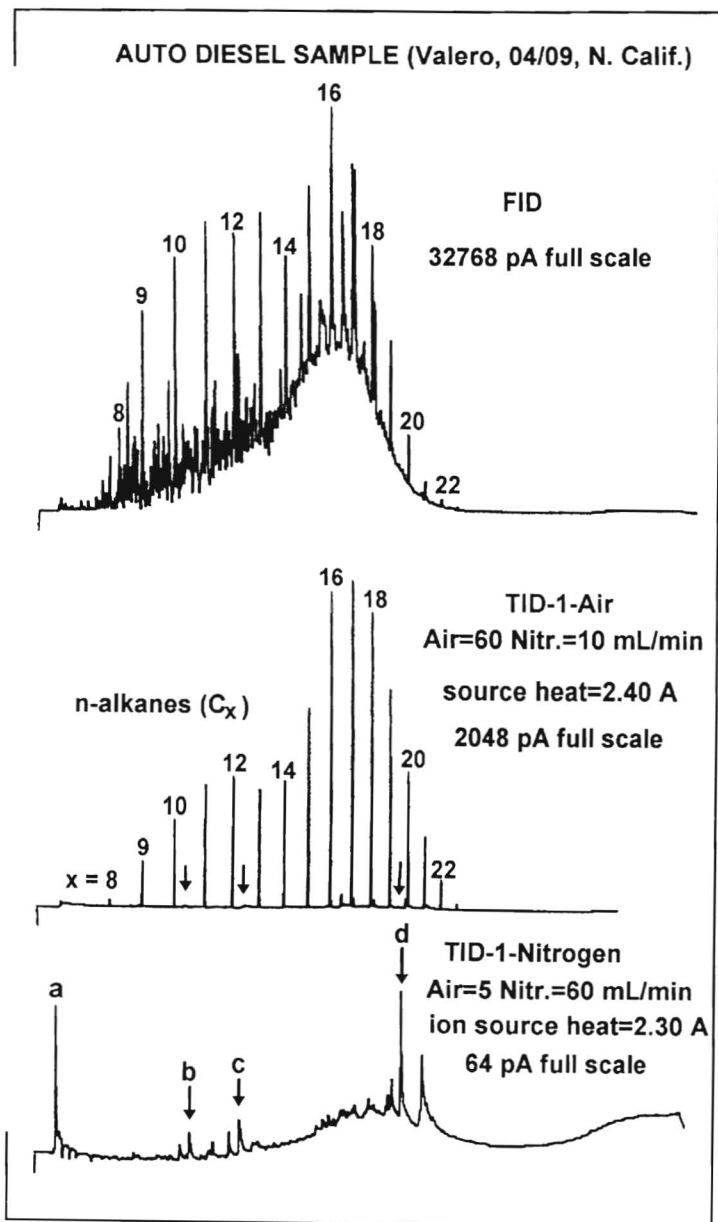
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## THERMIONIC SURFACE IONIZATION DETECTION FOR GC selectivity for OXYGENATED compounds (Alcohols, Phenols, Carboxylic Acids, Glycols, Phthalates, Water, etc.)

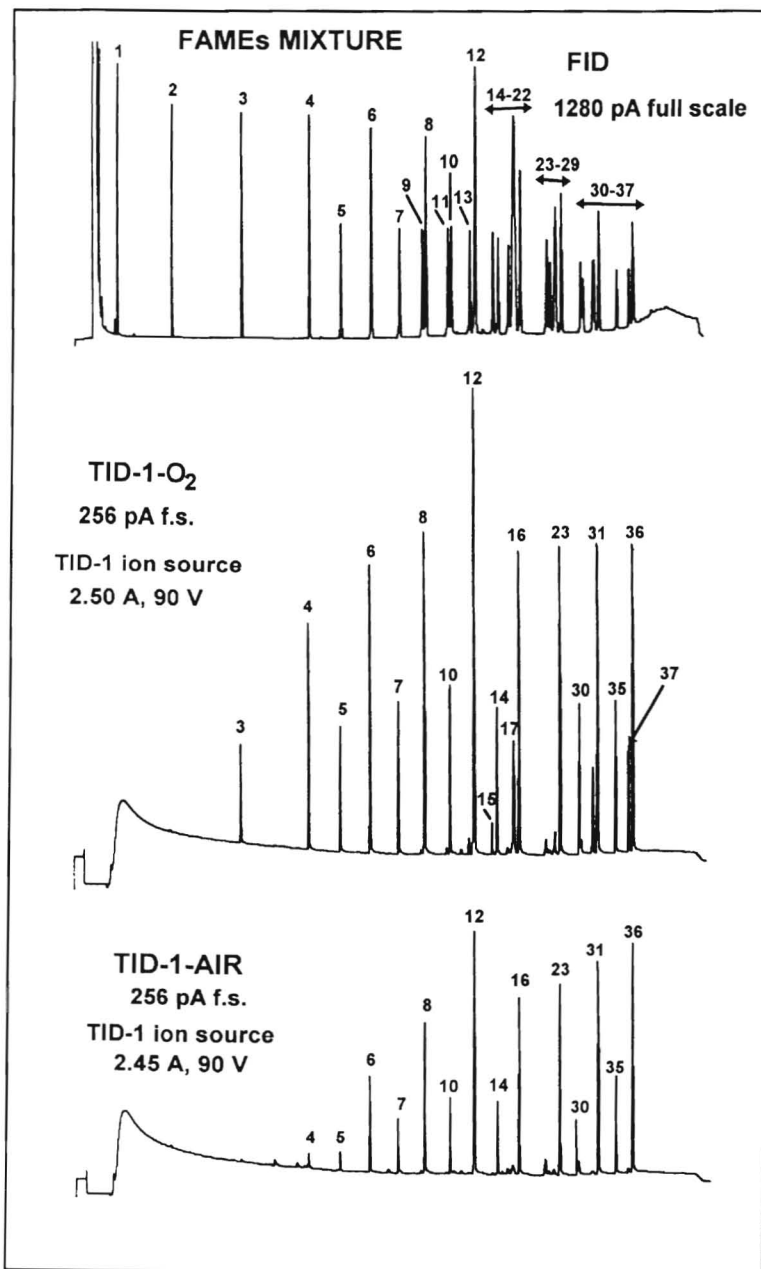




### CATALYTIC COMBUSTION IONIZATION DETECTION FOR GC selectivity for compounds containing chains of CH<sub>2</sub> functional groups in PETROLEUM, BIOFUEL, and FAME (Fatty Acid Methyl Ester) samples

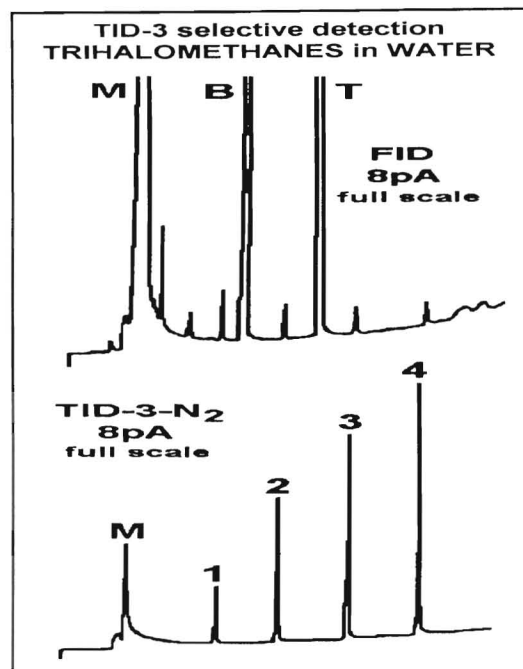
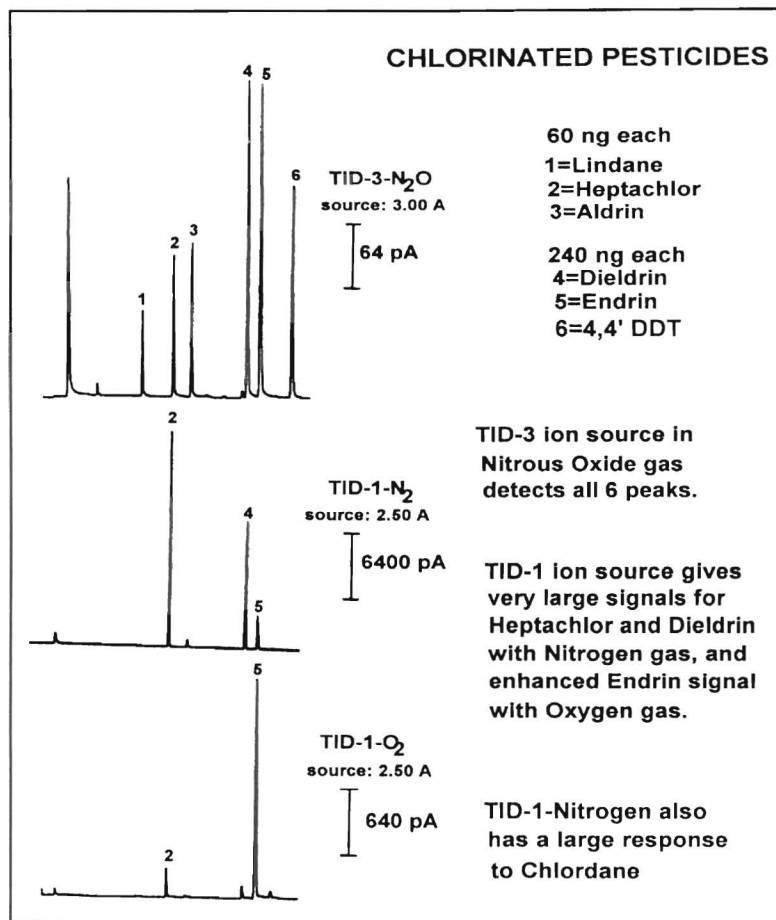


The conventional FID detected hundreds of compounds in this diesel sample, while the hot (300-400°C) TID-1 ceramic in the Air environment selectively ignited combustion ionization from just Methylene (CH<sub>2</sub>) groups in the Linear Alkane components of the sample.

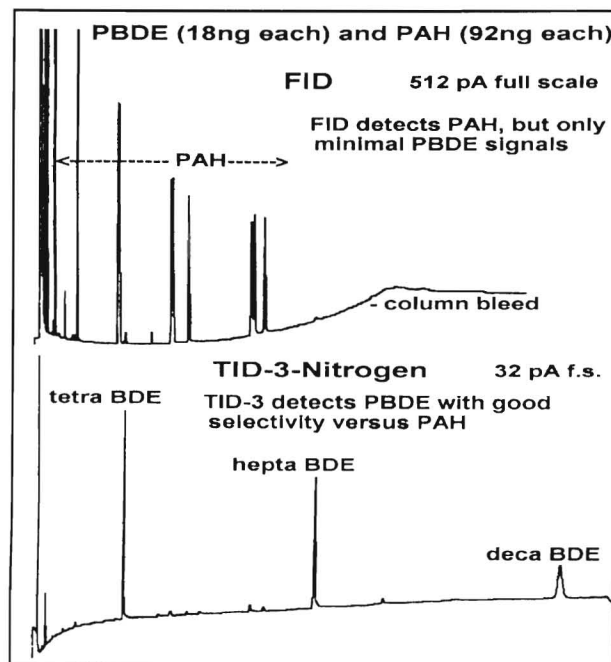
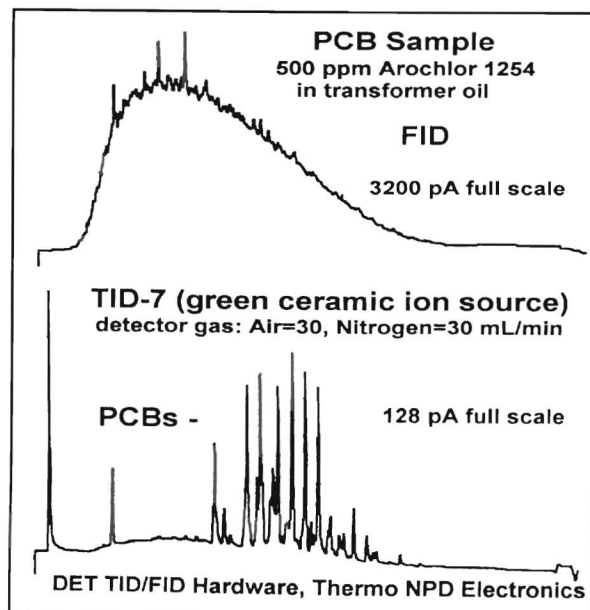


TID-1 detection of long chains of CH<sub>2</sub> groups in Fatty Acid Methyl Esters (FAMES). Mixture analyzed contained both Saturated and Unsaturated FAME compounds. TID-1-Air detected only the Saturates.

## THERMIONIC SURFACE IONIZATION DETECTION FOR GC selectivity for HALOGENATED (Cl, Br, I) compounds



Samples in Water solution:  
M=2500 ng Methanol,  
B & T=47ng each Benzene & Toluene,  
0.64ng each Trihalomethanes,  
1=CHCl<sub>3</sub>, 2=CHCl<sub>2</sub>Br, 3=CHClBr, 4=CHBr<sub>3</sub>





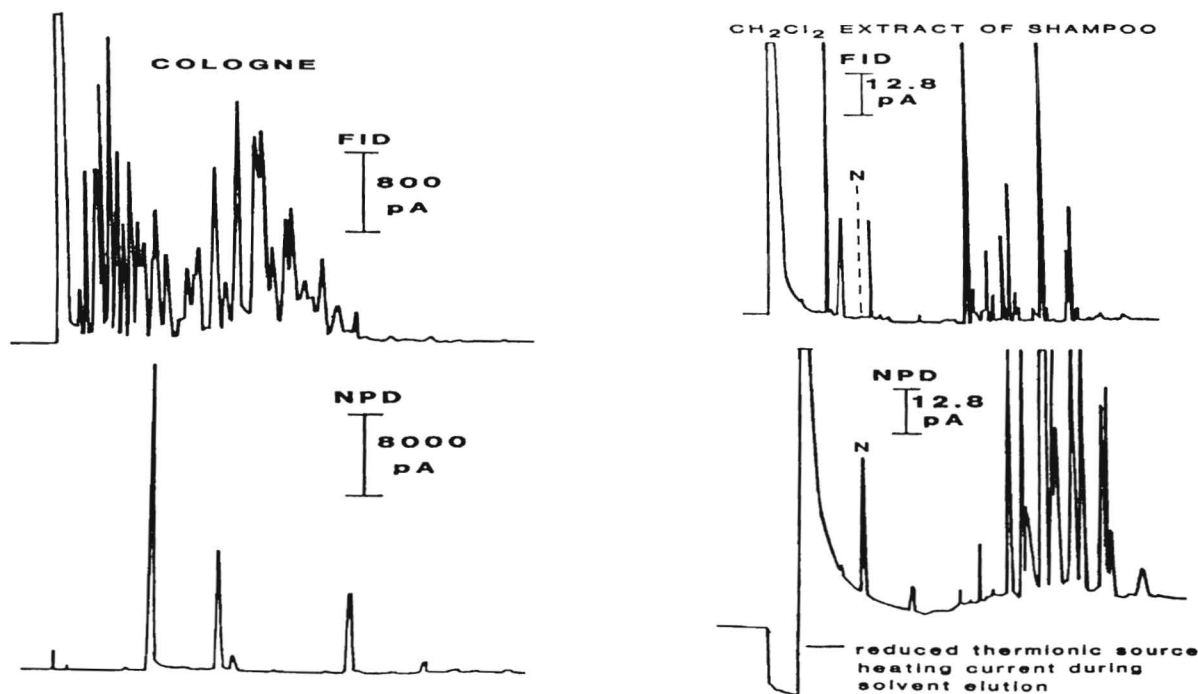
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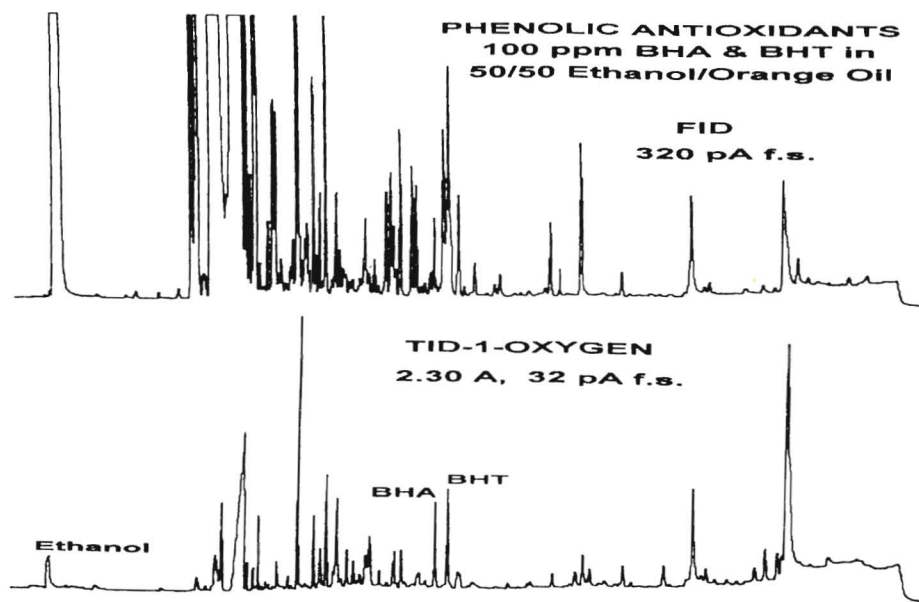
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**DET SELECTIVE DETECTORS SIMPLIFY GC ANALYSES OF COMPLEX SAMPLES**  
**THERMIONIC SURFACE IONIZATION** - no other chemical detection technology provides so many unique selectivity choices using the same inexpensive equipment.



**NPD - selectivity & enhanced sensitivity detects N constituents of Cologne & Shampoo**



**TID-1 ion source in an oxidizing gas environment provides large Phenol responses vs. other Oxygenates, and allows BHA & BHT antioxidant detection in a complex essential oil matrix.**

12/6

# DET

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## DET

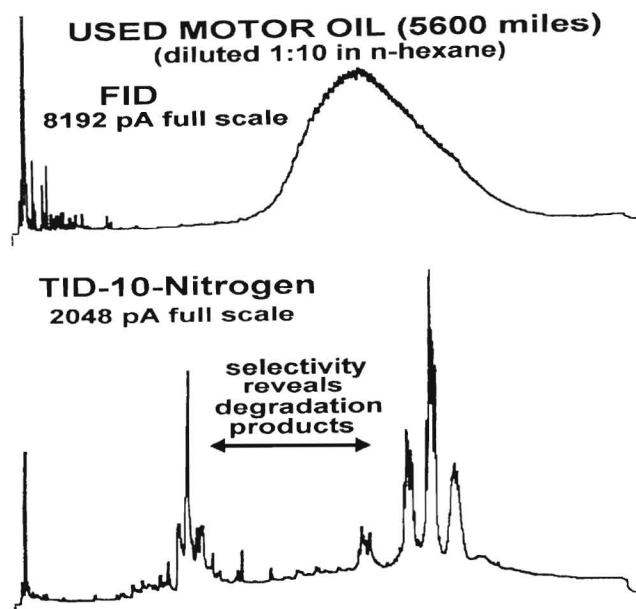
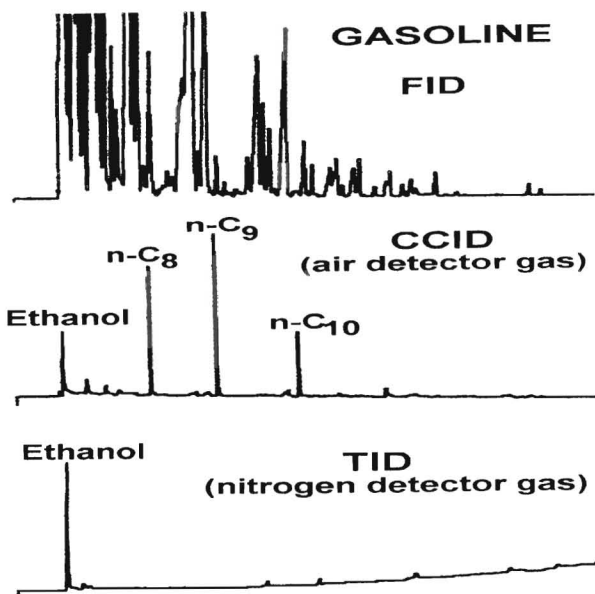
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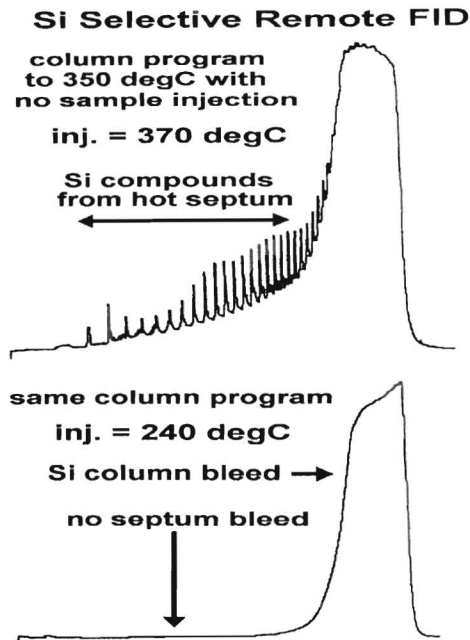
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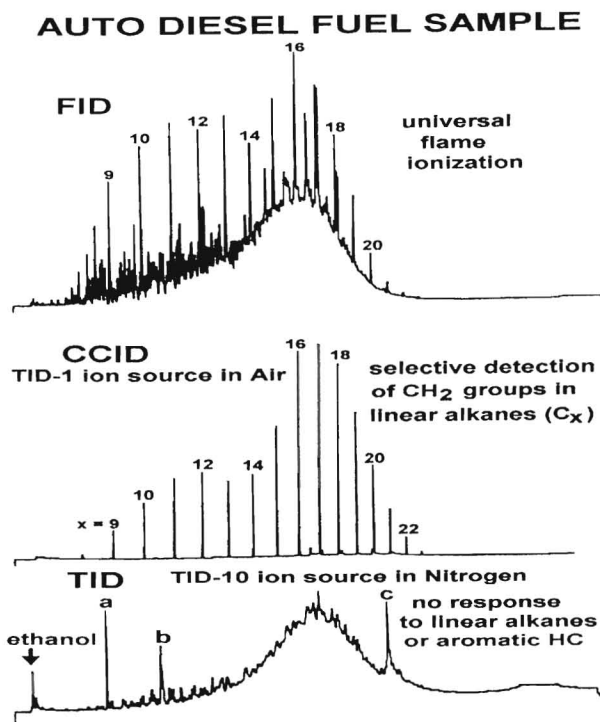


TID-1 selectively detects Ethanol in Gasoline  
CCID adds selectivity for  $\text{CH}_2$  groups in  $\text{C}_{8,9,10}$

TID-10 detection reveals oil degradation products obscured in FID chromatogram



very sensitive detection of Si bleed from septum (Supelco Thermogreen LB-2) & column (Phenomenex ZB-5HT)



compared to complex FID chromatogram, CCID reveals just linear Alkanes, while TID reveals constituents other than Linear Chain Alkanes and Aromatic Hydrocarbons

12/6/03



# DET

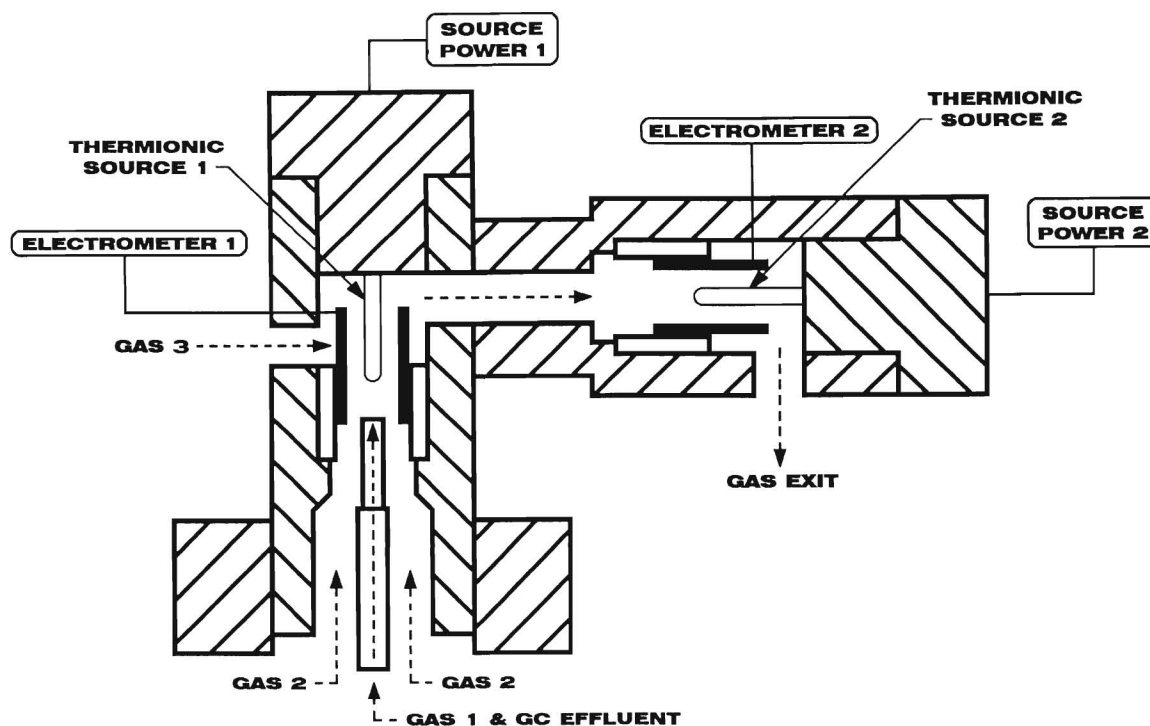
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## TANDEM TID

2 simultaneous signals, many possible combinations



detector hardware designed for custom retrofit onto an FID/NPD detector base already existing on a GC - detector gases 1 and 2 of various compositions supplied through the 2 gas lines normally used for H<sub>2</sub> and Air to the detector base - detector gas 3 used to purge volume between the 2 detection stages - separate ion source and supporting electronics required for each detection stage.

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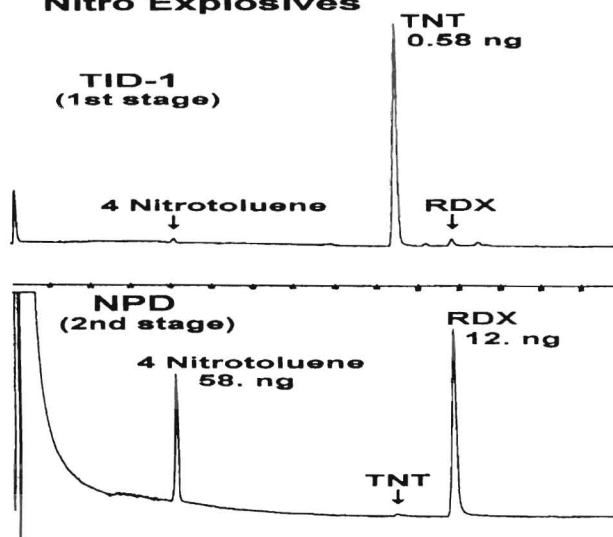
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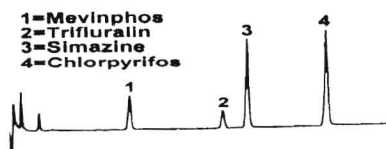
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### TANDEM TID on SRI 8610 GC 1 sample, 2 simultaneous signals Nitro Explosives

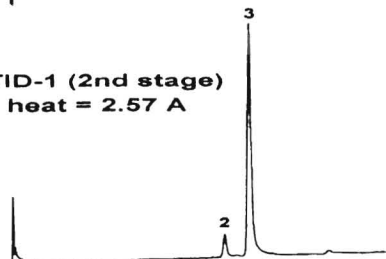


Series combination of DET TID-1 and NPD hardware mounted on SRI 8610 GC provided 2 simultaneous signals. TID-1 provided exceptional sensitivity to TNT while NPD responded in relative magnitude to all the Nitro compounds.

### NPD (1st stage) heat = 3.30 A

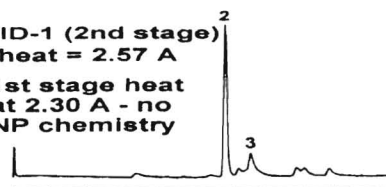


### TID-1 (2nd stage) heat = 2.57 A



### TID-1 (2nd stage) heat = 2.57 A

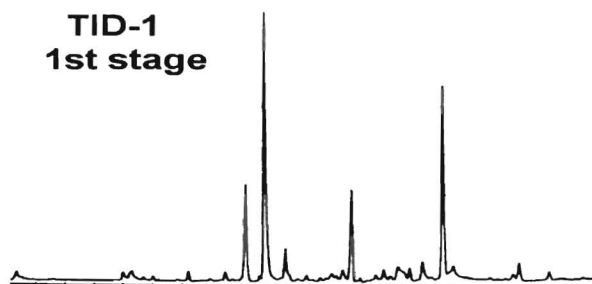
1st stage heat at 2.30 A - no NP chemistry



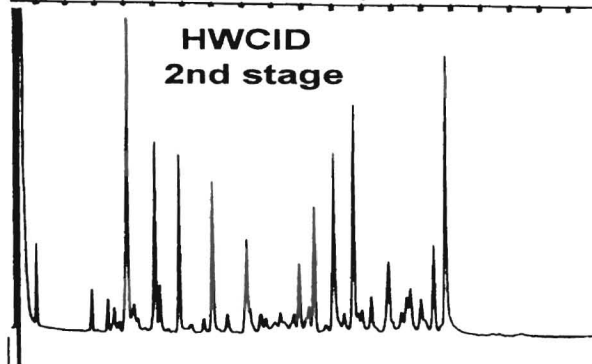
Simultaneous NPD/TID-1 of P pesticides with destructive NPD in first stage. Bottom chromatogram illustrates change in TID-1 selectivity when first stage chemistry was turned off.

### Poison Eau de Cologne

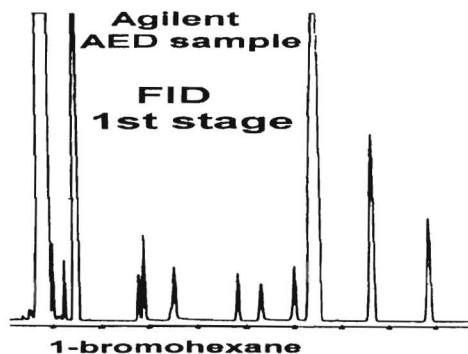
#### TID-1 1st stage



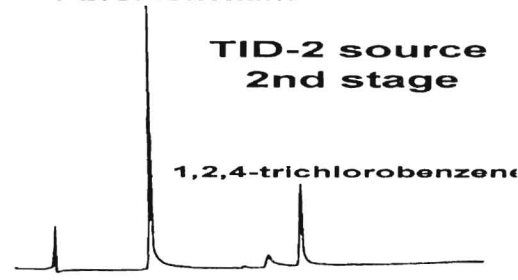
#### HWCID 2nd stage



Tandem combination of a selective TID-1 detector with a universal HWCID detector. HWCID (Hot Wire Combustion Ionization) maintains a flame like environment adjacent to a continuously heated bare wire.



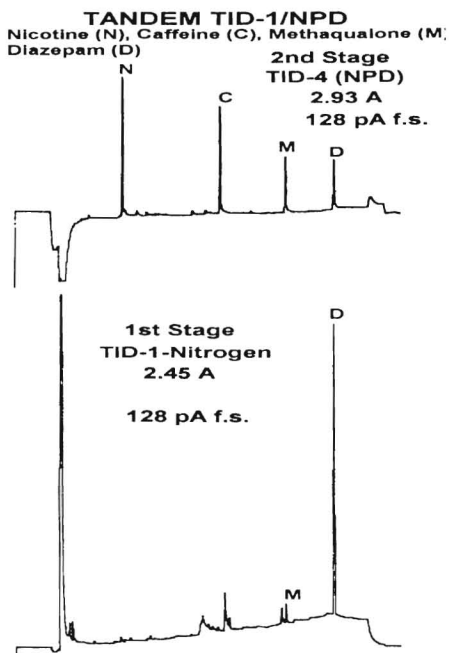
#### TID-2 source 2nd stage



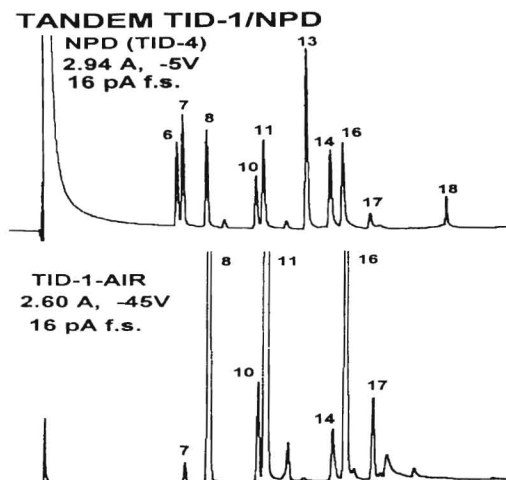
Simultaneous FID and FTID-2 detection where TID-2 ion source selectively detected Halogenate combustion products in effluent from first stage flame. Agilent AED sample contained a mixture of high concentration Alkanes along with lower concentrations of N, Cl, Br, S, O, and Si heteroatom compounds.,

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## Examples of Tandem Signal Combinations



Drug mix. Tandem TID/NPD on Varian 3800 GC.



Tandem TID/NPD on HP 5890 GC.

Explosives sample, 5 ng each compound:

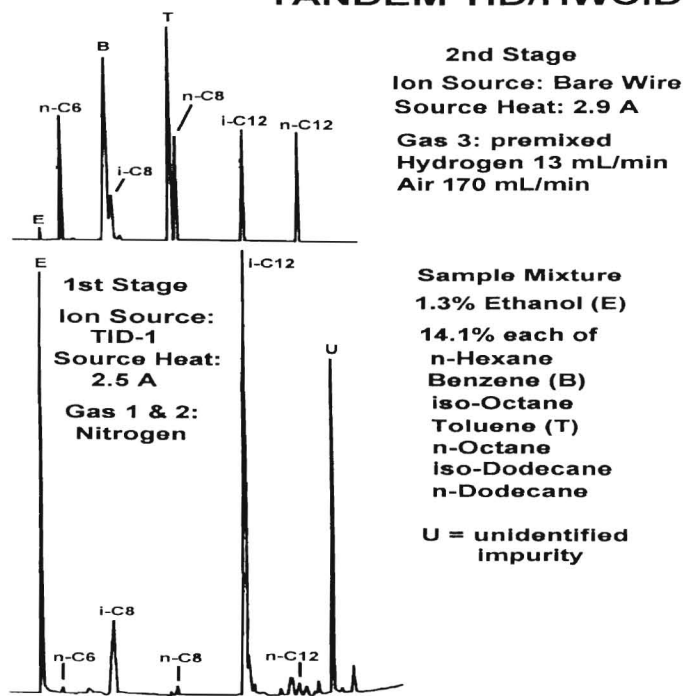
6=1,3-dinitrobenzene; 7=2,6-dinitrotoluene;

8=2,4-dinitrotoluene; 10= 1,3,5-trinitrobenzene;

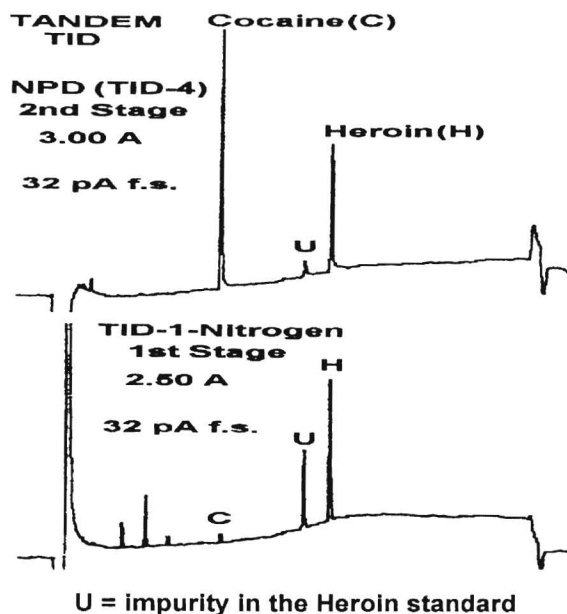
11=TNT; 13=RDX; 14=4-amino-2,6-dinitrotoluene;

16=2-amino-4,6-dinitrotoluene; 17=tetryl; 18=HMX

## TANDEM TID/HWCID



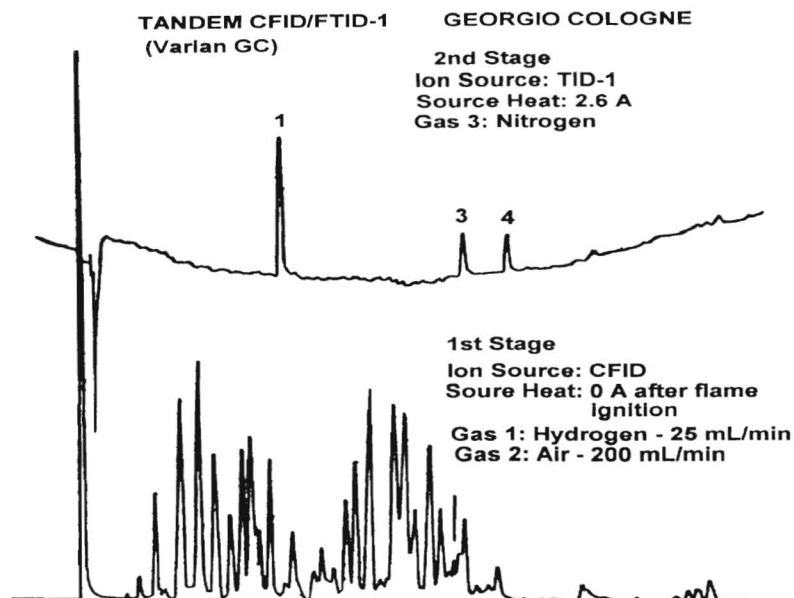
HWCID - universal flame environment around hot wire.  
TID-1 - selective to Ethanol and branched Alkanes.



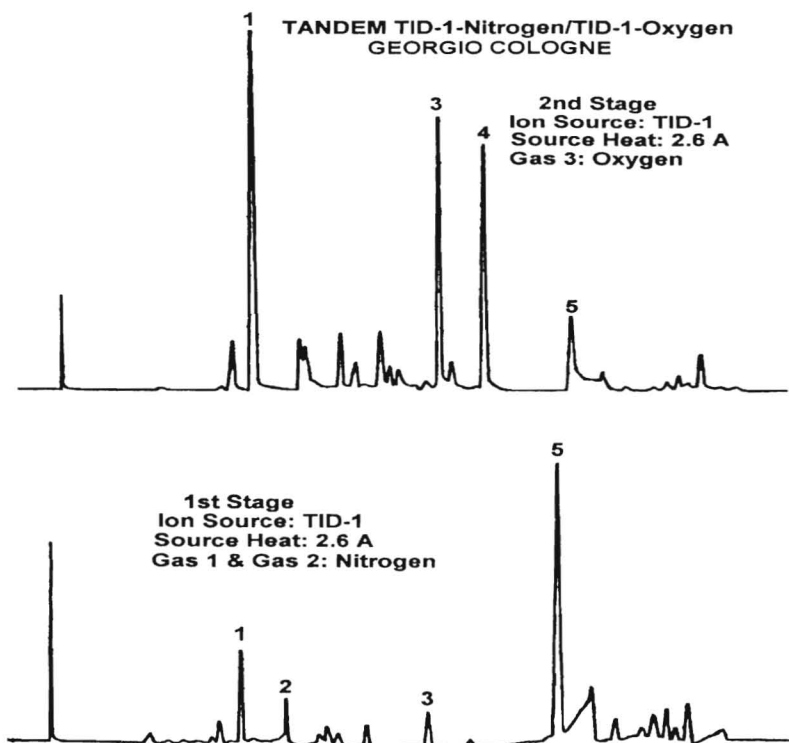
Tandem TID/NPD. Mix of Cocaine & Heroin standards.  
Varian GC.



## Examples of Tandem Signal Combinations



universal flame combustion in 1<sup>st</sup> stage, selective TID-1 detection of Nitrogen combustion products in 2<sup>nd</sup> stage.



comparison of TID-1 detection with 2 different detector gas environments.

# DET REPORT

NO.65 JANUARY 2012

**DET**  
Innovations in chemical detection

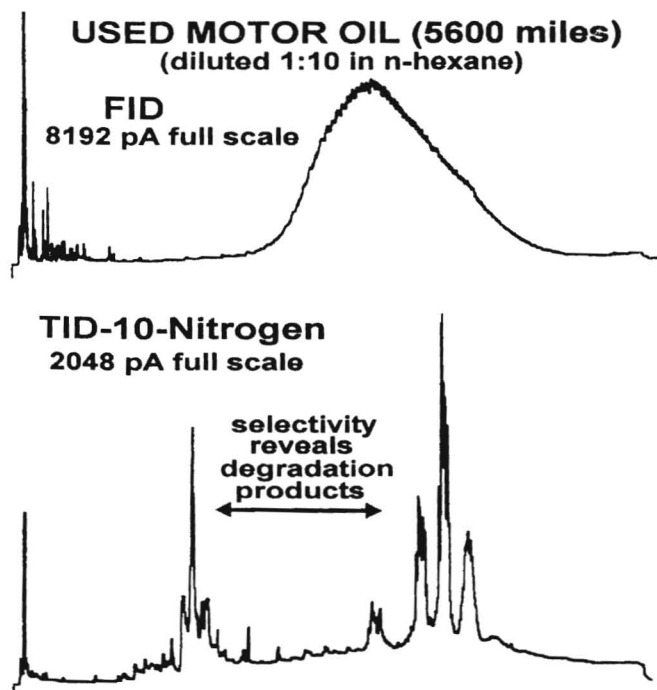
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- 1.) APPLICATION OF A NEW TID-10 CERAMIC ION SOURCE TO DETECTION OF DEGRADATION PRODUCTS IN USED MOTOR OIL.
- 2.) CATALYTIC COMBUSTION IONIZATION AND THERMIONIC SURFACE IONIZATION TECHNIQUES FOR SIMPLIFIED DETECTION OF SELECTED CONSTITUENTS IN GASOLINE AND AUTO DIESEL FUEL.
- 3.) SILICON SELECTIVE REMOTE FID DETECTOR PROVIDES A VERY SENSITIVE MEANS OF COMPARING THERMAL BLEED FROM GC SEPTA AND COLUMNS.
- 4.) INEXPENSIVE DET RETROFIT EQUIPMENT EXTENDS THE USEFUL LIFE OF GC EQUIPMENT AND PROVIDES A VERSATILITY FOR INTERCHANGEABLE SELECTIVE DETECTION MODES THAT IS UNMATCHED BY ANY OTHER DETECTION TECHNOLOGY.
- 5.) REACTOR THERMIONIC IONIZATION ANALYSIS (RTIA) METHOD OF SELECTIVELY SCREENING SURFACES FOR SECOND HAND SMOKE OR EXPLOSIVE RESIDUES.

## 1.) APPLICATION OF A NEW TID-10 CERAMIC ION SOURCE TO DETECTION OF DEGRADATION PRODUCTS IN USED MOTOR OIL.

DET chemical detection products are based on the science of Thermionic Surface Ionization, and feature a family of interchangeable, electrically-heated ion source elements made of proprietary ceramic materials. The method of fabricating DET ion sources provides an almost unlimited number of possibilities for new ceramic surfaces having different catalytic ionizing activities. Over the years, DET has evaluated hundreds of different ceramic formulations and is continually researching new ceramic additive combinations. A recent development is a very white ceramic formulation described as a "TID-10" type ion source which provides responses very similar to a previous TID-1 ion source. Generally, the TID-10 ceramic ion source is slightly more robust than the TID-1 ceramic, so our preference is to use the TID-10 wherever possible. However, there are some subtle differences where a TID-1 ion source provides better detection. These would be analyses where selectivity relative to Hydrocarbons is a critical concern, or where ultimate detectivity is required for Nitro and certain other heteroatom compounds.

Figure 1 shows analyses of a Used Motor Oil sample comparing FID detection versus Thermionic Surface Ionization detection using a TID-10 ion source operated in a detector gas environment of Nitrogen. The sample was comprised of drops of oil wiped off an automobile dip stick into a vial where n-Hexane was added to achieve approximately a 1:10 dilution. This dilution provided a sample viscosity that could be easily injected and volatilized



**Figure 1.** 0.5µL injected. 15m x 0.53mm x 0.15µm ZB-5HT, He=6mL/min, 50-350°C at 8°C/min, 350°C-1min, Inj.=360°C, Det=380°C, Nitrogen detector gas=60mL/min, Agilent 6890 GC & DET Current Supply, 2.25A ion source heat, - 45V polarization.



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in a heated GC inlet. The FID chromatogram of this sample exhibited a characteristic "hump-like" signal profile corresponding to unresolved Hydrocarbon peaks, whereas the TID-10 chromatogram revealed peaks associated with the oil degradation products that build up with extended usage in a car engine. Not only did the selectivity of TID-10 detection reveal peaks buried underneath the FID signal "hump", but the sensitivity of TID-10 detection also revealed peaks at earlier retention times where the FID chromatogram exhibited no signals at all.

Figure 2 compares TID-10-Nitrogen chromatograms of an unused sample of Motor Oil (Castrol GTX 10W30) versus a sample of that same Motor Oil after 5600 miles of its usage in a car engine. The comparison clearly shows the significant change in the pattern of chromatographic peaks that appear as the chemical composition of the oil degraded with increasing use. Figure 2 also compares chromatograms of 2 different types of New Oil samples (Castrol GTX 10W30 & Castrol Edge Synthetic 5W30). This comparison further illustrates how selective detection can provide simplified chemical fingerprint patterns to characterize and identify different types of samples.

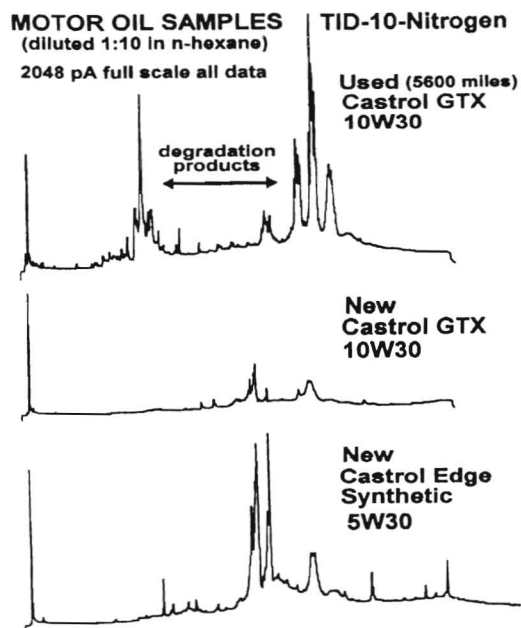


Figure 2. Same conditions as Figure 1.

## 2.) CATALYTIC COMBUSTION IONIZATION AND THERMIONIC SURFACE IONIZATION TECHNIQUES FOR SIMPLIFIED DETECTION OF SELECTED CONSTITUENTS IN GASOLINE AND AUTO DIESEL DUEL.

The unique compound selectivities achieved by DET's family of Thermionic Surface Ionization detectors can greatly simplify analyses of otherwise very complex samples. In analyses of Petroleum or Biofuel samples, the pattern of selective TID-1 or TID-10 peaks differs significantly depending on whether the ion source is operated in an inert or oxidizing gas environment, as well as on the operating temperature of the ionizing surface. Figure 3 compares analyses of a gasoline sample using an FID, CCID (Catalytic Combustion Ionization Detector), and TID (Thermionic Ionization Detector). As described in earlier DET Reports, CCID relates generally to the selective detection of Methylene ( $\text{CH}_2$ ) functional groups in high concentration Hydrocarbon compounds, whereas TID relates generally to selective detection of compounds containing electronegative heteroatom functionalities. In Figure 3, the TID and CCID data were generated using a TID-1 ion source in detector gas environments of Nitrogen and Air, respectively, and the ion source surface temperature was maintained at a relatively low value in the range of 300 - 400°C by supplying a heating current of 2.100 Amps through the ion source's wire core. With the inert  $\text{N}_2$  environment, Ethanol was virtually the only compound detected amongst the hundreds of compounds present in

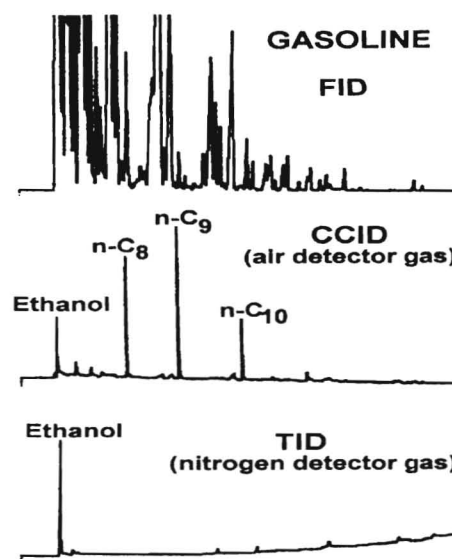


Figure 3. 0.6µL Chevron gasoline injected. Detector=230°C. 30m x 0.53mm HP1ms, He= 8mL/min, 50-160°C at 8°C/min Air = 60mL/min for CCID data,  $\text{N}_2$  = 60mL/min for TID data.

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gasoline. With the oxidizing Air environment, the corresponding chromatogram revealed the presence of the 3 linear chain Alkane components, n-Octane, n-Nonane, and n-Decane due to CCID ionization, as well as some residual Ethanol response due to TID type ionization.

The middle chromatogram in Figure 4 shows how the pattern of peaks detected by the CCID process can be further modified by operating the TID-1 ion source in an Oxygen environment instead of Air, and by increasing its surface temperature as achieved by a heating current of 2.40 A versus the 2.10 A used for the bottom chromatogram. These changes provided detection of more constituents in the gasoline sample, but still good selectivity for these constituents versus the many other peaks shown in the FID chromatogram.

Figure 5 compares FID, CCID, and TID detection for a sample of undiluted Auto Diesel Fuel. In contrast to the complex pattern of peaks in the FID chromatogram, the middle CCID chromatogram revealed only the Linear Chain Alkane components of the sample. These CCID data were generated using a TID-1 ion source in a detector gas

environment of Air. The bottom TID chromatogram was generated with a TID-10 ion source operated in a detector gas environment of Nitrogen. It revealed that this diesel fuel sample had an Ethanol component plus distinct peaks labeled "a", "b", and "c" which have not yet been identified. These latter three peaks are undoubtedly heteroatom compounds because their retention times do not coincide with any of the Linear Chain Alkanes, nor do they coincide with any other prominent Hydrocarbon peaks in the FID chromatogram. In addition, the TID chromatogram also exhibited a "hump" of signal due to unresolved constituents that was similar to the data "hump" underlying the sharp peaks in the FID chromatogram. Since it is known from previous work that TID-1 and TID-10 ionization in Nitrogen does not respond to either Linear Chain Alkane or most Aromatic Hydrocarbons, then the TID data "hump" must correspond to other types of Hydrocarbon constituents.

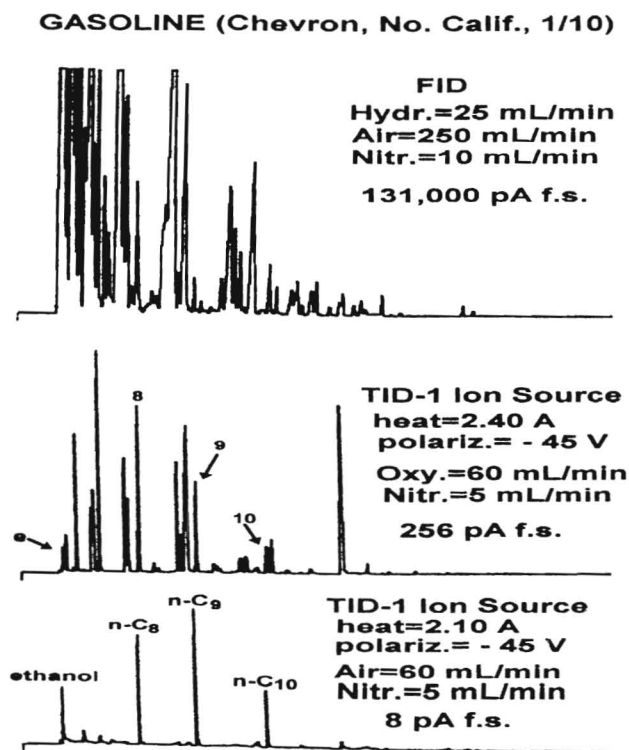


Figure 4. Same conditions as Figure 3.

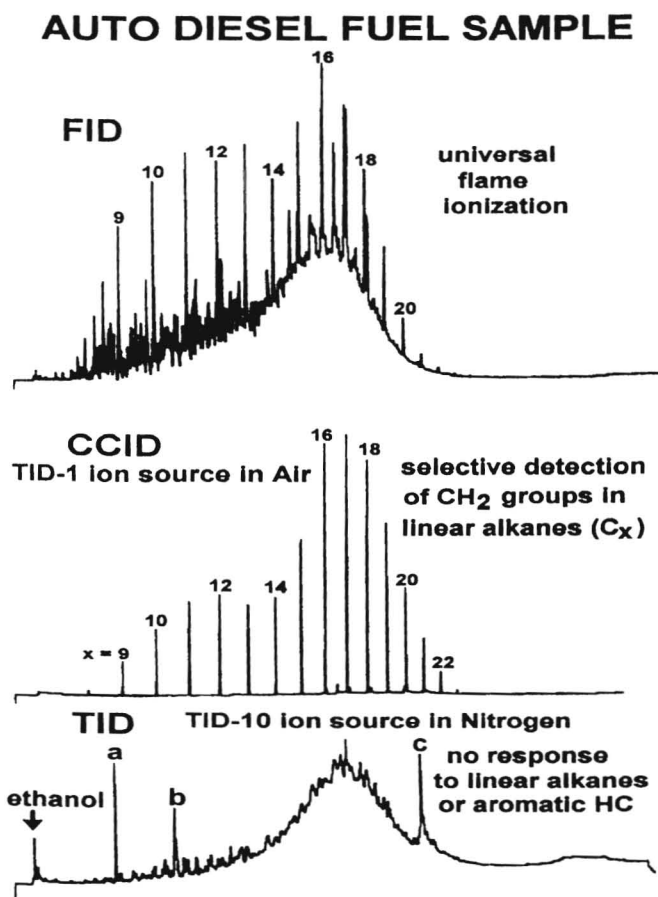


Figure 5. Agilent 6890 GC with DET TID-1 & TID-10 ion sources powered by a stand-alone DET Current Supply. Det.=340°C. 30m x 0.53mm HP-1, He=8mL/min, 50°C-2min, 50-320°C at 10°C/min, 320°C-4min, Inj.=320°C.



# DET REPORT

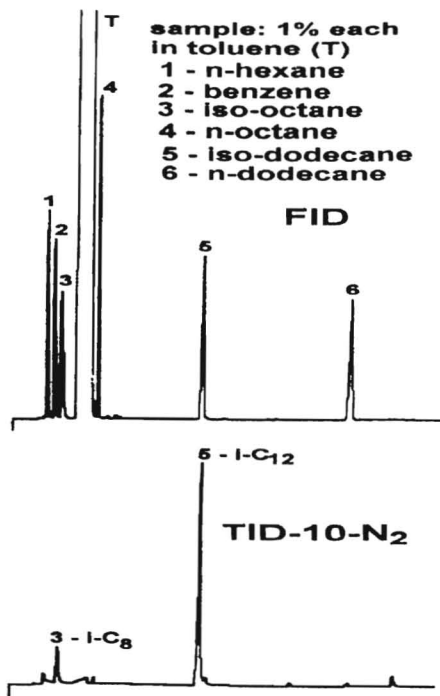
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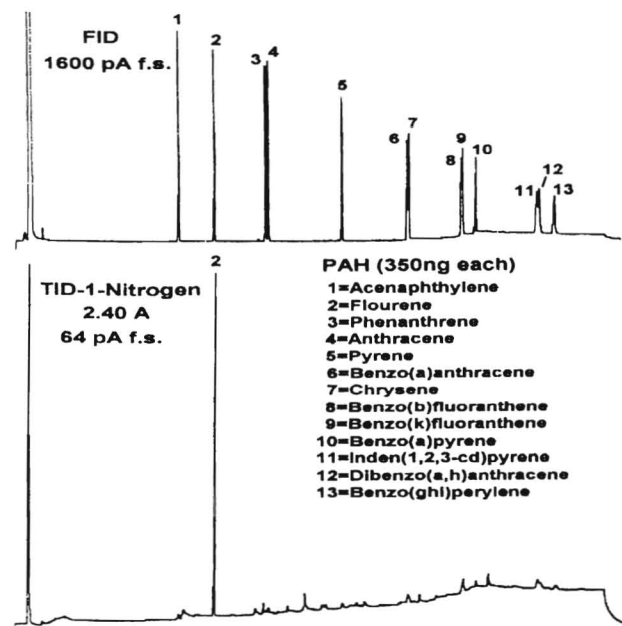
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Some candidate Hydrocarbons which are known from previous work to be responsive to TID-1 or TID-10 ionization in a Nitrogen environment are Branched Chain compounds and Polycyclic compounds like Indene and Flourene which contain 5 member carbon rings. (See Figures 6 and 7).

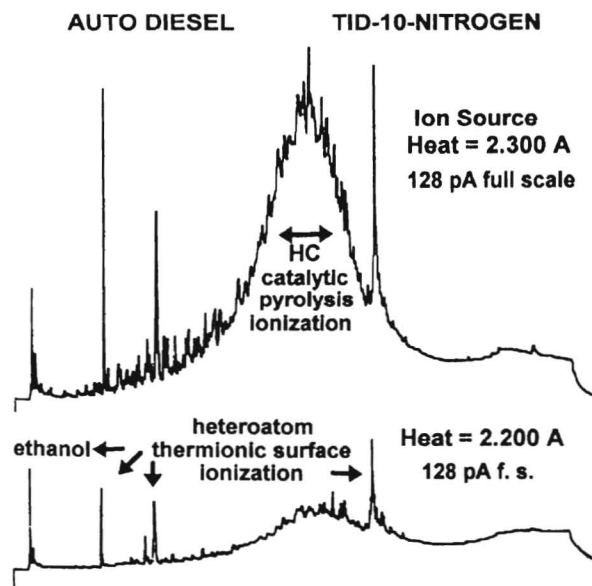
TID-1/ TID-10 ionization in a Nitrogen environment is known to be especially sensitive to Oxygenated compounds like Phenols, or Nitrogen heterocycles like Indoles and Carbazoles because the heteroatom functionalities impart an electronegative character to the compound and its possible dissociation products. However, the response of TID-1/TID-10 ion sources to Hydrocarbons is somewhat different, because C and H are not normally known as atoms with a strong affinity to form negative ions. Consequently, we have come to envision the "hump-like" Hydrocarbon signals illustrated in the bottom chromatogram of Figure 5 as a Catalytic Pyrolysis Ionization process as compared to a Thermionic Surface Ionization process applicable to heteroatom compounds. Whereas Thermionic Surface Ionization can often detect trace level constituents, Catalytic Pyrolysis Ionization is really limited to high concentrations of Hydrocarbons.



**Figure 6.** Example of TID-10-Nitrogen selectivity for Branched Chain Hydrocarbons amidst a mixture of Aromatic and Linear Chain Alkane compounds. Compound response increases with increasing numbers of branched Methyl (CH<sub>3</sub>) groups. iso-Octane has 3 CH<sub>3</sub> groups and iso-Dodecane has 5 CH<sub>3</sub>.



**Figure 7.** Example of TID-1-Nitrogen selectivity for the 5 member carbon ring in Flourene amidst other PAH compounds. Indene has similar selective response, as does TID-10 ion source.



**Figure 8.** Comparison of TID-10-Nitrogen analyses of Diesel Fuel at 2 different temperatures (i.e., heating current) for the TID-10 ionizing surface. Same conditions as Figure 5.

# DET REPORT

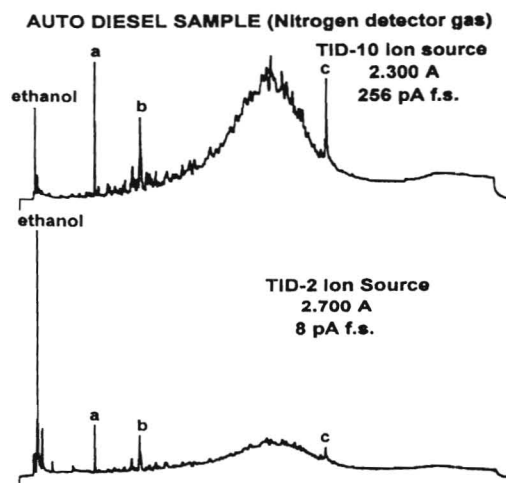
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Figure 8 illustrates how the pattern of TID-10-Nitrogen ionization of the diesel fuel is affected by changing the surface temperature of the ion source. Figure 9 shows how the response to the diesel fuel changes when the TID-10 ion source is replaced by a TID-2 ion source which has a lower level of catalytic activity. Note that the TID-2 ion source required a much higher surface temperature, and produced much lower signals than the TID-10 ion source.

The data presented in this section have demonstrated the versatility of DET's chemical detection technology for simplification of analyses of complex samples. Key ingredients in DET's methods are the catalytically-active ceramic surfaces and their effectiveness at converting selected chemical compounds into measurable electrical currents. As has been seen, variations in ion source surface temperature and detector gas environment are additional means of simply altering the chromatographic profile generated. The type of chemical detection described in this report is unprecedented, simple, and inexpensive, and can be implemented on a variety of different GC instruments as will be discussed in a later section.

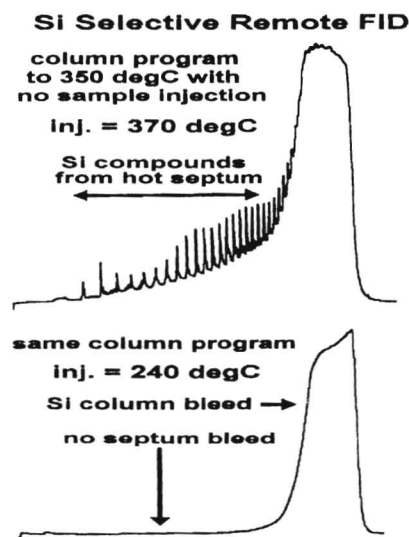


**Figure 9.** Comparison of Diesel Fuel analyses using 2 ion source types of different catalytic activity. TID-2 ion source is a Black Ceramic formulation normally used in an ignited Hydrogen-Air gas environment for selective NP detection. Used here in just a Nitrogen environment, TID-2 required a higher surface temperature to produce lower signals than the more catalytically-active TID-10 ion source.

### 3.) SILICON SELECTIVE REMOTE FID DETECTOR PROVIDES A VERY SENSITIVE MEANS OF COMPARING THERMAL BLEED FROM GC SEPTA AND COLUMNS.

The Remote FID mode of chemical detection was developed based on the discovery that flame combustion of certain chemical compounds produced long-lived ion species that persisted well downstream in the flowing effluent of the flame. Meanwhile, ions produced in flame combustion of Hydrocarbons were found to dissipate rapidly by positive ion-negative ion recombination processes in a relatively short distance downstream of the flame. Hence, there was identified a method of selective detection by locating an ion collector and polarizer downstream of the flame rather than immediately adjacent to the flame. The type of compounds found to be detectable by this means were those containing P, Pb, Sn, or Si atoms. Furthermore, the selectivity versus Hydrocarbons was so good that it was possible to use a flame fueled by a Hydrogen-Methane mixture rather than just Hydrogen to achieve even better selectivity versus complex Hydrocarbon matrices.

Figure 10 demonstrates that a Remote FID is a very sensitive means of detecting bleed from Si compounds in GC septa and GC column coatings. There was no sample injection for the data in Figure 10. The column temperature was simply programmed up to 350°C, and the baseline signal monitored with the Remote FID.



**Figure 10.** HP 5890GC equipped with DET retrofit Remote FID hardware & electronics. Supleco Thermogreen LB-2 septum. Phenomenex ZB-5HT column, 15m x 0.53mm x 0.15µm. Flame fuel: 20mL/min Hydrogen/20%Methane, 200mL/min Air.



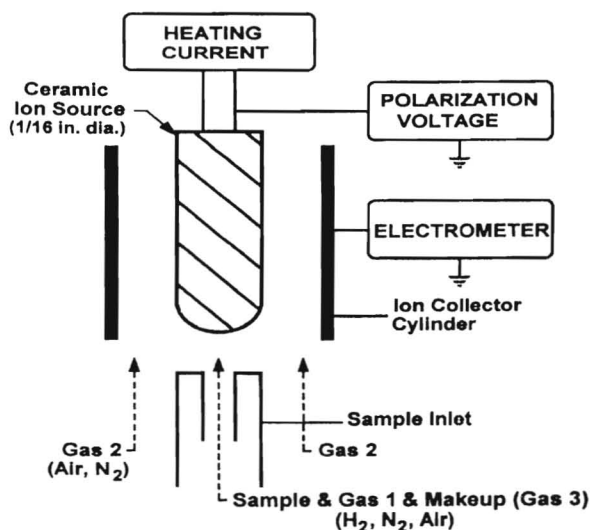
## 4.) INEXPENSIVE DET RETROFIT EQUIPMENT EXTENDS THE USEFUL LIFE OF GC INSTRUMENTS AND PROVIDES A VERSATILITY FOR INTERCHANGEABLE MODES OF SELECTIVITY THAT IS UNMATCHED BY ANY OTHER DETECTOR TECHNOLOGY.

One consideration in deciding whether to buy a new GC is often the need to acquire a mode of detection not currently available on an existing GC. However, if other parts of the GC are still operating well, then adding retrofit detector equipment from DET can often be an inexpensive alternative for extending the useful life of the existing equipment. As a good example of that life-extension concept, DET continues to use in its facilities a Hewlett Packard 5710 GC and a Varian 3700 GC, both of which were manufactured in the 1970's. All thermal zone controls and gas flow control elements on these instruments still work, so both have been retrofitted with 2 DET detector assemblies each, along with stand-alone DET supporting electronic modules where needed, and both are used daily to condition DET's NP ion sources under typical NPD operating conditions.

DET has available an assortment of detector hardware structures designed to custom fit existing FID or NPD detector bases on various GC models. All these hardware structures can accommodate any of the family of ceramic ion source elements manufactured by DET. Consequently, a DET retrofit not only can provide a performance upgrade to an existing NPD detector, but it also can provide the capability for expansion to many other types of selective detection. Mode changes are accomplished through simple changes in the type of ion source used, and the type of detector gases supplied.

Numerous previous DET Reports have discussed DET's equipment recommendations for achieving optimum NP and other modes of Thermionic Surface Ionization detection. All DET retrofit equipment conforms to the general design illustrated in Figure 11. DET ceramic ion sources are small cylindrical structures installed into the top of a tower structure such that the ion source is located on the axis of a surrounding ion collector cylinder. This basic hardware configuration provides for stream-lined gas flow through the detector volume, and efficient collection of ions formed at the ion source surface. DET ion sources are comprised of a wire core covered by layers of ceramic coatings, and they are optimally powered by electronics that provide Constant Current type heating control for the wire core plus a polarization voltage that can be adjusted in magnitude to provide the best possible signal-to-noise for different detection modes. As indicated in Figure 11, detector signals are measured with an electrometer which in most cases is an NPD electrometer already existing on the GC.

**THERMIONIC IONIZATION DETECTOR DESIGN  
(CONCENTRIC CYLINDER GEOMETRY)**



**Figure 11.** Schematic of the hardware configuration and electronic components used in all DET GC detectors and stand-alone transducers.

DET retrofit equipment for specific GC models is intended to provide optimum combinations of hardware and electronics, and is summarized as follows:

**AGILENT 6890/7890 GC:** The NPD hardware structure on Agilent 6890/7890 GC models was designed to use DET's style of ceramic ion sources, and those sources install into the preferred concentric cylinder geometry depicted in Figure 11. Therefore, the Agilent NPD hardware can accommodate all types of DET ion sources that have different catalytic ionizing activities. However, the 6890/7890 NPD Bead Voltage power supply is not the most optimum for heating ion sources because it provides Constant Voltage heating rather than Constant Current heating, and it is limited to a fixed polarization of - 4.4 V. While this low polarization is fine for NP detection, it provides about a factor of 10 worse signal-to-noise for most other modes of selective detection. Therefore, for use with Agilent instruments, DET has available a stand-alone Current Supply module that provides an optimum combination of Constant Current heating and switch selection of



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polarization voltages ranging from - 5 V to - 45 V. All DET ion sources compatible with the 6890/7890 NPD hardware structure are priced at \$385 each, and the Current Supply is \$1760.

**THERMO SCIENTIFIC TRACE GC** - Thermo's NPD electronics incorporate all of the most optimum features for operating NPD and TID detectors. These include Constant Current heating power, variable polarization voltages, ability to turn the heating current on/off as a timed event, and an indicating readout in the event of an open circuit in the ion source wiring. However, Thermo's NPD hardware structure installs DET manufactured ion sources into the side of a tower structure rather than the more optimum concentric cylinder orientation depicted in Figure 11. Therefore, DET has developed a hardware structure that retrofits onto the Thermo NPD or FID detector base, and that accommodates ion sources identical to those used on the Agilent equipment. This combination of DET hardware and Thermo NPD electronics provides the most versatile NPD/TID capability currently available. DET's Thermo retrofit hardware price is \$1800, and ion sources are \$385 each.

**VARIAN/BRUKER TSD GC MODELS** - The TSD (NPD) detector on Varian/Bruker instruments is a large hardware structure with an awkward side access for replacement of the NPD ion source (bead). DET retrofit hardware is more compact than the TSD hardware, it installs easily onto a TSD or FID detector base, it accommodates the same style DET ion sources used with Agilent GC models, and it provides the optimum concentric cylinder geometry depicted in Figure 11. Also, for NP detection, DET's innovative Black Ceramic type ion source can be used to achieve sharp Phosphorus peak shapes in contrast to the notorious P peak tailing characteristic of the TSD bead. As with Agilent and Thermo retrofit parts, the DET hardware also is easily converted to many other modes of selective detection. DET ion sources are compatible with the Constant Current heating supplied by TSD electronics. However, the TSD electronics are limited to a low polarization value for the ion source, so a stand-alone DET Current Supply provides a means of achieving higher polarizations for big response improvements in detection modes other than NP. DET retrofit hardware for Varian/Bruker GC modes is priced at \$1650, and ion sources and the stand-alone DET Current Supply are priced as indicated earlier.

**SRI INSTRUMENTS GC MODELS** - Like the Thermo and Varian/Bruker retrofits, a DET hardware retrofit for SRI GC

models consists of a tower assembly that mounts onto a heated FID/NPD base on the SRI GC. As with other DET retrofits, the DET hardware provides an optimum concentric cylinder geometry for stream-lined gas flow and efficient ion collection, and easy end mounting of the ion source. SRI's Constant Voltage type NPD electronics can be used to power the ion sources, but the stand-alone DET Current Supply provides better user friendly precision control of ion source heating and polarization. Like the previous GC brands, DET retrofit hardware for SRI GC models can accommodate all the different type of ceramic ion sources developed by DET. Consequently, an SRI GC equipped with DET hardware, ion sources, and stand-alone Current Supply provides exceptional chromatographic analysis capability in a relatively compact and inexpensive package. DET retrofit hardware for SRI GC models is priced at \$1850, with DET's interchangeable ion sources and Current Supply priced as previously cited.

**HP 5890 GC MODEL** - DET retrofit hardware for the HP 5890 fits onto an existing FID or NPD base on that GC, and provides optimum concentric cylinder detector geometry and compatibility with all the different ion sources developed by DET. However, the DET hardware and ion sources are not compatible with any of the 5890 detector electronics, so operation of the DET retrofit equipment requires the stand-alone DET Current Supply and a stand-alone Electrometer such as a Keithley Model 6485 Picoammeter. The price of the DET retrofit hardware is \$1850, the ion sources cost \$385 each, the DET Current Supply is \$1760, and the Keithley Electrometer is \$1800 if DET supplies it. Hence, the total cost of DET 5890 retrofit equipment is \$5795, which is somewhat higher than other GC retrofits where some of the existing electronics were useable. There are, however, some extenuating considerations regarding DET's retrofit equipment for the 5890. First, DET's 5890 retrofit provides the capability for an entire family of different selective detection modes; second, the stand-alone DET Current Supply can also be used for improved ion source power on Agilent 6890/7890, Varian/Bruker, and SRI GC models; third, the 5890 hardware structure will also fit onto the FID detector base on newer Agilent 6890/7890 GC models; and fourth, the combination of the DET Current Supply and Keithley Electrometer provides all the ion source power and signal measurement electronics needed to operate any stand-alone DET transducers. In other words, various parts of DET's 5890 retrofit equipment have other possible uses as well.



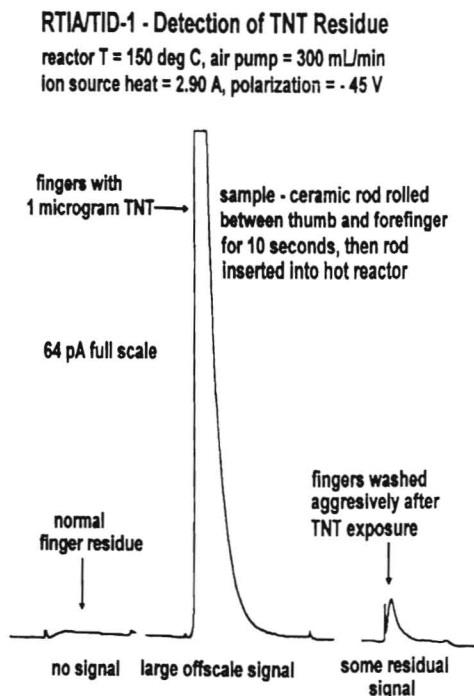
NO.65 JANUARY 2012

## 5.) REACTOR THERMIONIC IONIZATION ANALYSIS (RTIA) METHOD OF SELECTIVELY SCREENING SURFACES FOR SECOND HAND SMOKE OR EXPLOSIVE RESIDUES.

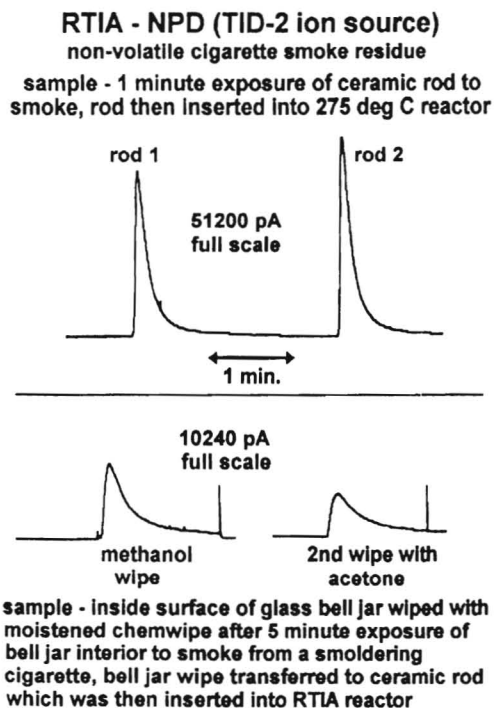
Previous DET Reports have periodically discussed stand-alone implementation of TID and NPD detection techniques in instrumentation identified by the nomenclature "Reactor Thermionic Ionization Analyzer" (RTIA). In this instrumentation, a TID or NPD transducer is attached to a heated inlet reactor chamber, and an Air sampling pump is attached to the transducer exit so as to pull a flow of ambient Air through both the reactor and transducer. The purpose of the reactor is to generate vapors from non-volatile substances, and the purpose of the transducer is to provide selective detection of the vapors generated. Since the sample volatilization process occurs in an Air environment, both Thermal Desorption and Thermal Oxidation processes can contribute detectable vapors. In some cases, the detected signal rises to a peak, and then falls back to baseline. This indicates that the detected substance has been completely volatilized at the prevailing reactor temperature. In other cases, the detected signal

risers to a plateau and stays there until the sample is removed from the reactor. This indicates detection of an enhanced vapor pressure from the substance, but not complete vaporization.

One versatile means of introducing non-volatile samples into the RTIA reactor is as a residue on a small diameter ceramic sampling rod. Data shown in Figures 12 and 13 illustrate that type of residue screening. Figure 12 demonstrates the extreme sensitivity TID-1 ionization has for detecting traces of TNT which is a compound that contains a Nitro functional group in a para location relative to other functionalities. Figure 13 demonstrates NPD screening for surface residues that accumulate from exposure to second-hand cigarette smoke.



**Figure 12.** RTIA/TID-1 detection of a TNT trace residue on a finger. Sampling procedure consisted of rolling the tip of a ceramic rod between the thumb and forefinger, and then inserting the rod into the RTIA reactor equipped with a TID-1 transducer which has exceptional sensitivity for Nitro explosives like TNT. Data demonstrate that some detectable residue is still left after vigorous washing of hands.



**Figure 13.** "THIRD HAND SMOKE". RTIA/NPD detection of non-volatile residues deposited on surfaces exposed to Second Hand Smoke. Top data illustrate signals from smoke residues deposited directly onto tips of 2 ceramic rods. Bottom data illustrate Methanol & Acetone wipes of a surface exposed to Second Hand Smoke, with the wipes then transferred to the tip of a ceramic rod. Data demonstrate simple means of monitoring ambient environments for exposure to potentially toxic non-volatile chemicals in those environments.

## DET innovations in chemical detection

### TID-1-N<sub>2</sub>(O<sub>2</sub>): selective for NITRO, OXYGENATED, or HALOGENATED compounds

#### Equipment:

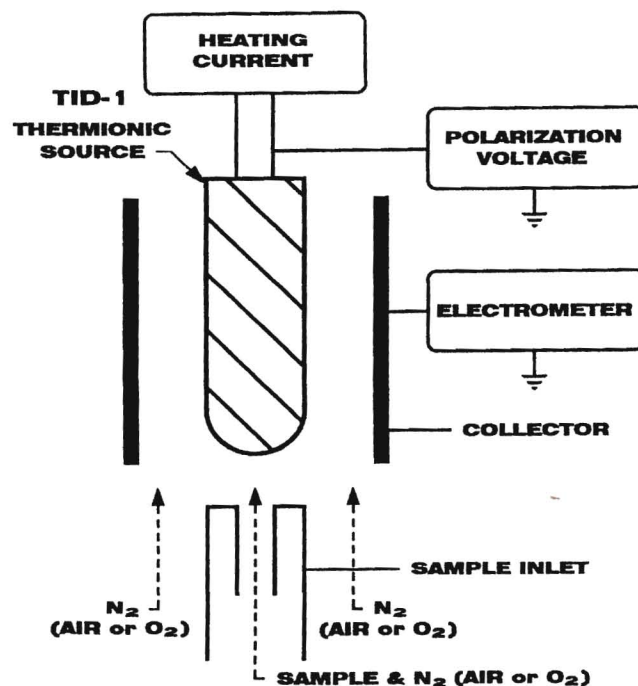
This detection mode uses a TID-1 type thermionic source mounted in either a TID/FID, REMOTE FID, FTID, PTID, or TANDEM TID tower. The detector gas is N<sub>2</sub> flowed through the gas lines which normally provide "H<sub>2</sub>" and "air" to an NPD or FID. (Air or O<sub>2</sub> are other possible 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<sub>2</sub> 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<sup>8</sup> 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<sup>7</sup> - 10<sup>5</sup>. 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<sup>4</sup> 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<sub>2</sub>. The presence of O<sub>2</sub> 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 or TID-10 MODE

### 1.) BASIC DESCRIPTION

In this mode of operation, a ceramic ion source (TID-1 or TID-10) of very low work function and high catalytic activity is operated in an inert gas environment of  $N_2$ , or oxidizing gas environments of Air,  $O_2$ , or  $N_2O$ . Sample compounds are ionized by a catalytic 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 (picogram and nanogram detectivity) are obtained for many Oxygenated compounds such as Alcohols, Phenols, and Carboxylic Acids. 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. This mode of detection is not totally destructive of the incoming sample, so tandem combinations with other detection modes are possible. Also, when operated in an oxidizing gas environment, TID-1 and TID-10 ion sources provide selective ionization of  $CH_2$  functional groups in high concentration (100 ng and above) Hydrocarbon, Fats, and Triglyceride samples according to a process that has been identified as Catalytic Combustion Ionization. Stand-alone transducer applications are also possible since TID-1 and TID-10 detection can function with ambient Air as the only supplied detector gas.

### 2.) DETECTOR GAS FLOWS

In this mode of operation,  $N_2$ , Air,  $O_2$ ,  $N_2O$ , or combinations thereof are supplied through the 3 detector gas lines that normally supply  $H_2$ , Air, and Makeup gas to an NPD or FID. The principal function of the detector gases is to maintain a well purged detector volume. A total flow rate of 50 - 70 mL/min generally suffices, although some stand-alone transducer applications have used flows up to 1000 mL/min.  $N_2$  or He are the preferred GC carrier gas.

### 3.) OPERATION

- a.) To become familiar with the response characteristics of a TID-1 or TID-10 ion source some initial experimentation with high responding test samples is recommended. Examples of good test sample compounds are the Nitro compounds Methyl Parathion or 2,4-Dinitrotoluene at concentration levels of about 1 - 10 ng. A good source of Methyl Parathion is a Varian/Bruker TSD test sample (#82-005048-04) or a Thermo Scientific NPD test sample (#33819006-1), and a good source of 2,4-Dinitrotoluene is a 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 gas flows in accordance with guidelines in IIIA.2. For first time users, we recommend starting with an inert N<sub>2</sub> detector gas environment, and later trying an oxidizing environment of Air to see how the response changes.
- 2.) Set the detector heater block at the desired operating temperature. (20°C higher than the hottest GC column oven temperature is recommended.)
- 3.) Connect the electrometer on the GC or a stand-alone electrometer 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 ion source heating current is increased. Set the electrometer and data system attenuations and range so the recorded display corresponds to approximately 10<sup>-11</sup> Amps for full scale signal.
- 4.) On a 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	2.6 - 2.9 Amps	2.5 - 2.8	2.7 - 3.0
200°C	2.3 - 2.6 Amps	2.2 - 2.5	2.4 - 2.7
300°C	2.1 - 2.3 Amps	2.0 - 2.2	2.2 - 2.4

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. If the equilibrated detector baseline signal is greater than 50 pAmps, reduce the ion source heating current by 0.1 Amps.

- 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 as with the original heating current.

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  $2 \times 10^{-14}$  Amps) occurs for background signal levels of  $10 \times 10^{-12}$  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  $10 \times 10^{-12}$  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<sub>2</sub> 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.

#### 4.) **TID-1 AND TID-10 ION SOURCE DIFFERENCES**

TID-10 is a newer, slightly more robust version of the TID-1 ion source. At comparable ion source temperatures and in an inert gas, TID-10 has about a factor of 3 less sensitivity for Nitro compounds, and about a factor of 3 more sensitivity to branched Methyl (CH<sub>3</sub>) functional groups in very high concentration (more than 1 microgram) Hydrocarbons. Otherwise, TID-10 and TID-1 appear to be interchangeable, although there is a much larger library of application data that has been obtained with the TID-1 ion source over the years.

#### 5.) **INERT VERSUS OXIDIZING GAS ENVIRONMENTS**

Long term operation of TID-1 and TID-10 ion sources at high source heating currents in an oxidizing environment sometimes causes a change in the ionization characteristics when that ion source reverts back to operation in an inert gas environment. Once it is established which environment is best for a given analysis, then for best results the ion source should be dedicated to continued operation in that environment.

## GUIDE TO TID-1 DETECTION ON AGILENT 6890/7890 NPD EQUIPMENT

### 1.) DETECTOR GASES

TID-1 detection requires a detector gas environment of Nitrogen, Air, or Oxygen, or some combination thereof. This gas environment can be achieved by supplying the appropriate gas type at the detector gas inlets normally used to provide Hydrogen, Air, and Makeup for the NPD. A total gas flow rate of 50 to 70 mL/min generally suffices.

### 2.) ION SOURCE SURFACE TEMPERATURE

TID-1 surface temperature is the one operating control that determines selectivity and sensitivity. The surface temperature depends on both the magnitude of the heating current supplied to the ion source, as well as on the operating temperature of the heated detector base. Typical heating currents for a Nitrogen gas environment are as follows:

detector base	heating current	Agilent bead voltage
100°C	2.5 - 2.7 Amps	2.8 - 3.1 Volts
200°C	2.3 - 2.5 Amps	2.6 - 2.8 Volts
300°C	2.1 - 2.3 Amps	2.4 - 2.6 Volts

Start with the DET Current Supply at 0 Amps, increase the current to the lower end of these ranges, and observe the detector baseline for an indication of signal increase as the heating current is increased from zero. Typically, an initial signal will rise rapidly from the zero baseline, reach a peak, and then equilibrate to some lower level. (Unlike an NPD, TID-1 background signal levels often equilibrate to a magnitude of 10 pA or less.) The hot thermionic source radiates some heat to the surrounding detector structure, and the thermal equilibration of the detector structure may require 15 to 20 minutes. To minimize this thermal equilibration time, set the detector heater base at as high a temperature as allowed by the application, so the thermal gradient between the ion source and the surrounding detector wall is minimized. (Example: Set the detector base temperature at least 20 °C higher than the highest temperature reached by the GC column.)

### 3.) INJECT SAMPLE OF INTEREST

Each new TID-1 source is accompanied by a chromatogram of the response of that source to a test sample. The conditions associated with that chromatogram provide a good starting point for examining the sample of interest. Inject the sample, see what the response is, then inject the sample again with a source heating current 0.1 Amps below and above the original heating current value. For best selectivity, operate at the lowest heating current that provides a signal magnitude sufficient for the analysis.

### 4.) OPERATION WITH AIR OR OXYGEN AS THE DETECTOR GAS.

Long term operation of the TID-1 source at high heating currents in an oxygen containing environment sometimes causes a change in the TID-1 surface characteristics such that subsequent operation in Nitrogen may yield a 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 the Nitrogen or Oxygen containing environment for best results.



## TID-1 Detection with the Agilent 6890 NPD Electronics

- 1.) TID-1 detection differs from NPD detection in several key ways:
  - a.) it does not require any Hydrogen flow - a detector gas environment of just N<sub>2</sub>, Air, or some combination suffices;
  - b.) the ion source surface is not as hot because there is no requirement to ignite any Hydrogen-Air chemistry (NP source glows an orange color whereas TID-1 source has no visible glow during normal operation);
  - c.) TID-1 signal gets bigger and bigger with increasing magnitude of the polarization voltage between the ion source and surrounding collector;
  - d.) TID-1 background signal is very low compared to an NPD background - therefore, the 6890 NPD ADJUST OFFSET FEATURE MUST BE DEACTIVATED FOR TID-1 OPERATION.
- 2.) Best TID-1 response is obtained with a stand-alone DET Current Supply replacing the 6890 Bead Voltage supply because the DET supply provides a higher polarization voltage (-45 V versus -4 V for the 6890 supply).
- 3.) TID-1 selectivity can also be obtained with the 6890 Bead Voltage supply, but the absolute magnitudes of response will be lower than with the DET supply.
- 4.) The magnitudes of TID-1 signals and background levels will generally increase with increasing magnitudes of the 6890 Bead Voltage. With a detector temperature of 250 - 300°C, we recommend starting with a Bead Voltage of 2.500 and/or a background output signal of 2 - 10 pA. Higher Bead Voltages will give larger signals, but may cause more rapid degradation of the ionizing activity.
- 5.) Each TID-1 source is accompanied by a final test chromatogram showing response on a 6890 NPD structure with power from a DET Current Supply. In operation, the resistance of the TID-1 source is about 1 Ohm. Hence, a final test power of 2.400 Amps from the DET supply corresponds to a source power of about 2.400 Volts from the 6890 Bead Voltage supply. Higher heating power from the Bead Voltage supply can compensate a little for its lower polarization magnitude versus the DET supply. However, there may be some small loss in selectivity because the TID-1 surface starts responding to a greater variety of chemical compounds as it is heated hotter and hotter.

# DET PARTS FOR THE AGILENT TECHNOLOGIES 6890/7890 NPD

## Improved Performance - - Extended Detection Modes

### THERMIONIC IONIZATION SOURCES (BEADS) - - - - - \$385. each

Durable cylindrical ceramic structure with a heater wire core, and mounted on a hexagonal shaped flange. Pre-tested for response. Interchangeable in Agilent 6890/7890 NPD assemblies, and in all DET detector assemblies. (Ion Sources made with a recycled electrical connector also available at \$350 each).

**TID-1 (010-901-00)** - Selective response to nitro-compounds, some halogenates, oxygenates especially phenols and carboxylic acids, chains of Methylene groups, and other electronegative functionalities - operates at 400 - 600°C in inert (N<sub>2</sub>) or oxidizing (air, O<sub>2</sub>) gas environments - femtogram detection for compounds like methyl parathion, 4-nitrophenol, pentachlorophenol, heptachlor, 2,4-dinitrotoluene, TNT, and acetaldehyde-DNPH when powered with -45 Volt polarization available from a DET Current Supply.

**TID-2 (010-902-00)** - Selective response to N,P compounds - Black Ceramic coating has long life and minimal tailing of phosphorus compounds - operates at 600 - 800°C in a dilute H<sub>2</sub> in air gas environment - low picogram detection for NP compounds - lower cost alternative to Agilent NP sources.

**TID-3 (010-903-00)** - Selective response to volatile halogenates - more uniform response to halogenates than TID-1 - operates at 600 - 800°C in inert (N<sub>2</sub>) or oxidizing (air, O<sub>2</sub>) gas environments - low picogram detection for trihalomethanes with minimal peak tailing and greater response for Br versus Cl - powered with -45 Volt polarization from a DET Current Supply.

**TID-4 (010-904-00)** - Our best coating for selective detection of N compounds (not recommended for P compounds because of tailing) - operates at same NPD conditions as TID-2 with 2 to 3 times better N detection than TID-2.

**TID-5 (010-905-00)** - Halogen selective detection - more uniform response than TID-3 - operates at same temperatures and gas environment conditions as TID-2, but with a higher polarization voltage (-45 V) available from a DET Current Supply - provides exceptional selectivity for Br versus Cl when configured with a stoichiometric H<sub>2</sub>/air mixture.

**TID-6 (010-906-00)** - P selective detection with suppressed N response - uses much higher Hydrogen, Air, and Nitrogen flows than the TID-2 and TID-4 NPD modes.

**TID-7 (010-907-00)** - NEW Green Ceramic for halogenated pesticides, PCBs - operates in N<sub>2</sub>, Air, or O<sub>2</sub>

### DETECTOR CURRENT SUPPLY - - - - - \$1760. each

**(001-901-01)** for 115 V. Stand-alone module provides heating current and a selection of -5, -15, or -45 V polarization voltages for DET thermionic sources or the Agilent NP source. May be used in place of the Bead Voltage supply on the Agilent NPD. Constant current operation supplies I<sup>2</sup>R heating power to the thermionic source versus V<sup>2</sup>/R constant voltage power provided by Agilent's Bead Voltage supply. R is a combination of the electrical resistance of the lead wires, the wire core of the source, and the resistivity of the ceramic material molded about the core. As the source ages, R increases slightly with time. With the Agilent constant voltage supply, the source heating power decreases with increasing R, and this contributes to the time decay in response of an NP source. To compensate for this, the Agilent Bead Voltage must be periodically increased in value. With the DET constant current supply, source heating power increases with increasing R, and this partially counteracts the response decay caused by loss of the NP source's ionizing activity. The DET supply also includes a green/red status light to immediately indicate that the source has burned out or the source power cable is not properly connected.

### WIDE BORE JET & COLUMN SPACING KIT

Allows capillary columns of 0.53 mm diameter or less to be inserted through the jet to a termination close to the ion source as defined by a spacer tool. Eliminates sample degradation from interaction with jet metal; eliminates jet clogging from sample matrices; and eliminates the need to ever replace the jet.

**(010-886-13)** - column spacer & 64 mm long jet for Agilent's adaptable fitting NPD base - **\$ 165. each**

**(010-887-13)** - column spacer & 43 mm long jet for Agilent's dedicated capillary base - **\$ 210. each**