

# CHEMICAL DETECTION PRODUCTS

by

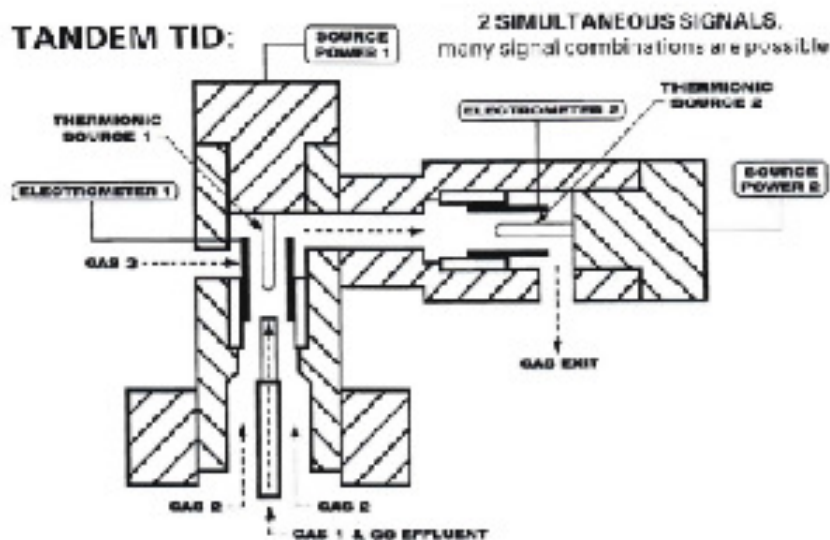
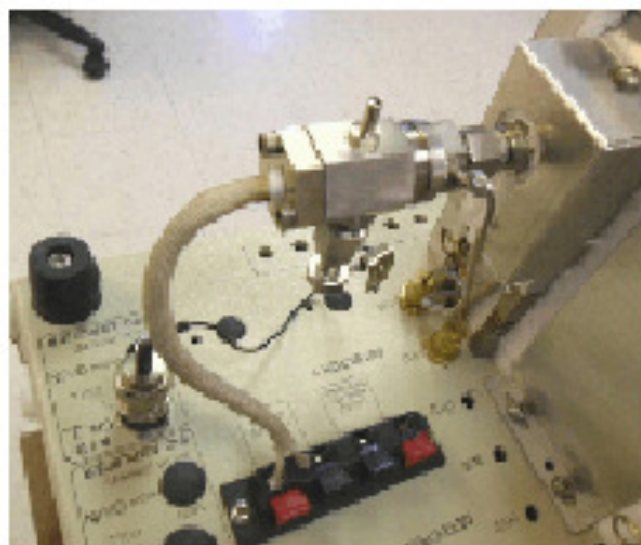
# DET

novel applications of the principles of  
Thermionic Surface Ionization  
and  
Flame Ionization

## GC DETECTION

- CERAMIC ION SOURCES (beads) for NPD and other modes of Thermionic Detection (TID)
- RETROFIT DETECTOR EQUIPMENT for Agilent, Thermo, Varian, HP5890, & SRI GCs
- COMPACT GC with NPD or TID selectivity

## STAND-ALONE TRANSDUCERS & DETECTION MODULES



# DET

innovations in chemical detection

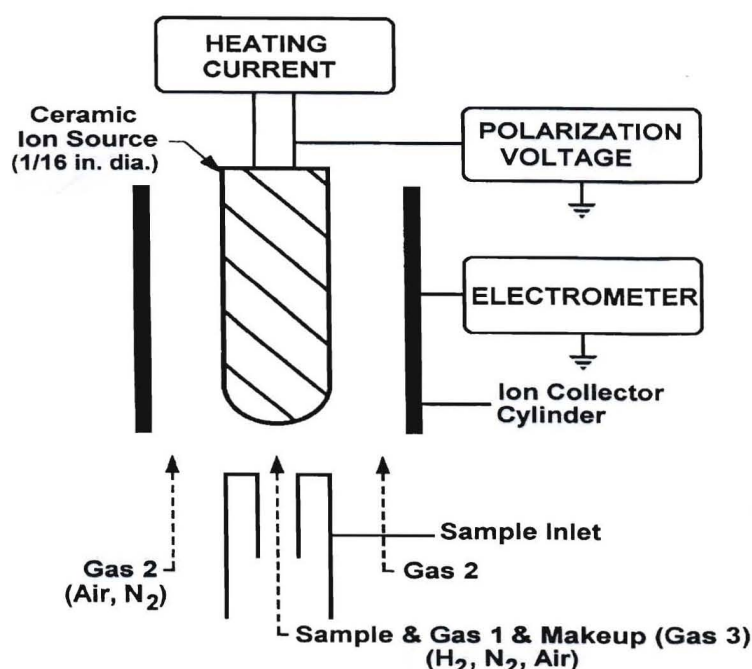
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# Thermionic Surface Ionization

(expanding the detection of GC NPD equipment)

THERMIONIC IONIZATION DETECTOR DESIGN  
(CONCENTRIC CYLINDER GEOMETRY)



## Optimum Geometry

(used on Agilent 6890/7890 NPD and all DET hardware)

cylindrical shaped ion source located on axis of collector cylinder provides streamlined gas flow and optimum electric field for ion collection

## Key Sensitivity and Selectivity Parameters:

1. ion source work function (surface composition);
2. ion source temperature (set by heating current);
3. composition of gases around the ion source;
4. polarization between ion source and collector.

Multiple modes of detection are achieved by easy permutations of these 4 parameters.

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## DET innovations in chemical detection

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

#### Equipment:

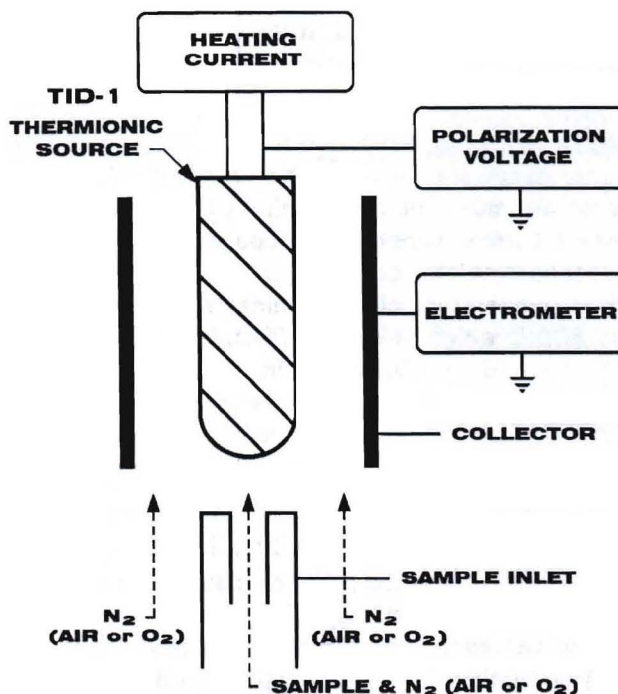
This detection mode uses a TID-1 type thermionic source mounted in either a TID/FID, REMOTE FID, FTID, PTID, or TANDEM TID tower. The detector gas is N<sub>2</sub> flowed through the gas lines which normally provide "H<sub>2</sub>" and "air" to an NPD or FID. (Air or O<sub>2</sub> are other possible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

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## TID-3-N<sub>2</sub>(O<sub>2</sub>): selective for VOLATILE HALOGENATES

### Equipment:

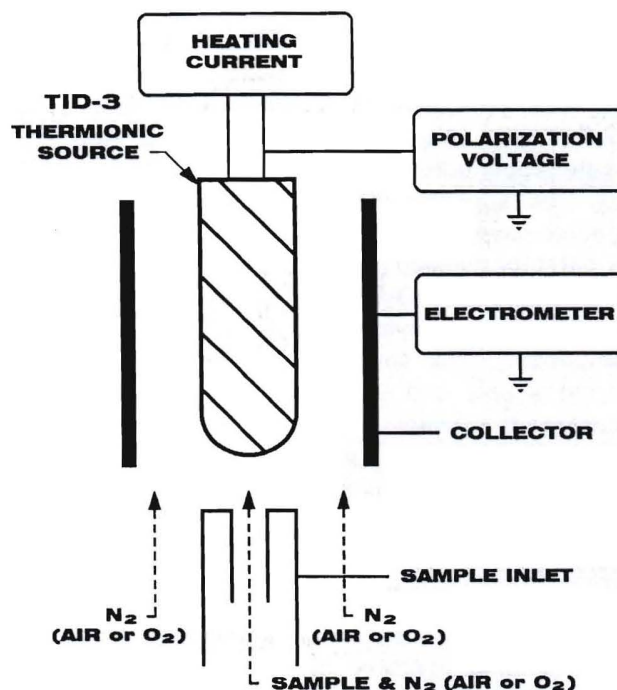
This detection mode is similar to the TID-1-N<sub>2</sub> mode except a TID-3 type source is used. The TID-3 source can be mounted in either a TID/FID, REMOTE FID, FTID, PTID, or TANDEM TID tower. Detector gas is N<sub>2</sub> through the lines which normally provide "H<sub>2</sub>" and air to an FID or NPD. (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 600-800°C which produces a visible orange glow.

### Principle:

This mode uses a thermionic surface of moderately high work function operated very hot 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 ionizing principle is essentially the same as the TID-1-N<sub>2</sub> mode except for the higher work function and higher operating temperature of the TID-3 ionizing surface. This mode was developed to eliminate a severe chromatographic peak tailing problem that otherwise occurs in using the TID-1-N<sub>2</sub> mode for volatile halogenated compounds. Assuming thermodynamic equilibrium between the thermionic surface and absorbed electronegative samples, the efficiency of surface ionization is given by the equation:

$$IE = \{1 + (g_o/g_n) \exp[(W - EA)/kT]\}^{-1},$$

where IE is the ionization efficiency, (g<sub>o</sub>/g<sub>n</sub>) is a ratio of statistical weights of negative ions and neutral species, W is the surface work function, EA is the electron affinity of the sample, k is Boltzmann's constant, and T is the surface temperature. In comparison to the TID-1 surface, the TID-3 surface has a higher work function W, so it must be operated at a higher temperature T in order to provide similar



magnitudes of ionization as the TID-1 surface. Because of the higher operating temperature, the TID-3 surface is less susceptible than the TID-1 surface to surface absorption of samples which can cause significant tailing especially for volatile halogenates.

### Response:

The detectivity for volatile halogenates such as methylene chloride, trihalomethanes, etc. is in the range of 1 - 2 pg/sec. The selectivity is greater than 10<sup>5</sup>:1 (bromoform : benzene), and the range of linear response exceeds 10<sup>4</sup>. Oxidizing environments such as air or O<sub>2</sub> are better than N<sub>2</sub> with respect to suppressing interferences from large concentrations of oxygenates such as alcohols.

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## DET innovations in chemical detection

### REMOTE FID: selective for LEAD, TIN, PHOSPHORUS, or SILICON compounds

#### Equipment:

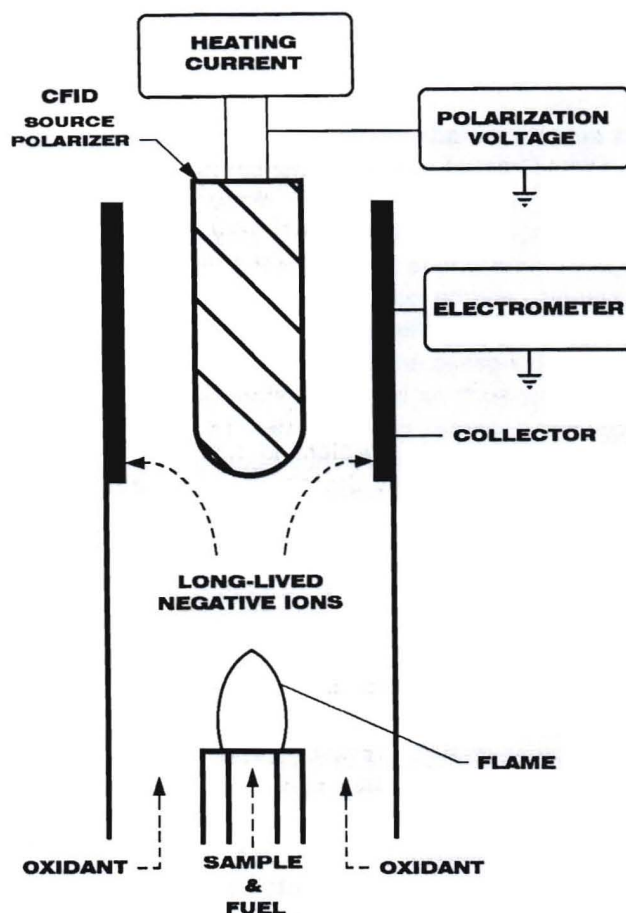
This detection mode uses a CFID type thermionic source mounted in either a REMOTE FID or FTID TOWER. The CFID source is used because it has the highest work function of the available source types, and in this mode the source is used simply as a flame ignitor and a polarizer electrode instead of as a source of surface ionization. The thermionic source polarizer and ion collector are located several centimeters downstream of a flame jet rather than immediately adjacent the jet as is the case in an FID. The detector gases are air and a mixture of  $H_2$  and an organic fuel such as methane. Heating current to the CFID source is increased to ignite a self-sustaining flame which flashes back and burns at the jet structure. After ignition, the heating current is reduced to zero or some low value. The source in this mode is normally polarized at -15 Volts relative to the collector for best sensitivity and dynamic range, or -5 Volts for best selectivity. Negative ion currents arriving at the collector electrode constitute the detection signal.

#### Principle:

This mode is based on the discovery that some heteroatom compounds form very long-lived negative ion species in flame combustion. These stable ions survive to be measured by the downstream collector, whereas ions from hydrocarbon combustion are dissipated by recombination processes before reaching the collector. The thermionic source serves only as a polarizer, and provides no additional ionization of samples. The detector uses an air-rich flame, and an organic fuel is added to further improve selectivity versus complex hydrocarbon matrices.

#### Response:

This mode provides selectivity for lead (Pb), tin (Sn), phosphorus (P), and silicon (Si), but it is unresponsive to N, O, S, or Cl. Detectivity for Pb, Sn, or P is 1pg (Pb, Sn, P)/sec, and the selectivity with an organic fuel



is greater than  $5 \times 10^5$  gC/g(Pb,Sn,P). Applications include detection of lead in gasolines and gasoline contaminated soil and water, organo-tin contaminants in water, phosphorus pesticides, and silicon bleed from gel implant prostheses. Since the ions detected in this mode are produced in the flame combustion process as in an FID, this detection mode is characterized by stable signal magnitudes over long operating times as long as the gas flows are maintained.

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**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.

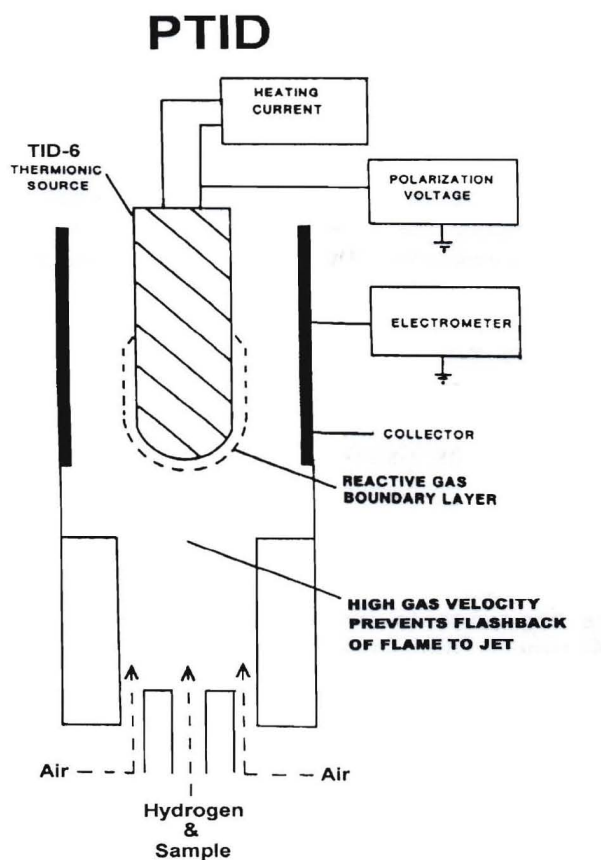
## Principle:

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 Hydrogen 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

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

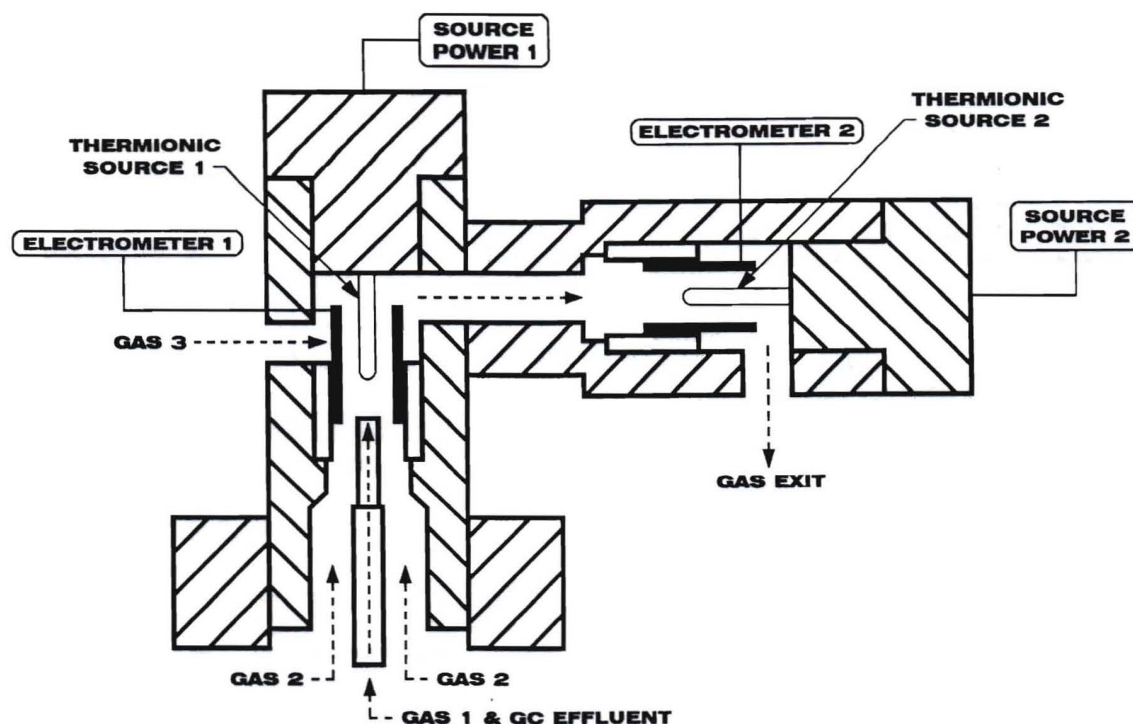


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## DET innovations in chemical detection

### 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<sub>2</sub>" 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<sub>2</sub>/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;

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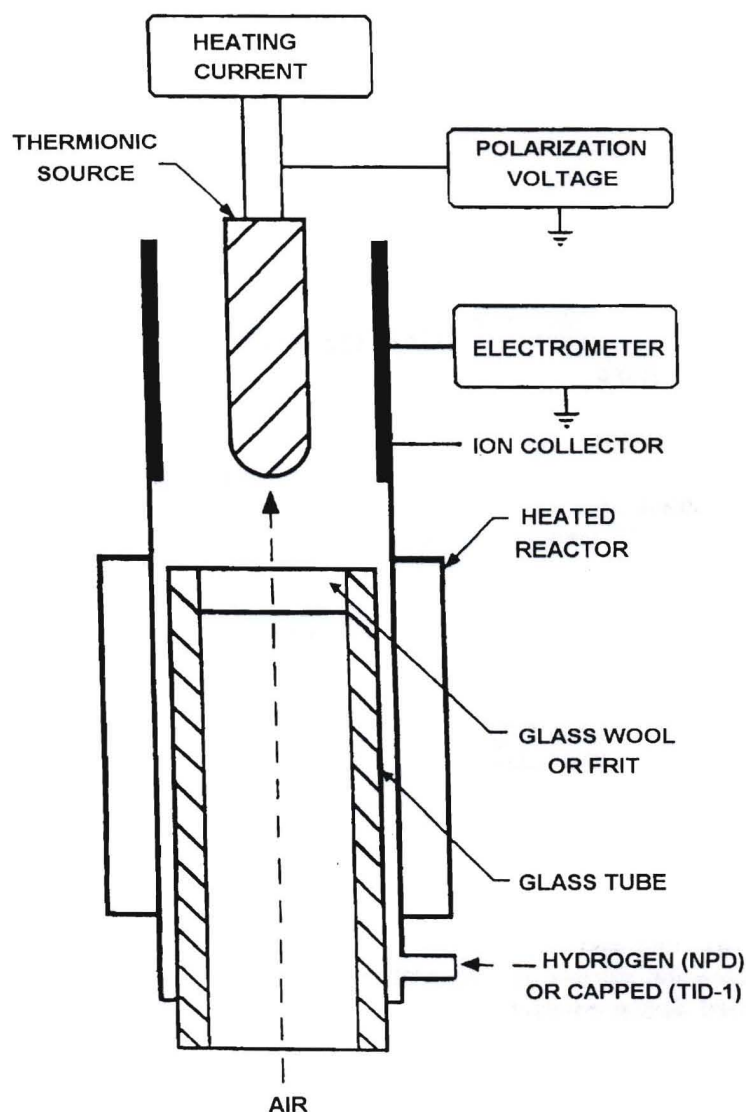
### RTIA: REACTOR THERMIONIC IONIZATION ANALYZER

#### 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 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<sub>2</sub>)**, **TID-3-Air(N<sub>2</sub>)**, or **TID-2-H<sub>2</sub>/Air** and **TID-4-H<sub>2</sub>/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 sampling pump attached to the module exit port. Ion Source power for the transducer in the RTIA module is provided by a **DET Current Supply**, and signals can be measured with a **Keithley 6485 Picoammeter** or equivalent.

#### 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.



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# **DET ION SOURCES and AGILENT 6890/7890 NPD EQUIPMENT**

## **Multiple Modes of Selective Detection**

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1. NPD - det. gas  $H_2 = 2 - 5$ , Air = 50,  $N_2 = 10$  mL/min  
TID-2 (black ceramic) - featuring sharp P peaks  
TID-4 (white ceramic) - best N response
2. PTID - det. gas  $H_2 = 20$ , Air = 200,  $N_2 = 100$   
TID-6 (blue gray ceramic) - P with suppressed N
3. TID-1\* (white ceramic) - det. gas  $N_2$ , Air, or  $O_2$   
oxygenates, nitro compounds, some halogenates,  
 $CH_2$  functional groups with an oxidizing environment
4. TID-3\* (white ceramic) - det. gas  $N_2$ , Air, or  $O_2$   
volatile halogenates like Trihalomethanes
5. TID-5\* (black ceramic) - det. gas  $H_2 = 5$ , Air = 12.5,  
 $N_2 = 30$  mL/min, Br and I with suppressed Cl
6. TID-7\* (NEW green ceramic) - det. gas  $N_2$ , Air, or  $O_2$   
halogenated pesticides, PCBs, PBDEs
7. POSITIVE IONS - DET Bare Wire Probe & Current  
Supply, Agilent NPD Hardware & FID Electrometer  
selective detection of triamines with Air det. gas,  
universal FID detection with  $H_2$ /Air flame

\* (Best Sensitivity Achieved With a DET Stand-alone Current Supply)

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# **DET NPD/TID/FID EQUIPMENT**

retrofit for the

## **THERMO TRACE GC**

---

- 1. DET Tower structure mounts onto the Thermo FID/NPD base - features a concentric cylinder geometry for streamlined gas flow and efficient ion collection.**
- 2. Tower assembly includes a Thermo jet modified with a ceramic liner and an extended ceramic tip.**
- 3. DET ceramic Ion Sources or Bare Wire FID Probe mount into the top of the DET tower for easy changes in multiple modes of selective or universal detection. (These are the same standard ion sources as used on Agilent 6890/7890 GC models).**
- 4. DET NPD/TID/FID equipment is very compatible with Thermo's versatile NPD electronics which provides Constant Current heating and a wide range of Polarization Voltages for the ion sources. The combination of DET hardware and Thermo's electronics provides unrivaled optimum capability for changing from one mode of detection to another.**

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# **DET NPD/TID/FID EQUIPMENT**

retrofit for

## **VARIAN GC MODELS**

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- 1. DET Tower structure mounts onto Varian FID/TSD base - about half the size of Varian's TSD tower - features a concentric cylinder geometry for streamlined gas flow and efficient ion collection.**
- 2. Tower assembly includes a ceramic-tipped jet that seals into Varian base with a non-crushable stainless steel ferrule.**
- 3. DET Ceramic Ion Sources or Bare Wire FID Probe (\$350 ea.) mount into top of DET tower for easy changes of multiple modes of selective or universal detection. (Same standard ion sources as used on Agilent 6890/7890 GC models at a much lower cost than Varian's \$1090 for a TSD bead replacement.)**
- 4. DET NPD/TID equipment compatible with Varian TSD electronics. Varian electronics suffice for NP detection, but big improvement in signal-to-noise for Oxygenate and Halogenate detection is achieved by powering ion sources with a stand-alone DET Current Supply.**

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# **DET NPD/TID/FID EQUIPMENT**

retrofit for

## **SRI GC MODELS**

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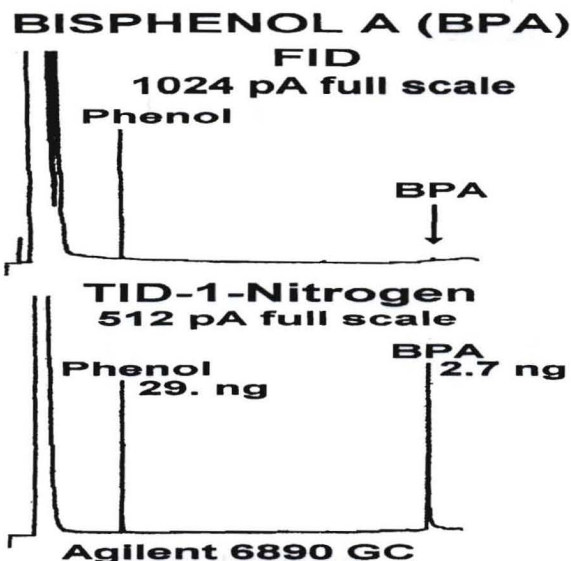
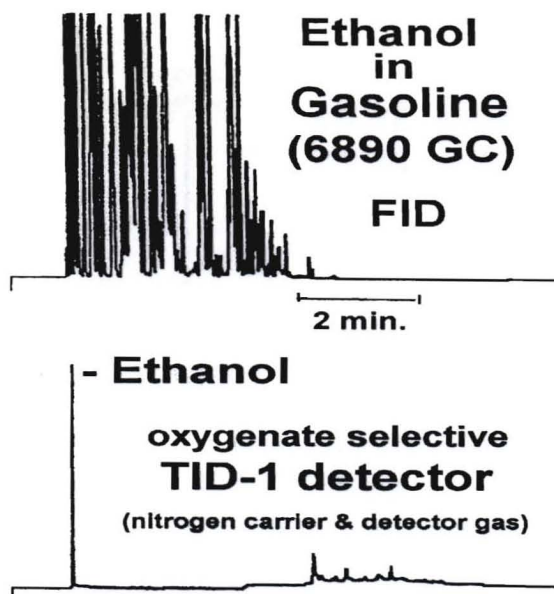
- 1. DET Tower structure mounts onto SRI FID base - includes a ceramic tipped jet and features a concentric cylinder geometry for streamlined gas flow and efficient ion collection.**
- 2. DET Ceramic Ion Sources or Bare Wire FID Probe mount into end of DET tower for easy changes of multiple modes of selective or universal detection.**
- 3. DET Ion Sources with bare wire terminations can be powered by the SRI NPD power supply with screw driver setting of ion source heating. A stand-alone DET Current Supply provides finer control of heating power and polarization voltages for DET Ion Sources that terminate in a Twinex electrical connector. (These are the same standard ion sources as used on Agilent 6890/7890 GC models.)**
- 4. SRI NPD amplifier suffices for signal measurement.**

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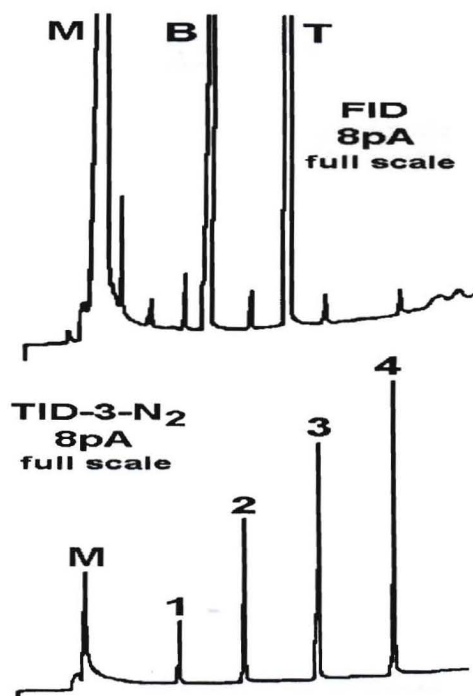
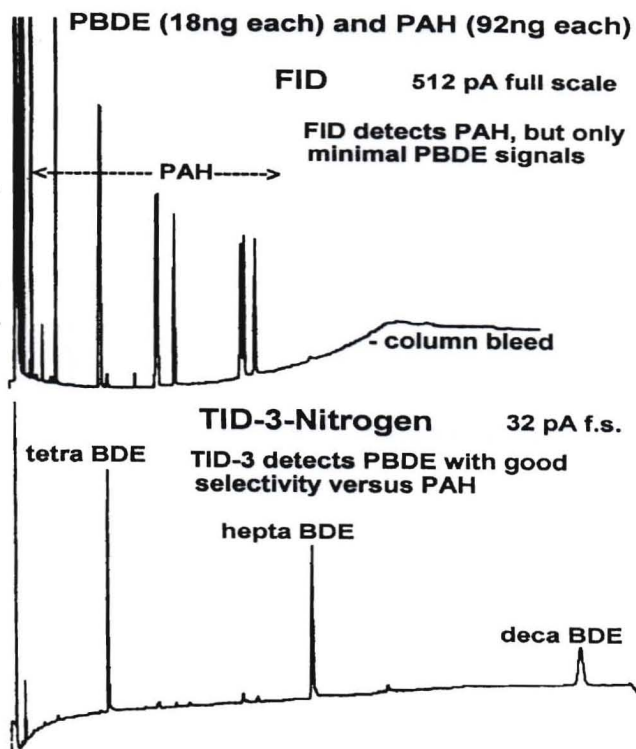
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Oxygenate selective TID-1 ionization provides easy analysis of Ethanol amidst many Hydrocarbons of Gasoline using a single Nitrogen supply for both GC carrier and detector gas.

Oxygenate selective TID-1 provides BPA detectivity which is 50 times better than an FID. TID-1 response to Phenols, Carboxylic Acids, Glycols, Salicylates, and Vanillin is especially large compared to other classes of Oxygenates.



Like TID-1, TID-3 ionization requires only Nitrogen as the detector gas, although TID-3 is designed to operate at a higher temperature to eliminate peak tailing.

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

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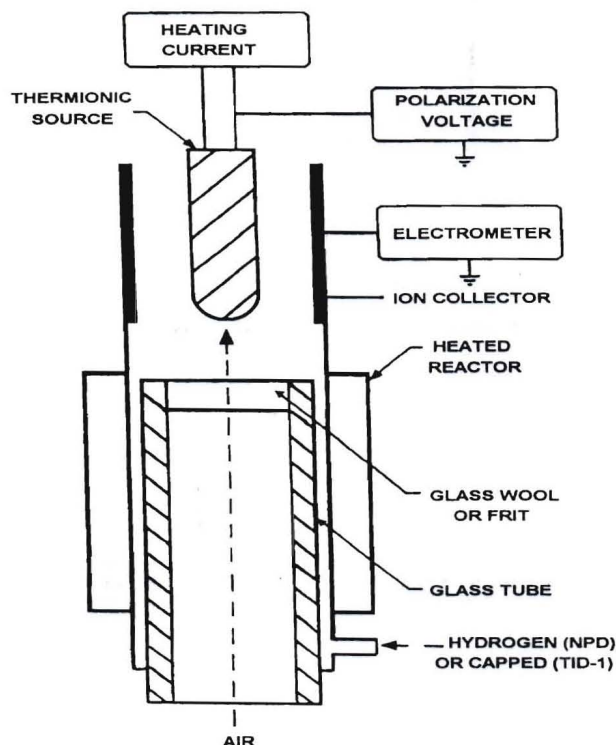
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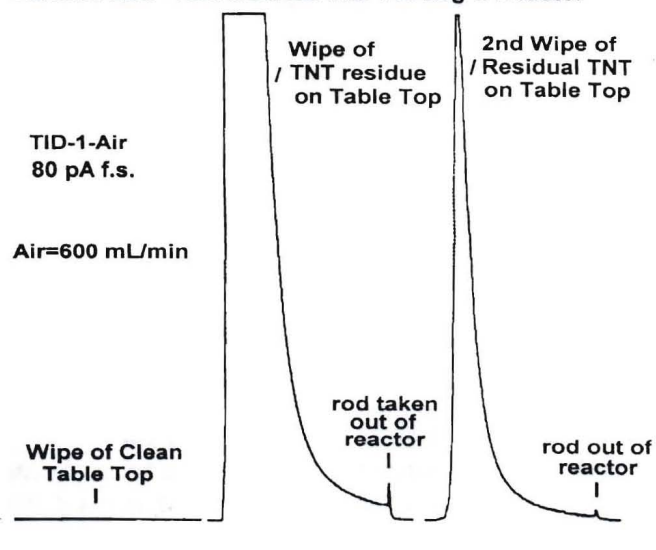
## Reactor Thermionic Ionization Analysis (RTIA)

selective TID/NPD transducer screening of vapors evolved from  
THERMAL DESORPTION/OXIDATION  
of nonvolatile liquid residues or solid sample constituents

**Background:** Thermal desorption continues to be an increasingly popular means of preparing real world samples for subsequent analysis by gas chromatography. Among the many different types of GC detectors, TID and NPD detectors have the distinctive characteristic that they can provide chemical species selectivity using Air as the primary detector gas. Consequently, these detectors are well suited to non-GC chemical screening applications where the gas environment is simply ambient Air drawn through a TID/NPD transducer by a sampling pump. In an **RTIA** configuration, such a transducer is preceded by a heated reactor chamber into which are inserted solid samples packed into a glass tube or liquid sample residues on a ceramic rod. The TID or NPD transducer provides selective responses to vapors evolved from thermal desorption and/or oxidation of the samples. At low reactor temperatures, thermal desorption usually accounts for most detected signals, while at high temperatures oxidative sample decomposition products often provide large signals. Good examples of the oxidative detection processes are large TID-1 signals from oxidation of sugars and proteins. For TID-1 and TID-3 thermionic detection, only Air is required as the operating gas, while for NPD a small flow of Hydrogen has to also be introduced into the incoming Air.

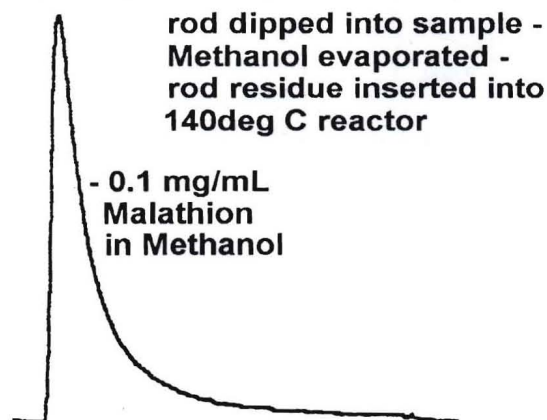


i-Propanol Wipe Transfer of Surface Residue to 1/16 in. Ceramic Rod - Rod inserted into 140 deg C Reactor



Malathion Residue on Quartz Rod

NPD, 160 pA f.s., Hydr.=4.3, Air=200



dried TNT residue on a table top wiped with an iso-propanol rod and transferred to ceramic rod

small quartz rod dipped into a 0.1mg/mL solution of Malathion in Methanol

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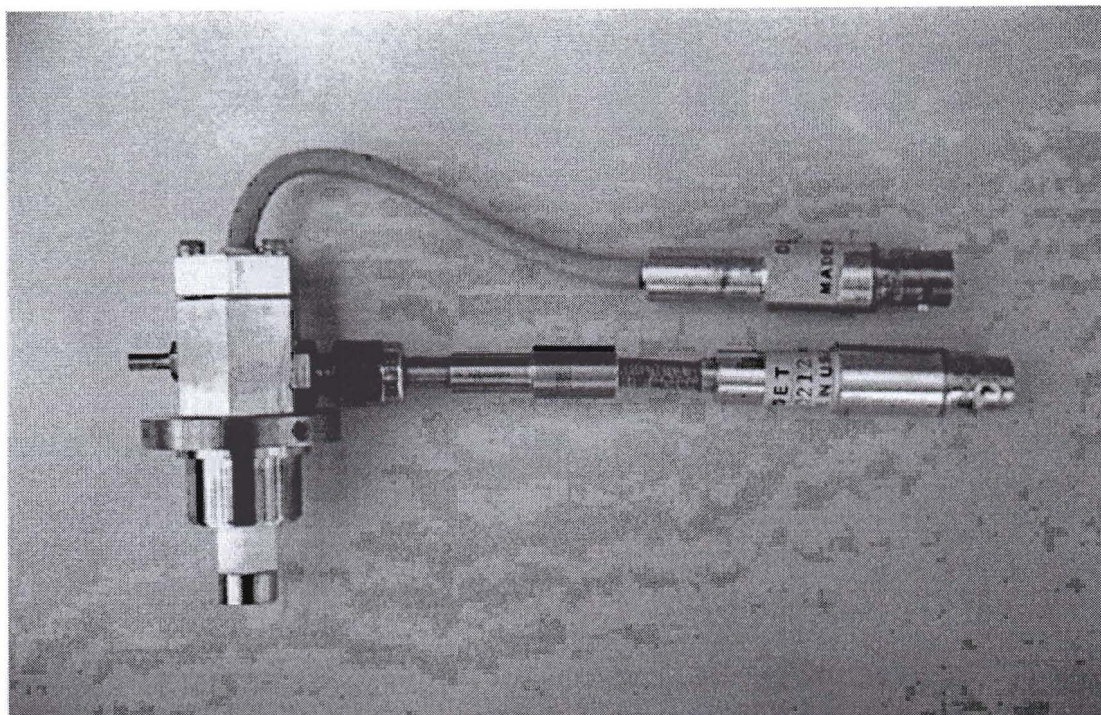
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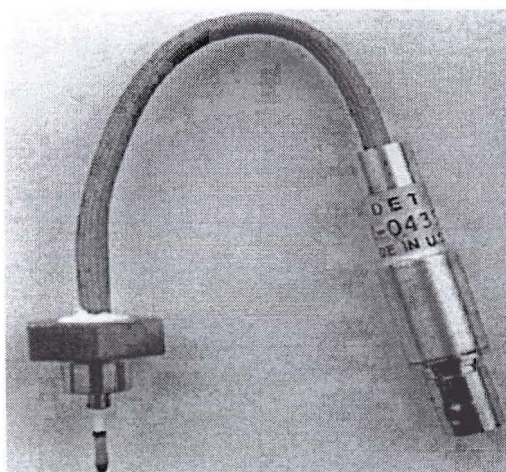


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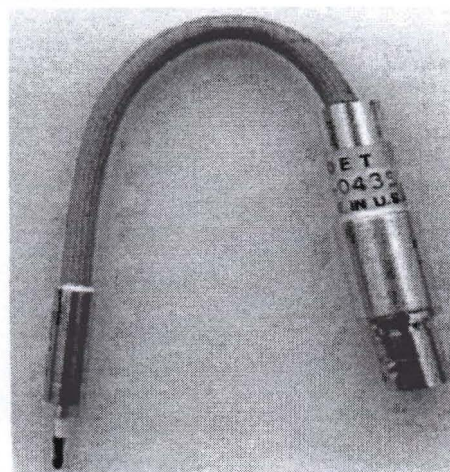


**DET NPD/TID/REMOTE FID HARDWARE**  
**MOUNTS ONTO AGILENT 6890 FID BASE OR HP 5890 FID/NPD BASE**

### **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-ELECTRON AND SRI GCs.**

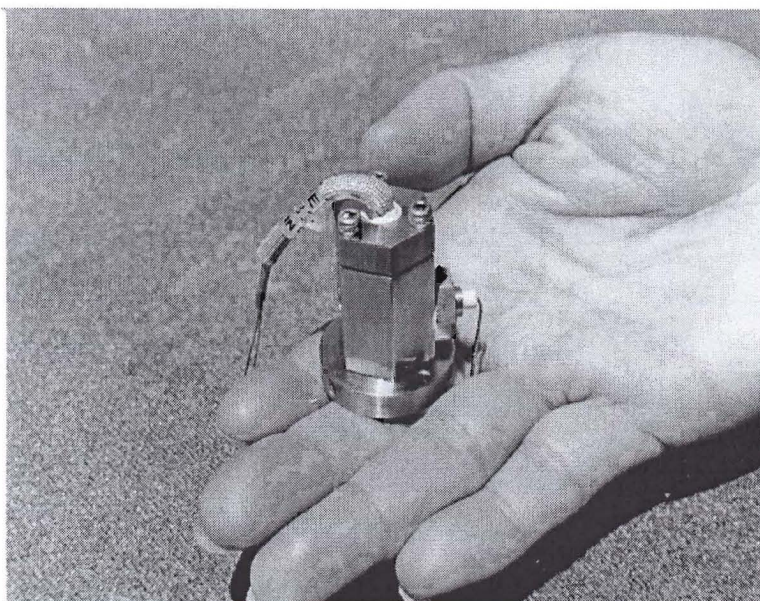
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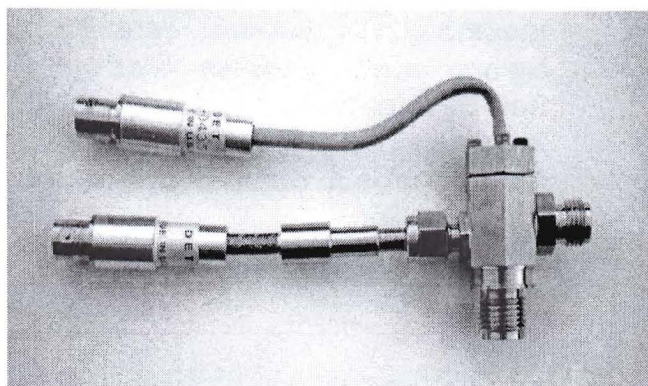
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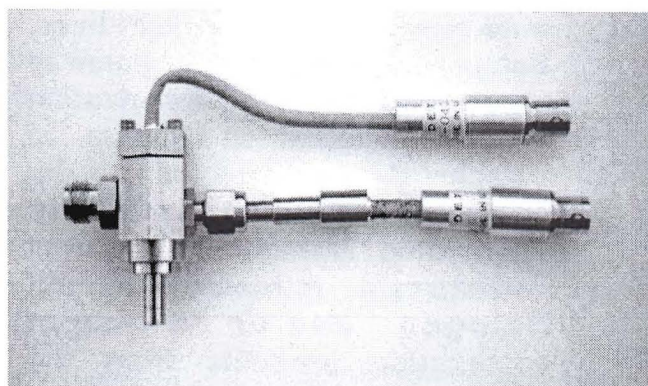
## EXAMPLES OF DET HARDWARE STRUCTURES



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**

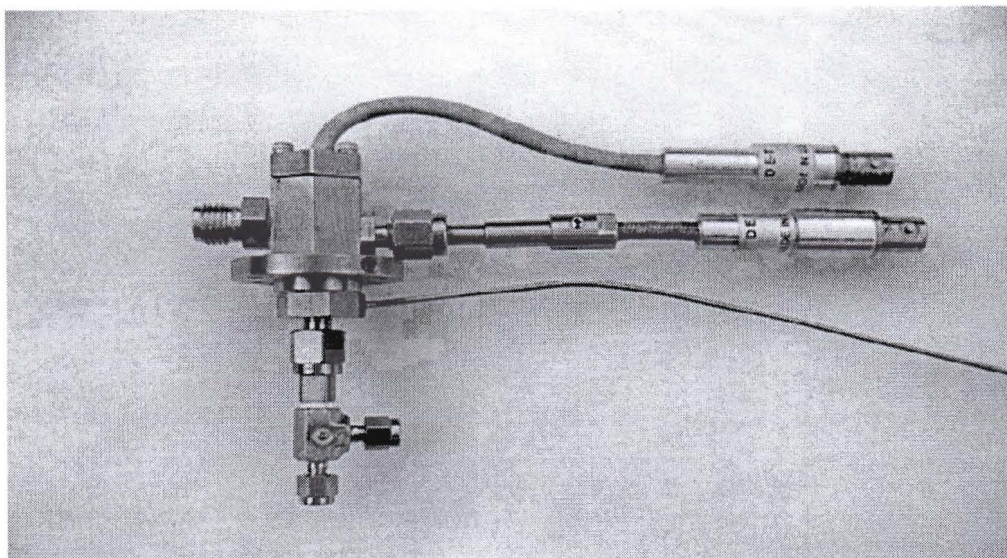
innovations in chemical detection

**HROMalytic** +61(0)3 9762 2034  
**ECH**nology Pty Ltd

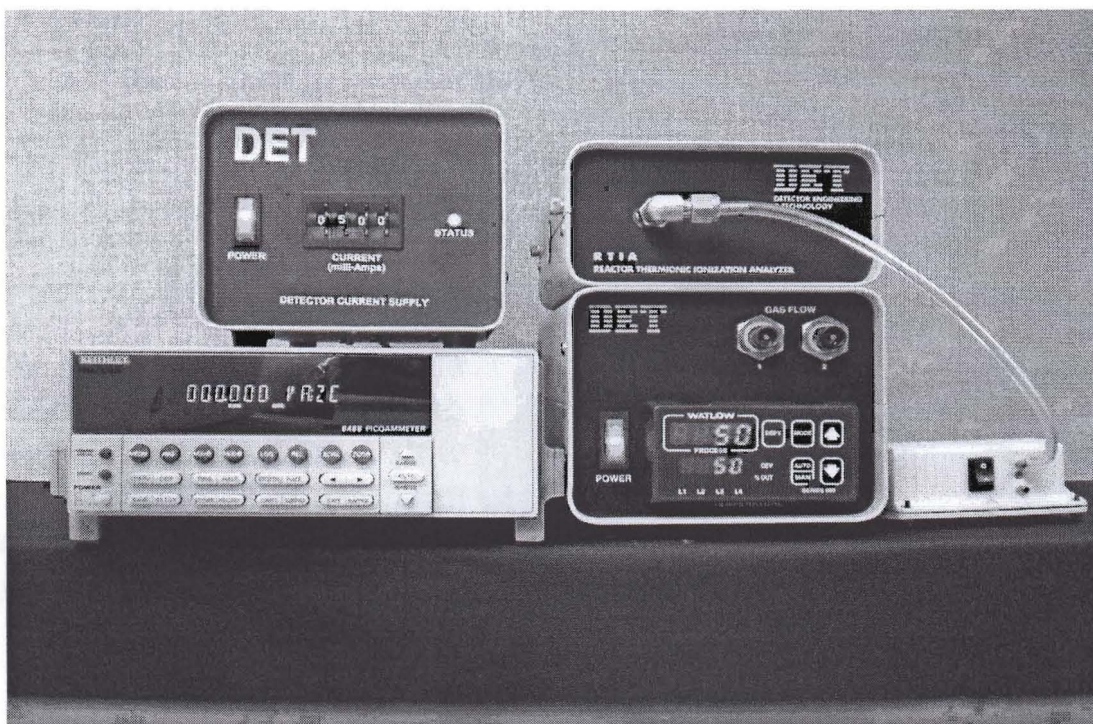
Australian Distributors; Importers & Manufacturers



**DET** innovations in chemical detection



**FID/TID TRANSDUCER - 1/16 SWAGE INLET TEE**



**DET CURRENT SUPPLY, KEITHLEY ELECTROMETER,  
AND RTIA MODULE WITH AIR SAMPLE PUMP**

**DETECTOR Engineering & Technology, inc.**



**Flame Thermionic Ionization (FTID)** – Samples are decomposed in a self-sustained Hydrogen-Air or Hydrogen-Methane-Air flame, and the neutral decomposition products are re-ionized and detected by a thermionic ion source and collector located well downstream of the flame.

**Catalytic Combustion Ionization (CCID)** – Hydrocarbon and Fatty Acid Methyl Ester (FAME) compounds containing large concentrations of CH<sub>2</sub> functional groups are selectively detected by forming momentary bursts of flame ignition as each compound impacts a hot catalytic ceramic surface in a detector environment containing Oxygen.

**Tandem Thermionic or Thermionic/Flame Ionization (Tandem TID, Tandem TID/FID)** – Two different detector stages are combined in series, and many different combinations are possible depending on the choices of ionizing elements and detector gases used in each stage. In some cases, the first detection stage is non-destructive, while in other cases, a destructive process in the first stage may be used to generate decomposition products that are then detected in the second stage.

**Reactor Thermionic Ionization Analysis (RTIA)** - In an 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 heated 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.

#### **INTERCHANGEABLE ION SOURCE ELEMENT CHOICES:**

**TID-2 (Black Ceramic)** – selective NPD detection with negligible tailing of P peaks;

**TID-4 (White Ceramic)** – selective NPD detection with the best possible N response;

**TID-1 (Very White Ceramic)** – selective detection of Oxygenates, Nitro compounds, some Halogenates, Pyrrole versus Pyridine functional groups, and Methylene groups in linear chain Hydrocarbons and Fatty Acid Methyl Ester (FAME) compounds;

**TID-3 (White Ceramic)** – selective detection of volatile Halogenates like Trihalomethanes;

**TID-5 (Black Ceramic)** – selective detection of Br and I compounds with suppressed Cl;

**TID-6 (Blue Gray Ceramic)** – selective detection of P compounds with suppressed N;

**TID-7 (NEW Green Black Ceramic)**- selective detection of Halogenates like PCBs;

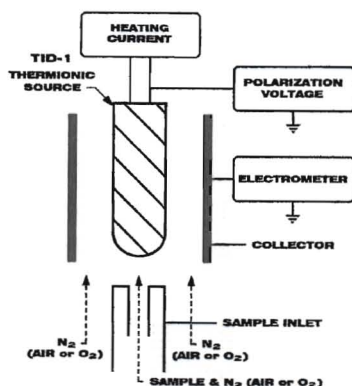
**CFID (Black Ceramic)** – used with the Remote FID mode for selective detection of P, Pb, Sn, or Si compounds;

**FID Probe (Uncoated Bare Wire)** – used as flame ignitor/polarizer for universal FID detection.

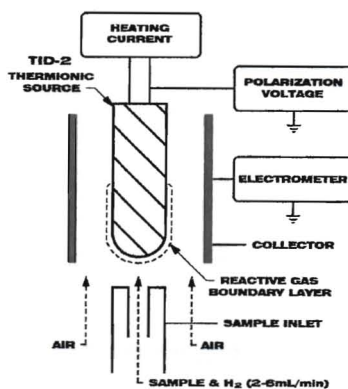


## GC DETECTOR INNOVATIONS by DET (different implementations of the same basic detector geometry)

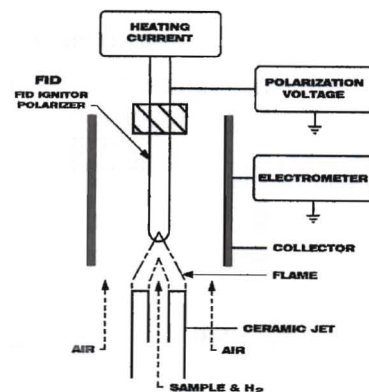
**TID**



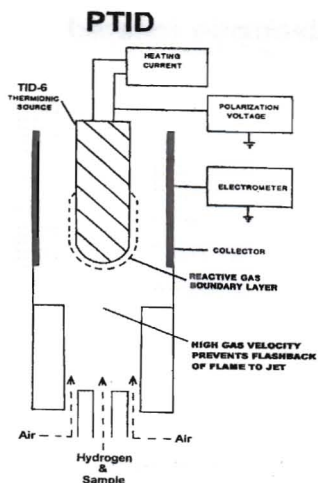
**NPD**



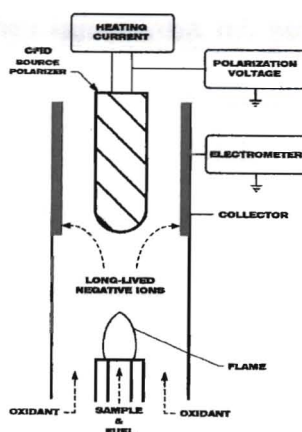
**FID**



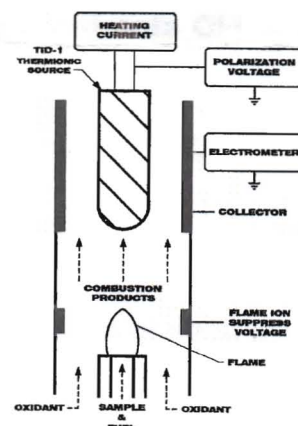
**PTID**



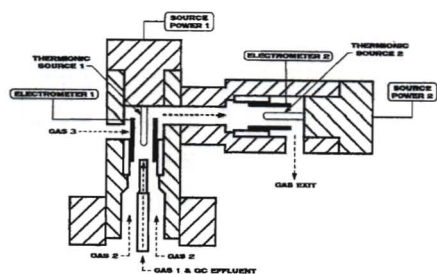
**REMOTE FID**



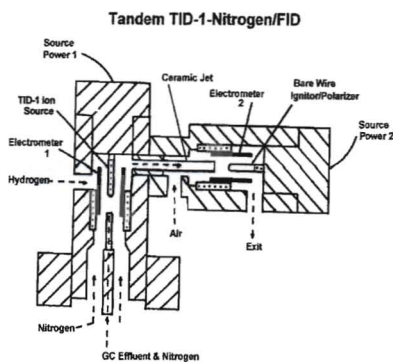
**FTID**



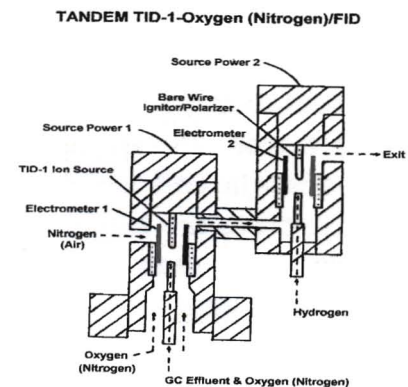
**TANDEM TID**



**TANDEM TID-Nitrogen/FID**



**TANDEM TID-Oxygen/FID**



**DET RETROFIT NPD/TID/FID TOWER ASSEMBLY THAT MOUNTS ONTO THE FID/TSD BASE ON VARIAN GC MODELS AND USES VARIAN TSD ELECTRONICS (\$1550):**

Accommodates the same ionizing elements as the Thermo retrofit. 10 times improvement in signal to noise achieved for TID modes by substituting the stand-alone DET Current Supply for Varian's TSD power supply.

**DET RETROFIT NPD/TID/FID TOWER ASSEMBLY THAT MOUNTS ONTO THE FID/NPD BASE ON SRI INSTRUMENTS GC MODELS (\$2350):**

Accommodates the same ionizing elements as the Thermo retrofit. NPD, TID, and FID modes can be powered by SRI NPD electronics, but better user friendly precision control is provided by the stand-alone DET Current Supply.

**DET RETROFIT NPD/TID/REMOTE FID TOWER ASSEMBLY THAT MOUNTS ONTO THE FID/NPD BASE ON AN HP 5890 (\$1850):**

Accommodates the same ionizing elements as the Thermo retrofit, plus a CFID (Black Ceramic) type source for use in an exclusive Remote FID detection mode which is selective for P, Pb, Sn, or Si compounds. DET hardware IS NOT compatible with 5890 detector electronics, so the stand-alone DET Current Supply (\$1760) and a stand-alone Electrometer (Keithley 6485 picoammeter, \$1800) are also required.

**APPLICATION EXAMPLES USING DET RETROFIT EQUIPMENT:**

sub-picogram NPD detection of pesticides and drugs of abuse;

femtogram TID-1 sensitivity for Nitro explosives like 2,4-Dinitrotoluene and TNT, as well as Nitro pesticides like Methyl Parathion;

sub-picogram TID-1 detection for some Halogenated pesticides like Heptachlor, Dieldrin, Chlordane, Pentachlorophenol, and Atrazine;

low picogram TID-3 detection of Trihalomethanes in drinking water;

selective TID-1 detection of Ethanol and other Alcohols in petroleum and biofuels;

selective TID-1 detection of Acetic, Formic, and other Carboxylic Acids in wine and other food and flavor analyses;

picogram TID-1 detection of BisPhenol (BPA) and Phthalates in food packaging products;

**DETector Engineering & Technology, inc.**  
486 N. Wiget Lane, Walnut Creek, CA 94598 USA  
ph: 925-937-4203, fx: 925-937-7581; email: [detplp@aol.com](mailto:detplp@aol.com), [www.det-gc.com](http://www.det-gc.com)



**VISIT DET at PITTCON 2011, March 13 – 17, Atlanta, Georgia, USA**  
**Booth 4078                      Sunday Poster 180-16P**

**CHEMICAL DETECTION PRODUCTS by DET**  
**featuring novel applications of the principles of**  
**THERMIONIC SURFACE IONIZATION and FLAME IONIZATION**

**GC detectors and stand-alone transducers manufactured by DET all have an original common design feature consisting of an electrically heated, cylindrically shaped ion source element positioned on the axis of an ion collector cylinder. Ion source elements are fabricated from proprietary ceramic coatings; are mounted on a flange for easy self-aligning installation into detector tower structures; and are available with different ceramic coatings for multiple modes of chemical detection using the same basic equipment.**

**DETECTION PRINCIPLES USED IN DET PRODUCTS:**

**Thermionic Surface Ionization (TID & NPD) – 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, like the widely used NPD, 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 gas phase chemistry.**

**Conventional Flame Ionization (FID) – Samples decompose and form ions in gas phase reactions with radical species like H, O, and OH that are present in self-sustained Hydrogen-Air flames. A polarizer voltage and ion collector located near the flame effectively measure ions formed by combustion of organic compounds.**

**Remote Flame Ionization (RFID) – Like an FID, samples are decomposed in a self-sustained flame, but the polarizer and collector electrode are located further downstream of the flame. In this detection, hydrocarbon ions dissipate by recombination processes near the flame, and only long lived ion species remain to be selectively measured at the collector. Detectable ion species include decomposition products of compounds containing P, Pb, Sn, or Si atoms, and the selectivity versus Hydrocarbon interferences is greatly improved by using a Hydrogen-Methane-Air fueled flame.**



## DETECTOR HARDWARE STRUCTURES by DET (visit DET at Pittcon 2011, booth 4078)

### GC DETECTOR TOWER CONFIGURATIONS:

**NPD/TID/FID Tower Structure** – This type of detector structure includes a ceramic tipped jet and a tower assembly that positions an ion source and collector electrode in close proximity to the top of the jet. Selective NPD and TID, and universal FID modes of detection are available depending on the choice of ion source element and the detector gases.

**NPD/TID/Remote FID Tower Structure** – This type of detector structure includes a wide bore jet, and a tower assembly that positions the ion source and collector electrode several centimeters downstream of the top of the jet. The internal diameter of the jet is sufficient to allow fused silica columns of 0.53 mm diameter or less to be inserted clear through the jet. For NPD and TID modes of detection, the GC column is terminated above the jet in close proximity to the ion source/collector. For the Remote FID mode of detection, the column end terminates right at the top of the jet, a self-sustaining flame is ignited at the jet, and long lived ions formed in the flame are carried downstream to the ion collector.

**NPD/TID/Remote FID/FTID Tower Structure** – This type of detector structure is similar to the Remote FID structure except it has an additional Ion Suppress electrode located near the top of the flame jet. The purpose of the Ion Suppress is to prevent ions formed in a flame at the jet from moving downstream to the ion collector. Remote FID detection is also achieved by turning Off the Ion Suppress voltage.

**NPD/TID/PTID Tower Structure** – This type of detector structure is similar to the Remote FID structure except it has a small restricted internal diameter between the jet and ion source that produces a high gas velocity to prevent a flame front formed at the hot ion source from flashing back to a self-sustained flame at the jet.

**Tandem TID & Tandem TID/FID Tower Structure** – This detector structure consists of 2 detection stages coupled together in a series combination. The first stage is either an NPD/TID/FID tower or Remote FID Tower each modified with an auxiliary gas flow input to sweep any dead volume between the 2 stages. The second detection stage can be either an NPD/TID transducer or an FID transducer. In the case of an FID transducer in the second stage, another auxiliary gas input is provided to achieve the appropriate fuel mixture for a self-sustaining flame.

### STAND-ALONE DETECTOR STRUCTURES:

DET tower structures can be configured with various choices and sizes of either Swage or Tube Inlets and Outlets for use as stand-alone transducers. A mounting flange is available to attach to the transducers, as well as Aluminum heater blocks. A transducer attached to a heated inlet reactor is used in DET's Reactor Thermionic Ionization Analyzer (RTIA) module for selective screening applications.



VISIT DET at PITTCON 2011, March 13-17, Atlanta, Georgia, USA  
Booth 4078 Sunday Poster 180-16P

## GC DETECTION IDEAS FROM DETECTOR ENGINEERING & TECHNOLOGY

### RETROFIT THERMIONIC IONIZATION DETECTORS ADD NEW APPLICATIONS AND EXTEND USEFUL LIFE FOR EXISTING AGILENT, THERMO, VARIAN, SRI, AND HP 5890 GC MODELS

DET has developed a family of inexpensive GC detectors that operate according to the principles of Thermionic Surface Ionization and Flame Ionization, and that feature ion source elements made of proprietary ceramic materials. The ion sources are a standard mounting design identical to that used on Agilent 6890/7890 NPD equipment, and are interchangeable in compact detector tower structures designed to custom mount onto existing FID/NPD bases on different model GC instruments.

#### DET ION SOURCE TYPES FOR USE IN AGILENT 6890/7890 NPD EQUIPMENT (\$350 each):

TID-2 (Black ceramic) – selective NP detection with negligible tailing of P peaks;

TID-4 (White Ceramic) – selective NP detection with best possible N response;

TID-1 (Very White Ceramic) - selective detection of Oxygenates, Nitro compounds, some Halogenates, Pyrrole versus Pyridine functional groups, and Methylene groups in linear chain Hydrocarbons and Fatty Acid Methyl Ester (FAME) compounds;

TID-3 (White Ceramic) - selective detection of volatile Halogenates like Trihalomethanes;

TID-5 (Black Ceramic) - selective detection of Br and I compounds with suppressed Cl;

TID-6 (Blue Gray Ceramic) - selective detection of P compounds with suppressed N;

TID-7 (NEW Green Black Ceramic) - selective detection of Halogenates like PCBs.

#### STAND-ALONE DET CURRENT SUPPLY FOR IMPROVED NPD AND TID DETECTION ON AGILENT 6890/7890 GC MODELS (\$1760):

Provides optimum Constant Current heating of NPD and TID ion sources, and variable polarization voltages for 10 times signal to noise enhancement for TID detection modes.

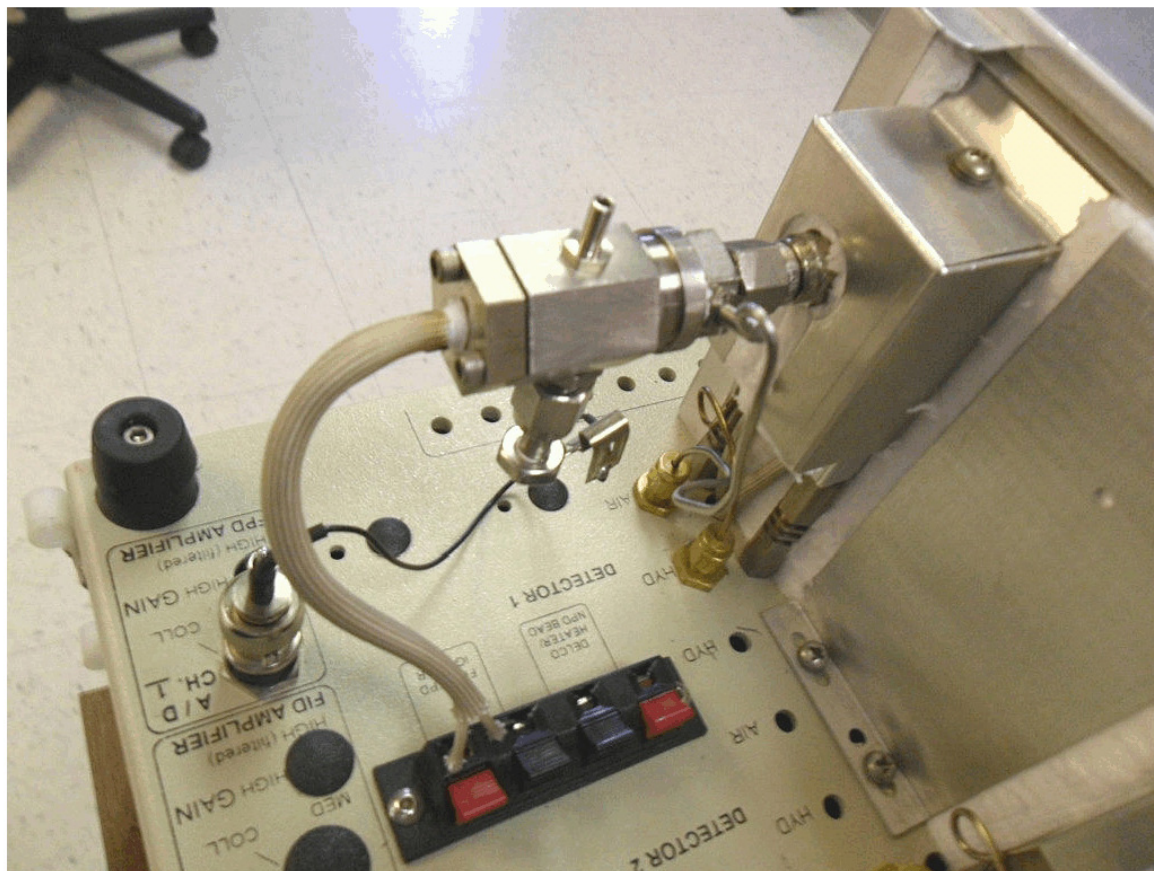
#### DET RETROFIT NPD/TID/FID TOWER ASSEMBLY THAT MOUNTS ONTO THE NPD BASE ON A THERMO SCIENTIFIC TRACE GC AND USES THERMO NPD ELECTRONICS (\$1800):

Accommodates any of the interchangeable ion source types listed above plus a bare wire probe for universal FID detection. Combination of DET hardware and Thermo NPD electronics provides unmatched performance capability for all modes of detection.

# DET

innovations in chemical detection

## DET NPD/TID/FID DETECTOR HARDWARE RETROFIT ON SRI GC WITH ION SOURCES POWERED BY SRI ELECTRONICS



**DET Retrofit for SRI Instruments GC Models 310 & 8610:**

**NPD/TID/FID Tower/Jet Assembly, part # 050-864-98, \$1850 USD**

- includes a ceramic tipped jet and tower structure with a concentric cylinder detector geometry that provides a stream-lined gas flow and efficient ion collection comparable to the NPD detector design on Agilent GC models - interchangeable ceramic coated ion source elements (part 010-90X-01, price \$315) mount into the end of the tower and bare lead wires connect to the SRI power terminals - "X" in the part number specifies the type of ion source and its intended selectivity of detection.

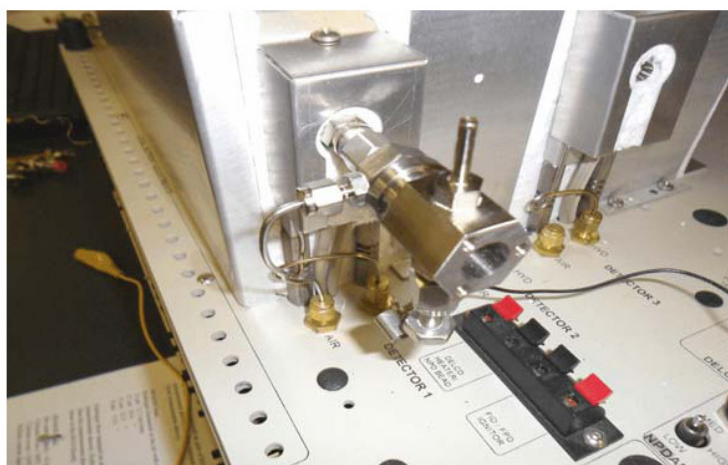
Available ceramic coated ion source elements include:

TID-2 & TID-4 ("X" =2 & 4) for NP selectivity; TID-1 ("X"=1) for selectivity to Oxygenates, Nitro compounds, some Halogenates, and certain other functional groups; TID-3 ("X"=3) for selectivity to volatile Halogenates and many Brominated compounds; and a few others.

Also available is a bare wire FID Probe element (\$315 USD) for conversion to a universal FID detection mode (part # 020-902-01 for power with SRI NPD electronics, or part #022-902-01 for power with SRI FID electronics).



## DET innovations in chemical detection



**DET RETROFIT NPD/TID/FID HARDWARE TO FIT SRI GC MODELS.** DET equipment has an optimum concentric cylinder geometry that provides better stream-lined gas flow and efficient ion collection, and it is compatible with the same ion source mountings as used on AGILENT GC models.



**COMPACT ANALYZER** - portable size SRI GC modified with glass lined flash vaporization injector, 0.32 mm dia. fused silica column, DET detector hardware with ceramic ion sources, and DET Current Supply for precision ion source power.

# DETector Engineering & Technology, inc.

- 1.) ELIMINATE NPD PHOSPHORUS PEAK TAILING WITH A BLACK CERAMIC ION SOURCE (BEAD) FROM DET.
- 2.) DIFFERENCES BETWEEN CERAMIC AND GLASS NPD ION SOURCES.
- 3.) SCIENCE OF THE NPD.
- 4.) LIFETIME CONSIDERATIONS FOR NPD ION SOURCES.

## 1.) ELIMINATE NPD PHOSPHORUS PEAK TAILING WITH A BLACK CERAMIC ION SOURCE (BEAD) FROM DET.

Years ago, Phosphorus peak tailing was a well known characteristic of NP detectors. In 1997, DET announced the development of a durable NPD ion source with a Black Ceramic coating specifically formulated to eliminate the P tailing, while still maintaining excellent P detectivity (e.g., 70 fgP/sec). That Black Ceramic ion source is currently available direct from DET, or as an NPD option from Agilent, Thermo Scientific, SRI Instruments, and several other GC manufacturers.

In recent years there has been increasing use of a so-called "Blos" glass NPD bead, and that has re-introduced the problem of tailing P peaks. Figure 1 demonstrates how detection of trace level peaks U1, U2, and U3 is obscured when they elute shortly after large tailing P peaks.

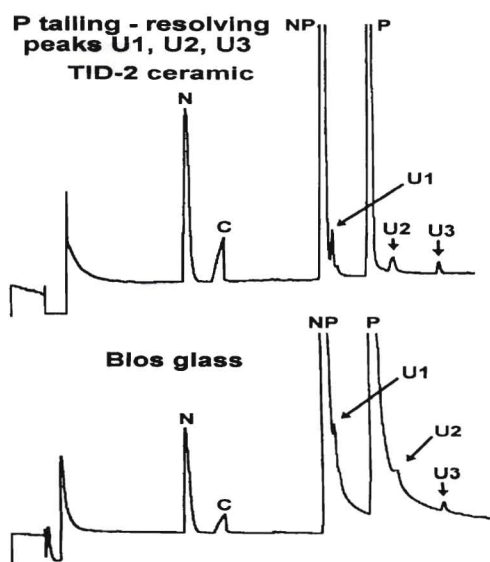


Figure 1. NP=2ng Methyl Parathion, P=4ng Malathion.

Figure 2 demonstrates that peak tailing results in a very long term recovery of the detector baseline to a stable level, and that is an important downtime consideration when waiting for baseline stabilization before injecting the next sample.

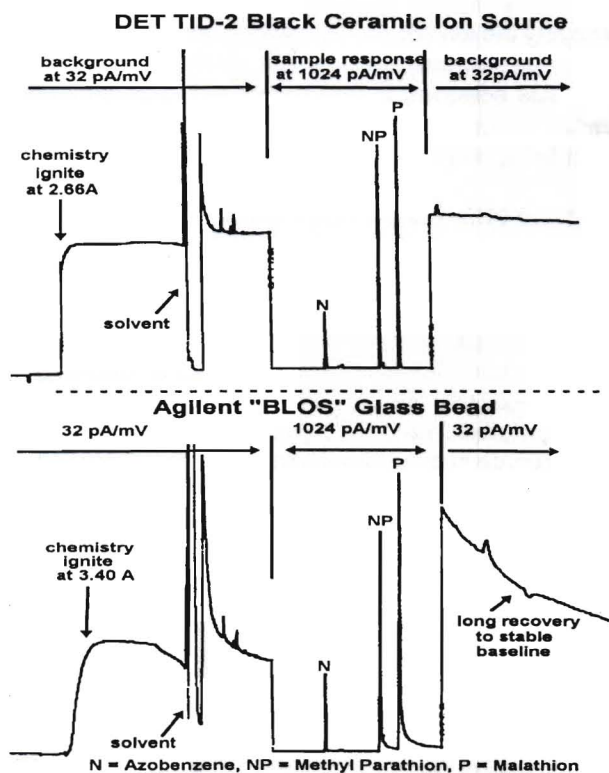


Figure 2. Expanded display sensitivity before and after elution of sample components. Agilent 6890 NPD hardware with DET Current Supply for ion source power. Ion source heating current initially increased to magnitude required for NP chemistry ignition. 3ng Azobenzene, 3ng Methyl Parathion, and 6ng Malathion sample injected. Sensitivity changed after solvent elution to show peak responses.



## 2.) DIFFERENCES BETWEEN CERAMIC AND GLASS NPD ION SOURCES

### Ceramic vs. Glass in an NPD Environment.

The ion source in an NPD must be hot enough to ignite a boundary layer of Hydrogen-Air chemistry, and that requires a surface temperature in the range of 600 - 800°C. At that temperature, a Bloss glass NPD bead, and previous glass beads, are in a softened state, and operating parameters must be carefully controlled to prevent overheating and melting the bead. This concern over glass melting is a major constraint on the type and quantity of additives that can be used in a glass bead matrix.

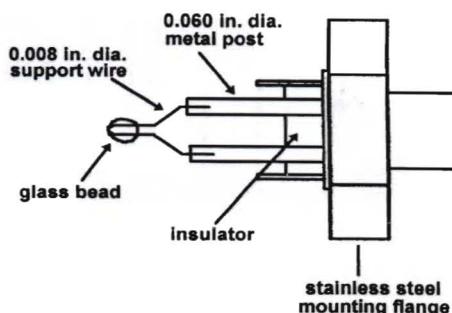
In contrast, the ceramics and additive chemicals used in DET ion sources are all chosen to withstand temperatures in excess of 1000°C, so that a wide range of operating conditions are allowed without destroying the ion source. Also, the method of forming ceramic ion sources allows an almost limitless number of possible additives to be used to enhance ceramic material properties such as hardness, electrical conductivity, and catalytic/ionizing activity.

### Structural Differences - DET Ceramic Ion Sources vs. a Bloss Glass Bead.

Figures 1 and 2 illustrate the structures of a Bloss glass bead and a DET ion source as they are configured to mount onto Agilent 6890/7890 NPD equipment. In both cases, the ion sources are attached to a hexagonal shaped mounting flange which provides easy top access installation into the Agilent NPD, and positions the ion source in an optimal location in the center of a collector electrode.

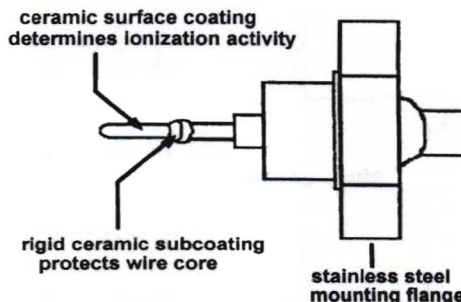
As indicated in Figure 1, the Bloss NPD ion source consists of a small glass bead attached to a loop of bare supporting wire that also is the means of electrically heating the bead. The supporting wire is a very small diameter that can easily be bent out of shape with the slightest touch. Also, the glass bead is a very small diameter so positioning the bead relative to an incoming gas orifice can be critical to ensure samples impact the bead surface.

In contrast, the DET ion source illustrated in Figure 2 is a more substantial rigid structure consisting of layers of ceramic materials coated over an internal heating wire core. A sub-layer coating covers the wire core to protect it from corrosion, and provides a hardened substructure that resists cracking at high temperatures. A surface coating applied over the sublayer contains ceramic additives that define the ionizing and catalytic activity of the outer surface. Many different surface coating formulations are possible because the sublayer prevents surface ingredients from direct, potentially corrosive, contact with the ion source's wire core. For example, for NP detection, DET has available a choice of 2 different ion source surfaces. One is a Black Ceramic (TID-2 type) formulated to eliminate tailing of P peaks. The other is a White Ceramic (TID-4 type) formulated to provide the largest possible N response for applications where there isn't concern about tailing P peaks. Other ceramic coated ion sources are available to provide selective detection of Oxygenates, Nitro compounds, Halogenates, Methylene functional groups, etc.



**Bloss Bead for Agilent NPD**

**FIGURE 1.** Schematic of Agilent's Bloss glass bead.



**DET Ion Source Construction  
 (fits Agilent & DET structures)**

**Figure 2.** Schematic of DET ion sources.

## Electrical Differences - DET Ceramic Ion Sources vs. a Bloss Glass Bead.

In a Bloss glass bead, the wire used to electrically heat the glass must have a large enough diameter to also provide support for the bead. In operation, the electrical resistance of the Bloss ion source is just 0.19 Ohms, which means that ion source heating power heats lead wires and connectors in addition to the ion source, and the temperature of the ion source is extremely sensitive to the stability of the heating power supply.

In DET ion sources, the heating wire is encased in a supporting ceramic structure so that a higher resistance 1.2 Ohm wire core is achieved. This assures that ion source heating power is mainly dissipated in the ion source rather than in the electrical leads and connectors.

Figure 3 compares a DET ion source and the Bloss bead with regard to the magnitude of NPD baseline changes associated with step function changes in the heating power (i.e., Agilent Bead Voltage). A 1 millivolt change in the Bloss power produced almost the same magnitude baseline change as a 10 millivolt change in the DET TID-2 power. Clearly, the Bloss bead demands much better power supply stability.

## 6890 NPD Sensitivity to Changes in Bead Voltage and Hydrogen Flow

2 pA full scale

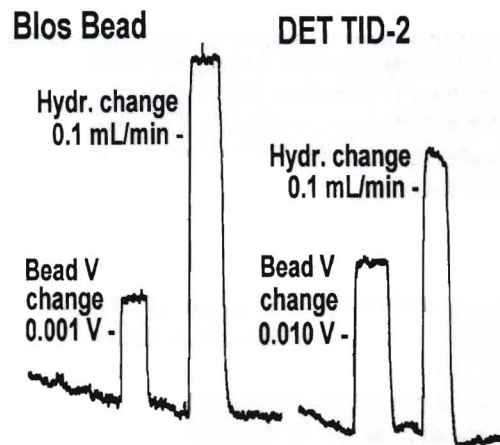


Figure 3. Baseline changes when Ion Source Heating (i.e., Bead Voltage) and Hydrogen flow were changed by incremental amounts. Comparison of Bloss glass bead and a DET TID-2 (Black Ceramic) ion source.

## 3.) SCIENCE OF THE NPD

### Science of the NPD Detection Process.

For any GC detector, defining the science of the detection process is an important part of designing reliable and reproducible detection equipment. For an NPD with a Bloss glass bead, the science is complicated by the fact that the glass bead is a non-rigid physical structure which appears to continually evolve with operating time with respect to color changes, internal bubble formation, particulate surface growths, and migration movement about the heating wire core. Furthermore, both the glass and the exposed metal support wire can contribute to the detectable ionization, and there is likely also some volatilization of glass material occurring due to its semi-molten state. As a consequence, the science of a Bloss NPD cannot be easily defined.

The NPD detection process can be more easily described when the ion source is a rigid ceramic cylinder positioned on the axis of a collector electrode such as illustrated in Figure 4. As depicted in this

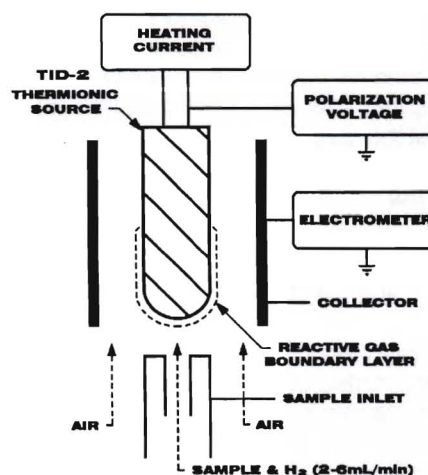


Figure 4. Schematic illustration of an NPD configuration.



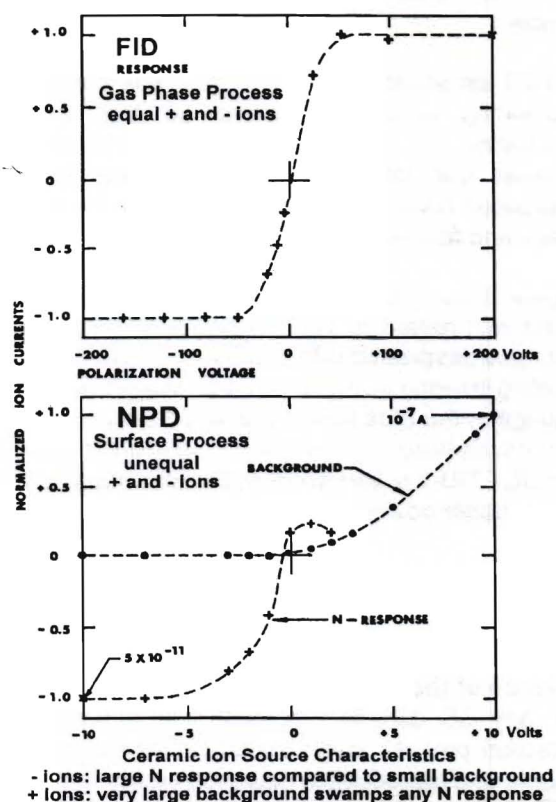
figure, NP selectivity turns on when the ion source is heated sufficiently to ignite the Hydrogen-Air detector gases. An important NPD parameter is that the Hydrogen is maintained at a low enough flow that the ignited chemistry does not flash back and form a self-sustained flame at the Hydrogen/sample inlet orifice. Instead, the ignited chemistry remains as a chemically reactive boundary layer in the vicinity of the hot ion source. Incoming samples are decomposed in this reactive boundary layer, and electronegative N and P decomposition products extract electrons from the ion source surface to form gas phase ions that subsequently move to the collector electrode for detection.

Data shown in Figure 5 were a milestone in demonstrating that NPD ionization was a Surface Ionization process rather than a Gas Phase process. These data show a comparison of FID and NPD ion currents measured as a function of positive and negative polarization voltages.

As is well known, FID ionization is a Gas Phase process that produces equal numbers of positive and negative ions. That is clearly shown by the symmetry in the FID data.

In contrast, ion current data measured with an NPD equipped with a ceramic ion source demonstrated that the ion source was a prolific emitter of large magnitudes of positive ion background with positive polarizations, but a negligible emitter of background current at negative polarizations. At the same time, there was a significant ion current response to the test N compound at negative polarizations, while any response at positive polarizations was swamped by the high background. The unsymmetrical NPD data clearly indicated that the response mechanism in that detector was a Surface Ionization process rather than a Gas Phase process.

From the recognition that the NPD mechanism is a surface process, it has been possible to identify other surfaces and other detector gas environments that produce other modes of selective detection. This expansion to other modes has been facilitated by ceramic fabrication technology which allows development of a many different ion source coatings.



**Figure 5.** Positive and Negative Ion Current versus Positive and Negative Polarization Voltages. FID and NPD.

## 4.) LIFETIME CONSIDERATIONS FOR NPD ION SOURCES.

A unique characteristic of NP detectors is that the absolute magnitudes of signal and noise can be varied over a wide range by changes in the ion source heating current and the Hydrogen flow. Therefore, signal-to-noise as well as selectivity should be the main considerations in judging NPD performance rather than absolute signal magnitudes.

The necessary and sufficient condition for turn on of

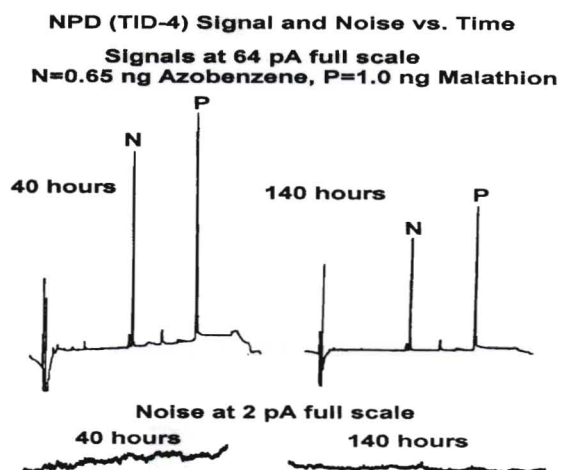
NP selectivity is that the ion source must be hot enough to ignite the Hydrogen-Air chemistry. While absolute signal magnitudes can be increased by heating the ion source beyond its ignition value, that practice leads to shorter operating life for the ion source. Some GC-NPD manufacturers have incorporated a flawed operating concept (e.g., Agilent Adjust Offset feature) that automatically increases the ion source heat in order to maintain a constant NPD

background signal. However, that procedure keeps heating the ion source hotter and hotter, and operating life is greatly shortened. Longest ion source operating life is achieved by leaving the heating current close to that magnitude just needed to ignite the boundary layer chemistry. Chemistry ignition in an NPD is indicated by a sudden increase in detector background signal as the ion source heat is slowly increased. This was illustrated in the data displayed in Figure 2.

It is not unusual for the absolute signal of an NPD to decay slowly with operating time, but the noise also decays, so signal-to-noise remains more constant. This characteristic is illustrated in Figure 6.

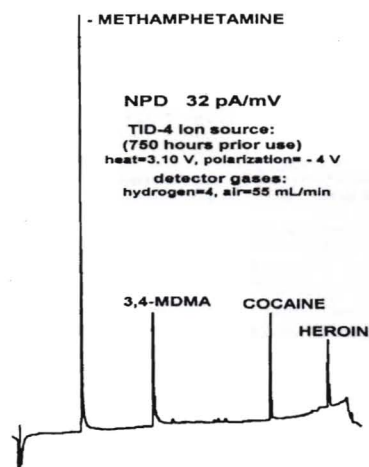
To account for any NPD response decay, use of an internal standard reference compound is usually recommended for the NPD. As an NPD ion source is used for long times, increases in Hydrogen flow and ion source heat can also be used periodically to get larger signals for extended time. DET'S TID-2 and TID-4 NPD ion sources can provide good NP response for operating times in excess of 1500 hours, and they have unlimited shelf lives when not in use.

NPD ion sources are consumable components, and DET provides a recycling service as an environment friendly way of disposing of depleted ion sources. This recycling experience has revealed that NPD end users have widely ranging criteria when determining that it is time to replace the ion source.

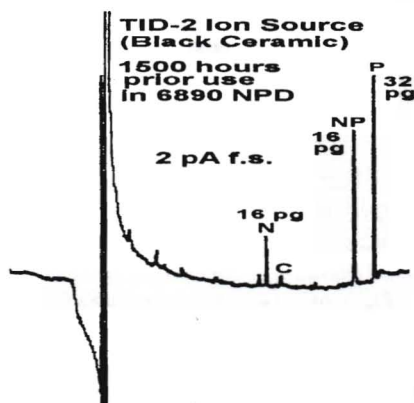


**Figure 6.** Absolute magnitudes of both signals and noise decrease with NPD operating time, but signal-to-noise (i.e., detectivity) remains more constant.

Many ion sources returned to DET still have hundreds of hours of useful life remaining when judged with regard to signal-to-noise and selectivity. Although the absolute response of a used NPD source may be 10 times lower than when it was new, the noise is also lower, so there remains good detectivity and selectivity. Figures 7 - 11 provide some examples from ion sources that have had extensive prior use. For some of these examples, judicious adjustments of Hydrogen flow and ion source heat were used to gain further enhancement of NPD responses in the later stages of ion source operating life.



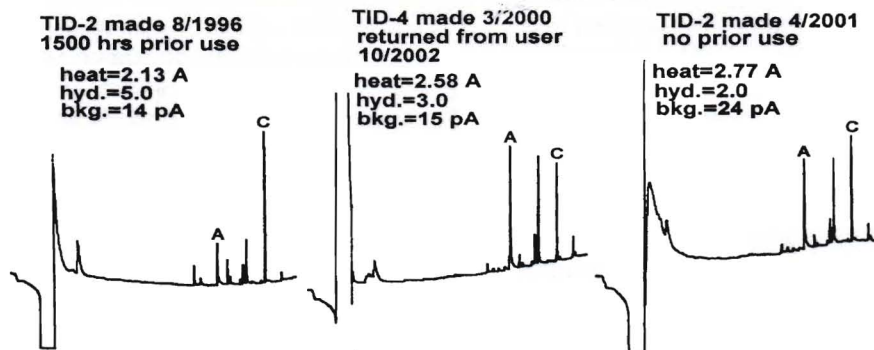
**Figure 7.** DET TID-4 White Ceramic ion source used 750 hours prior to these data. Signals 4.4 times less than when new, noise 5.5 times less, signal-to-noise 20% better than new.



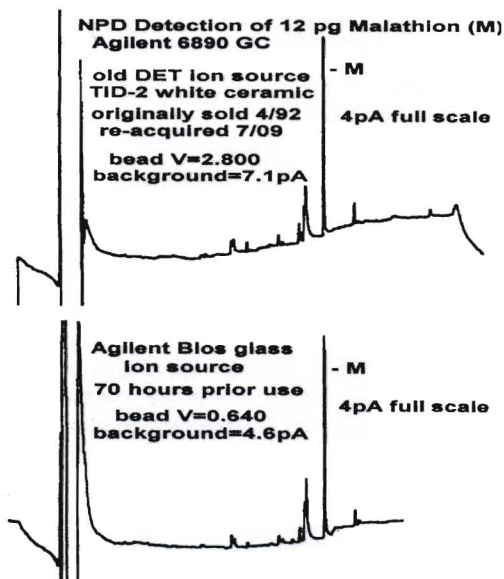
**Figure 8.** DET TID-2 Black Ceramic ion source used 1500 hours prior to these data. Still sharp P peaks, good selectivity of N and P vs. C, and low picogram sensitivity. N=Azobenzene, NP=Methyl Parathion, P=Malathion C=32,000 pg n-Heptadecane.



**DET Ceramic Ion Sources After 6 Plus Years Storage In Lab Drawer**  
 30 pg Atrazine (A) and Chlorpyrifos (C)  
 6890 NPD Equipment - all data at 16 pA full scale



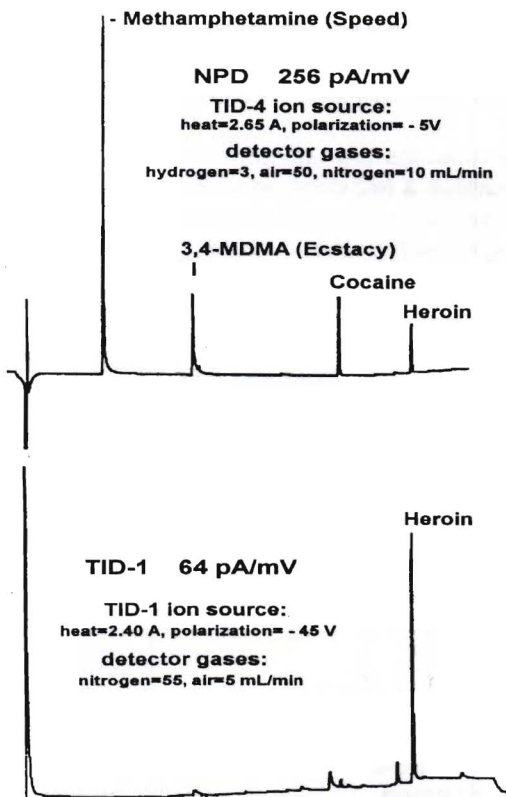
**Figure 9.** Demonstration that DET ceramic ion sources have unlimited shelf life.



**Figure 10.**

Figure 10 is an ultimate example of durability of a DET Ceramic Ion Source versus time. This NP ion source was originally manufactured in 1992. It was used for some time in a DET retrofit NPD on an HP 5890 GC by an end user in a tobacco company. The GC equipment was subsequently sold as surplus to a used equipment dealer. A new end user purchased the DET detector in 2009, and returned it to DET for refurbishment. The ion source had a frayed cable, but the ceramic surface was intact. When the well worn ion source was installed into an Agilent 6890 NPD, the data shown here indicated that its detectivity for low picogram amounts of Malthion was comparable to a recent Agilent "Blos" glass ion source.

## DRUGS OF ABUSE



**Figure 11.** Data from a new TID-4 ion source that stored on the shelf for 5 years prior to these data. The response was comparable to a freshly made new ion source. Note also how the selectivity of detection was easily changed to another mode by changing the type of ion source and the detector gases.



# DET

Innovations in chemical detection

**HROMalytic** +61(0)3 9762 2034  
**ECH**nology Pty Ltd  
Australian Distributors; Importers & Manufacturers

## Ceramic Coated NPD Ion Sources from DET

DET ion sources are 1/16 inch diameter ceramic cylinders attached to a hexagonal mounting flange that is compatible with the Agilent 6890/7890 NPD, as well as DET NPD hardware retrofits for Thermo, Varian/Bruker, SRI Instruments, and HP 5890 GC models. (DET sources are also available in a 1/4 inch tube mounting for custom applications.)

### **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 **NO 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 \$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), \$690.

### **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<sub>2</sub> functional groups**, and other compounds.



## **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<sub>2</sub>, CH<sub>2</sub>, 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.

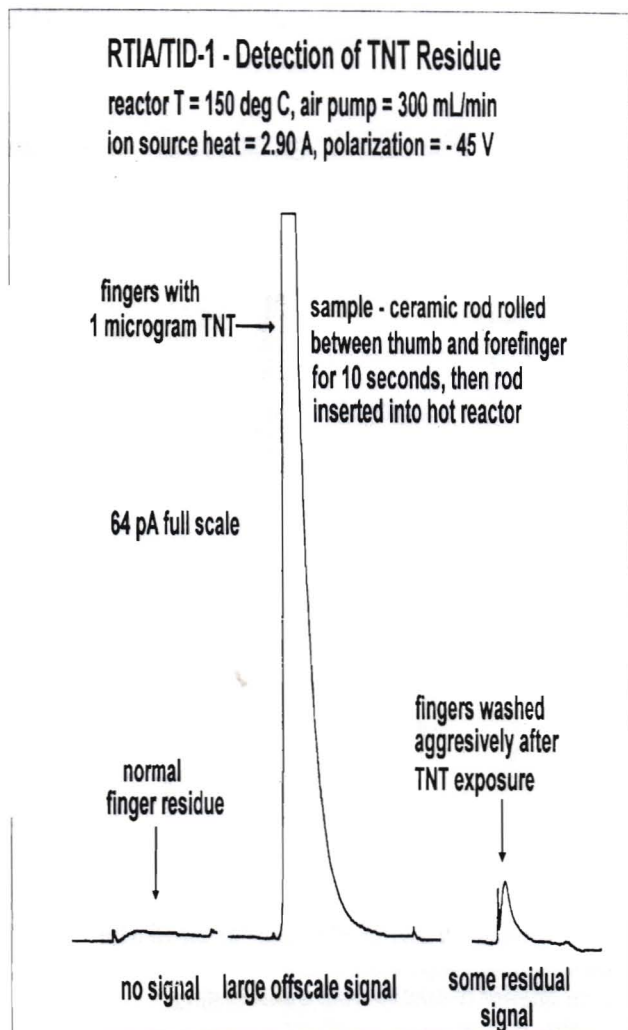
**(versatile detector capability helps sell the entire GC instrument)**



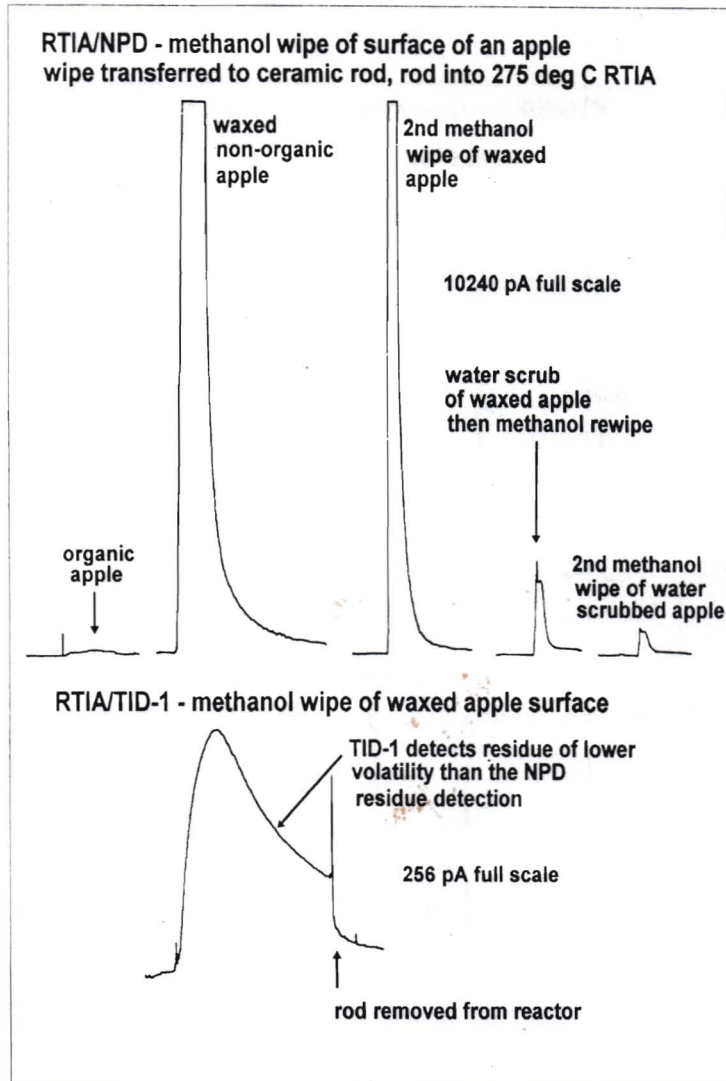
**AN EXTENSIVE LIBRARY OF SELECTIVE DETECTION APPLICATIONS:**

- 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).





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 detector which has exceptional sensitivity for Nitro explosives like TNT.

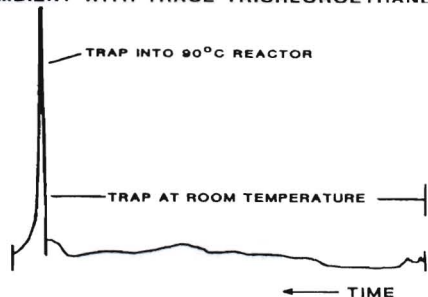


RTIA/NPD & RTIA/TID-1 detection of an Apple's Wax coating. Sharp rise and fall of NPD signal corresponded to a more volatile component than the slower oxidizing components detected by TID-1. The TID-1 signal was likely due to CH<sub>2</sub> groups in the wax compounds. However, it is not clear what compounds produced the NPD signal, since that detector has high sensitivity to N or P compounds, but discriminates against Hydrocarbons.

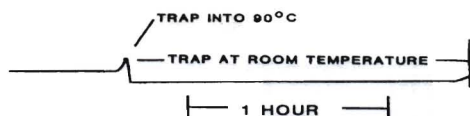
## Examples: RTIA/TID-1 Analyses

### TRAP-DESORB-DETECT

**AIR SAMPLING THROUGH CARBOTRAP**  
**AMBIENT WITH TRACE TRICHLOROETHANE**

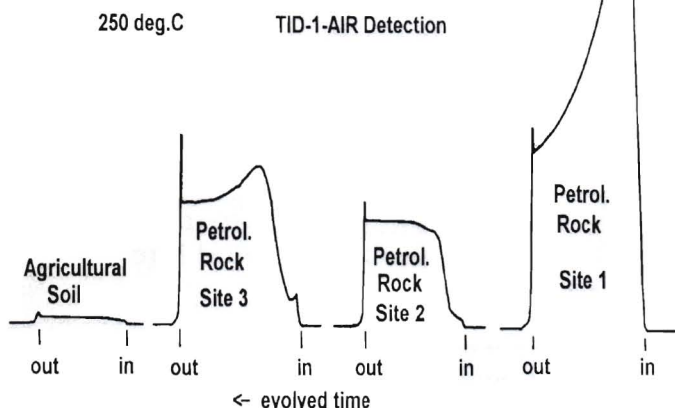


**AMBIENT WITHOUT TRICHLOROETHANE**



RTIA/TID-1. 1 L/min ambient Air - 1 hour through unheated trap, then trap into 90°C reactor.

Petroleum Source Rock from 3 Different Geological Sites  
 4mm dia. x 13mm Column of Sample into Hot RTIA Reactor

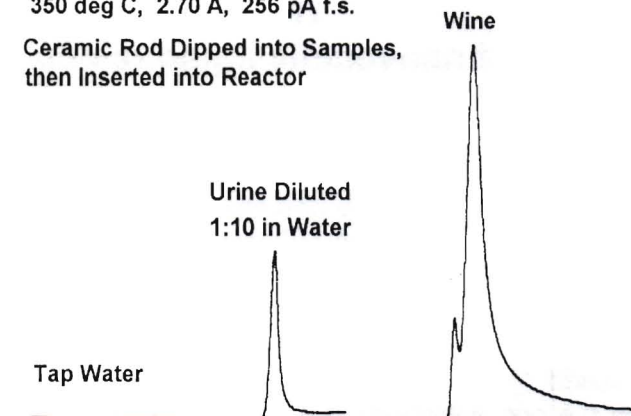


crushed rock/soil loosely packed into ½ inch long column inside 6mm OD x 4mm ID glass tube - tube inserted and sealed into reactor so incoming Air flowed through tube ID and the samples - sample tubes inserted/removed as indicated - peak in signals followed by decay indicates constituent being volatilized and removed - steady signal plateau indicates constituent vapor pressure, but no volatilization/removal.

### DESORB/OXIDIZE & DETECT

350 deg C, 2.70 A, 256 pA f.s.

Ceramic Rod Dipped into Samples, then Inserted into Reactor

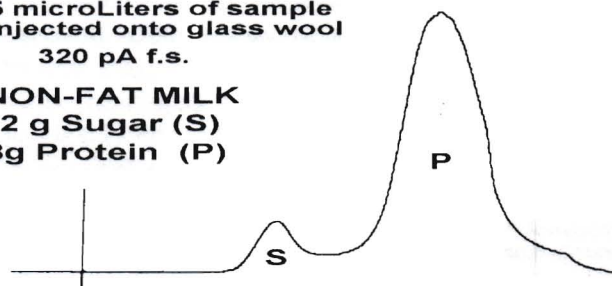


water based liquid samples - ceramic sample rod moist with both water and residual organic material when inserted into the reactor - signals mostly due to oxidation products of the organics.

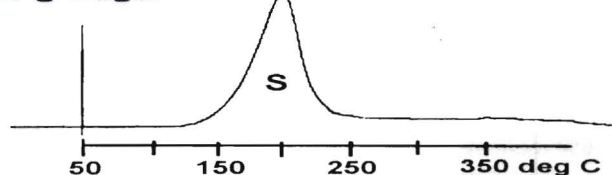
### RAMPED TEMPERATURE OXIDIZE & DETECT

5 microLiters of sample injected onto glass wool  
 320 pA f.s.

**NON-FAT MILK**  
 12 g Sugar (S)  
 8g Protein (P)



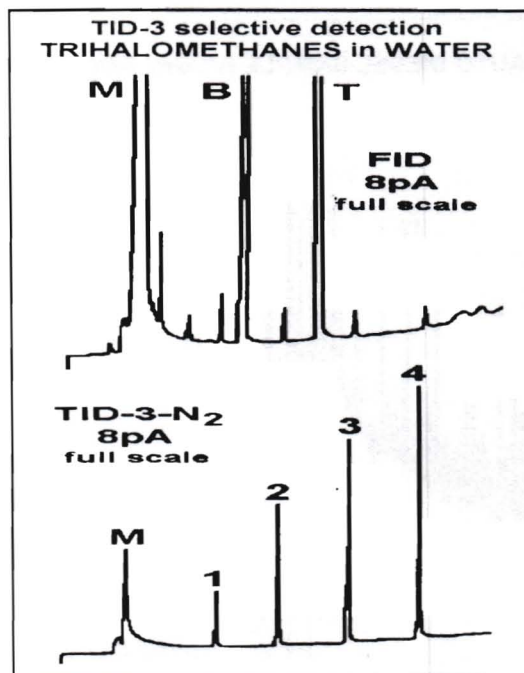
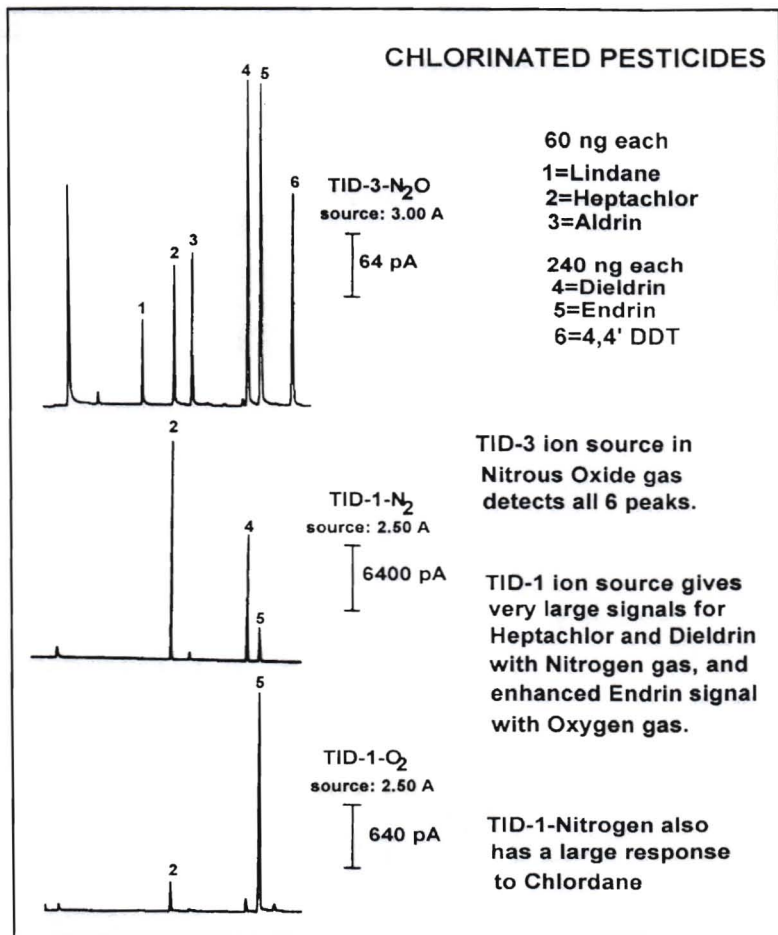
**FLAVORED JUICE DRINK**  
 26 g Sugar



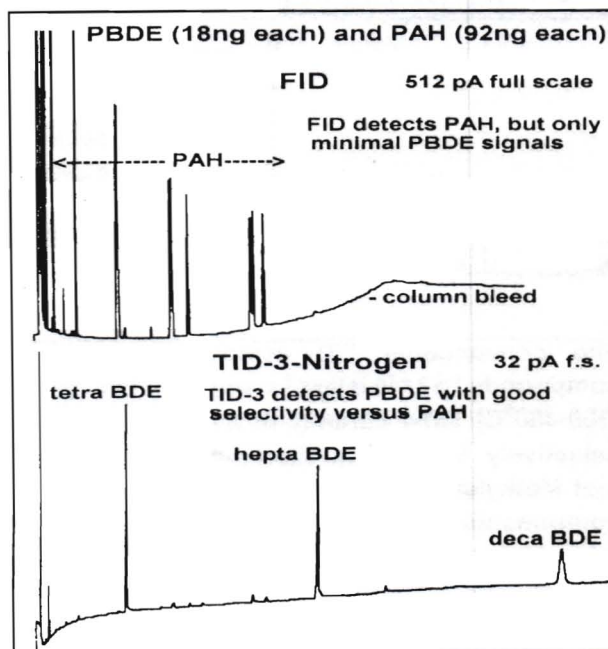
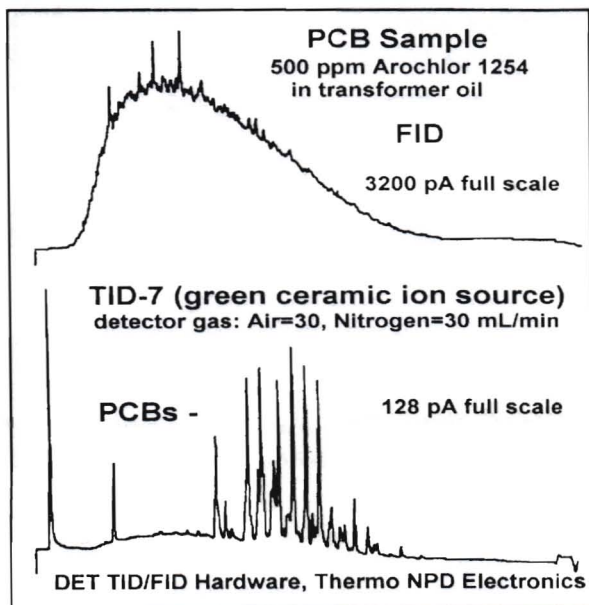
variation of the RTIA technique - TID-1 detector mounted onto a GC - 2 inch long 6mm OD x 4mm ID open end glass tube packed with glass wool located inside GC oven and connected to detector inlet - sample pump at detector exit pulled Air through the system - liquid samples injected onto glass wool - column oven temperature programmed to provide profile of oxidation product signals vs. temperature.



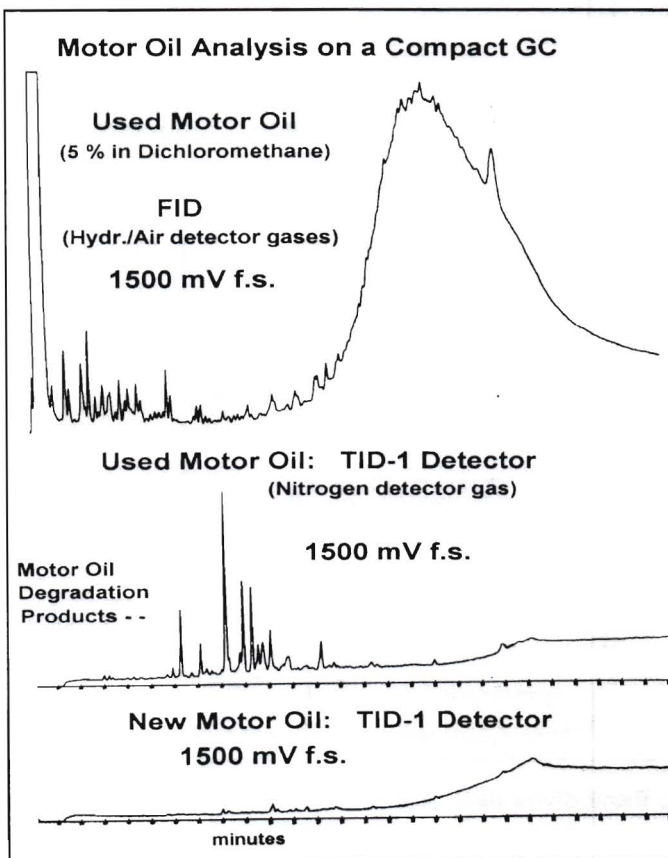
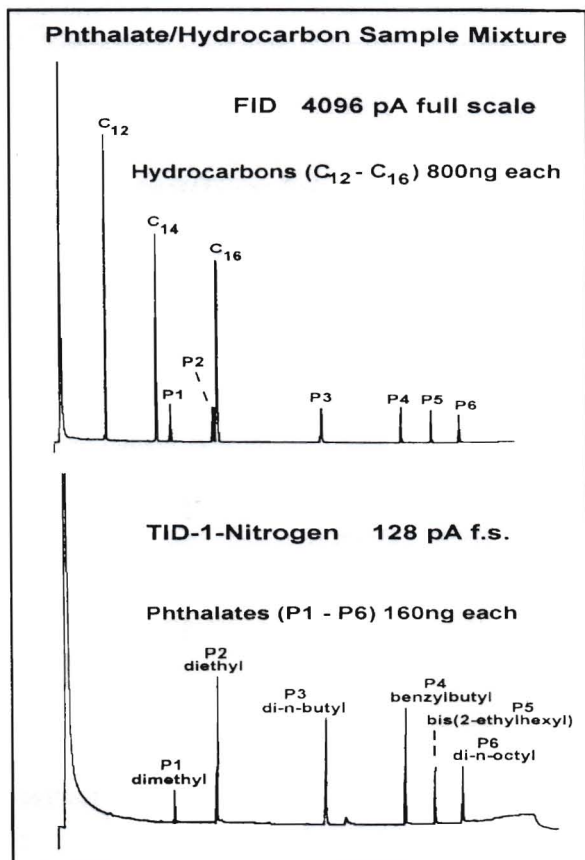
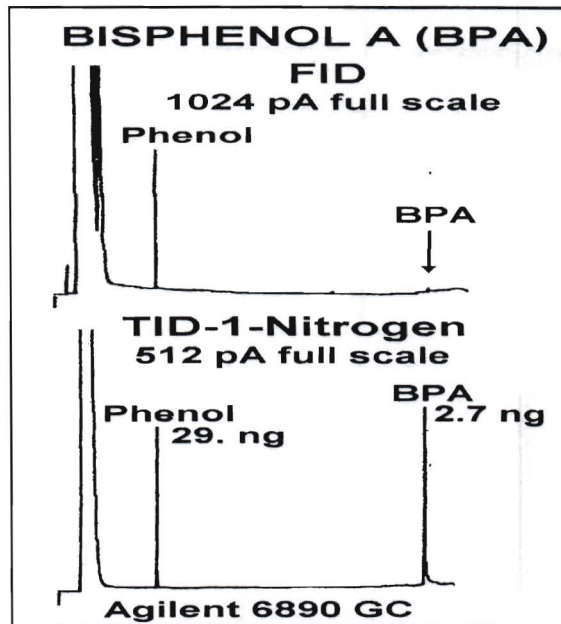
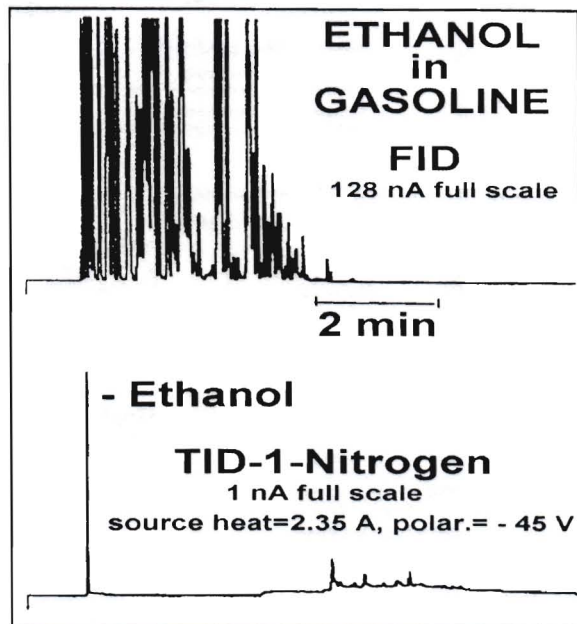
## THERMIONIC SURFACE IONIZATION DETECTION FOR GC selectivity for HALOGENATED (Cl, Br, I) compounds



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<sub>2</sub>, 4=CHBr<sub>3</sub>

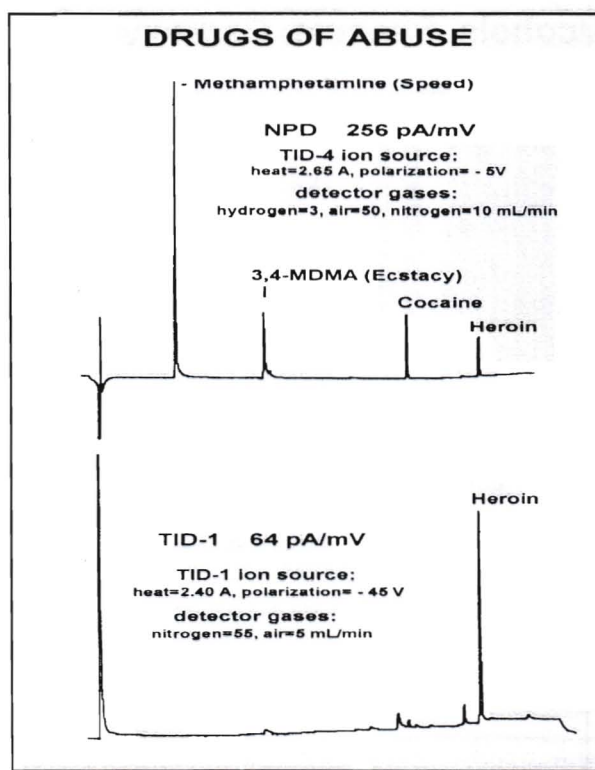
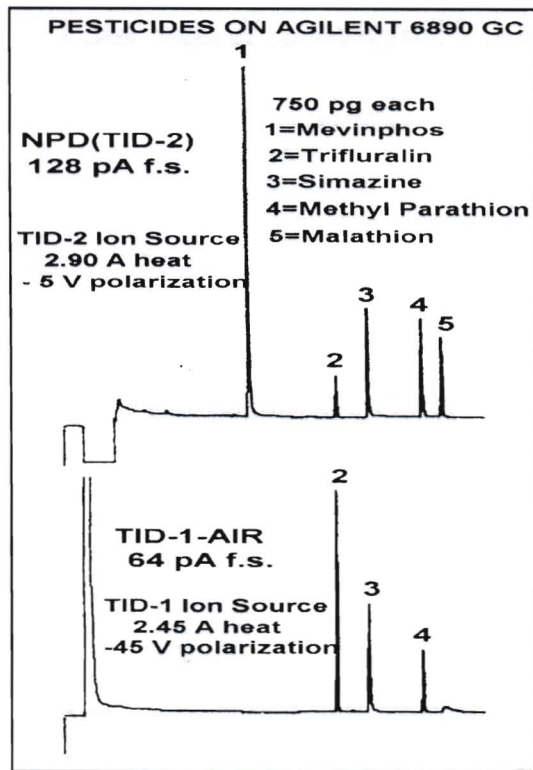


**THERMIONIC SURFACE IONIZATION DETECTION FOR GC**  
**selectivity for OXYGENATED compounds**  
(Alcohols, Phenols, Carboxylic Acids, Glycols, Phthalates, Water, etc.)





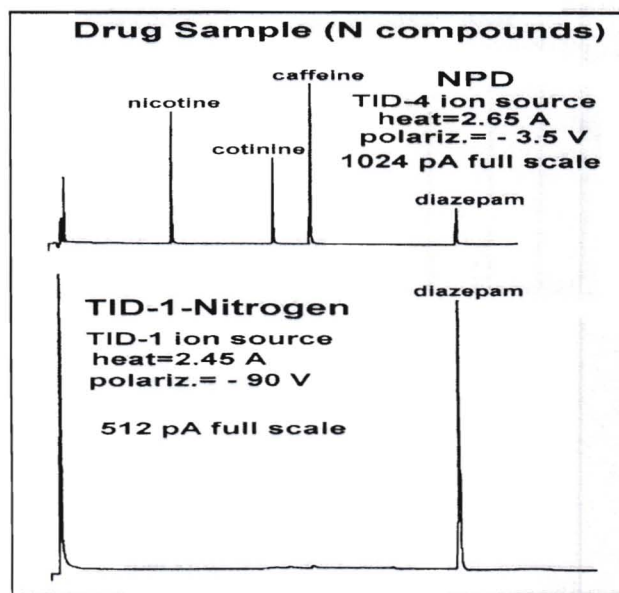
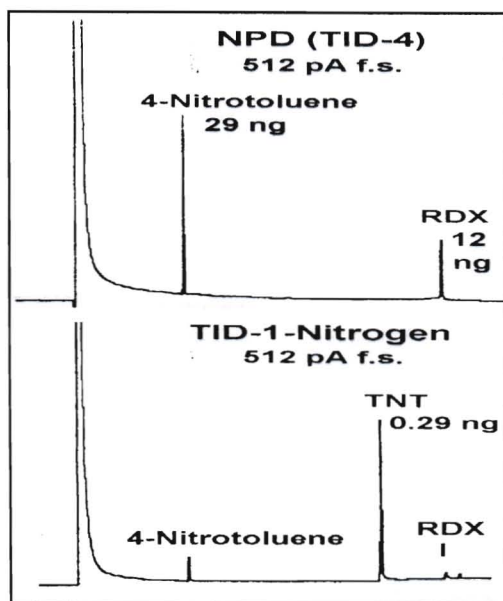
## THERMIONIC SURFACE IONIZATION DETECTION FOR GC selectivity for NITROGEN and PHOSPHORUS compounds (NPD)



TID-2 Black Ceramic designed for sharp P peaks

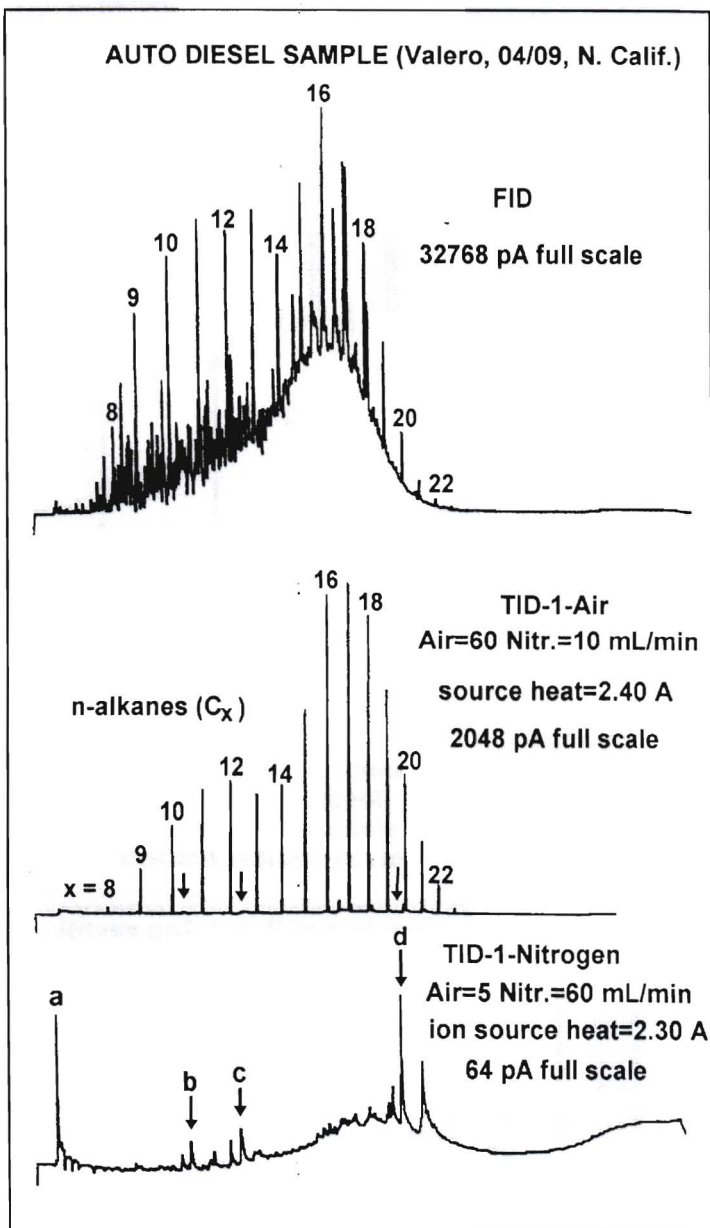
TID-4 White Ceramic designed for best N response

TID-1 mode is more compound selective than NPD

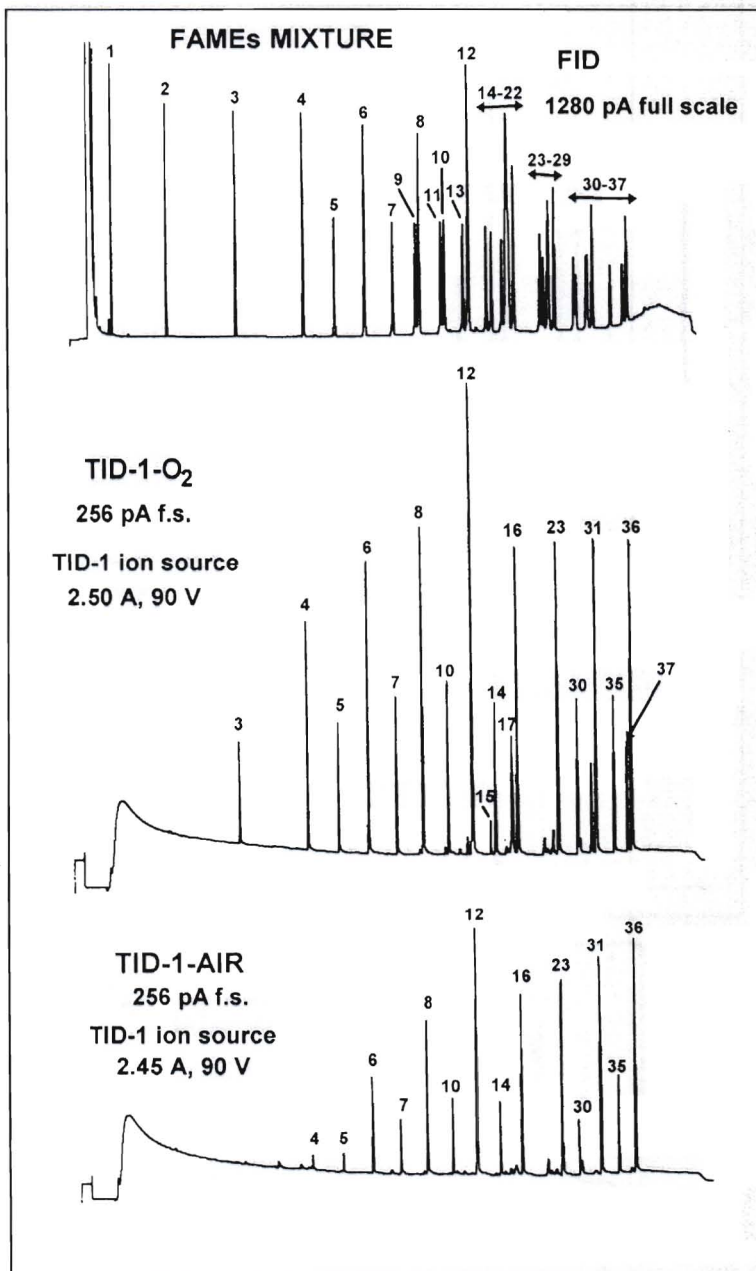


Nitro Explosives detection – NPD detects all N compounds – TID-1 mode has exceptional sensitivity for TNT

## 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 GAS CHROMATOGRAPHY (GC)

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

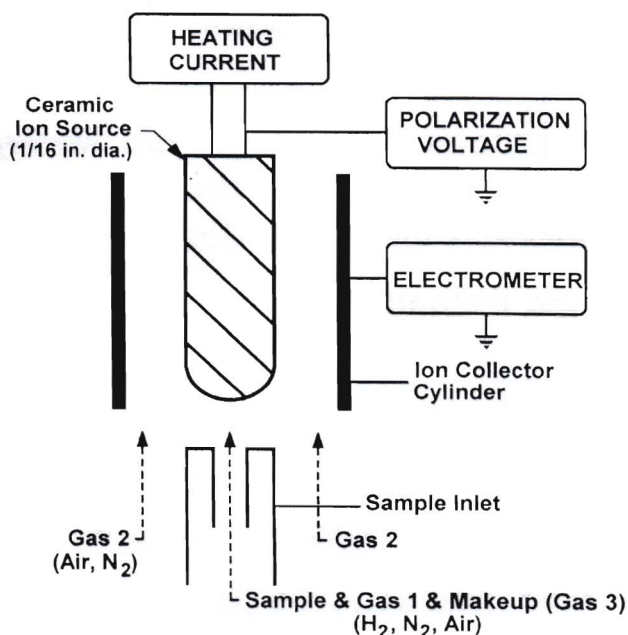
### basic detector components:

an electrically heated, ceramic ion source cylinder is positioned on the axis of a collector cylinder

### basic detector science:

samples extract electrons from the ion source to form negative ions which are measured at the collector

THERMIONIC IONIZATION DETECTOR DESIGN  
(CONCENTRIC CYLINDER GEOMETRY)



### selectivity/sensitivity determined by:

1. chemical composition of the ion source ceramic;
2. temperature of the ion source;
3. composition of the gas environment about the ion source;
4. magnitude of the polarizing voltage between the ion source and collector electrode;

multiple modes of detection are achieved using the same basic equipment, a choice of 8 different ceramic ion sources, and various permutations of these 4 operating parameters.

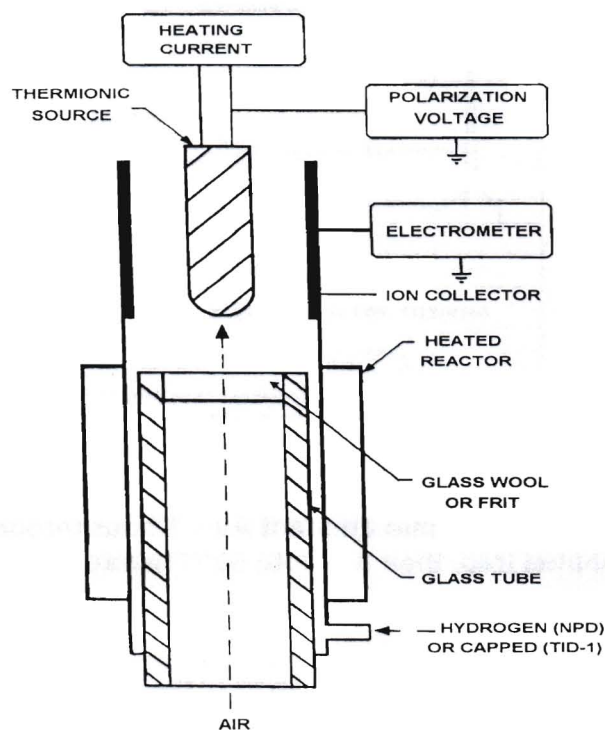
**SELECTIVITY CHOICES INCLUDE COMPOUNDS CONTAINING N, P, O, Cl, Br, I, Pb, Sn, OR Si ATOMS, OR NO<sub>2</sub>, PYRROLE, CH<sub>2</sub>, AND CERTAIN OTHER FUNCTIONAL GROUPS.**

**THERMIONIC DETECTORS OFTEN REVEAL TRACE SAMPLE CONSTITUENTS NOT DETECTED BY OTHER TYPE GC DETECTORS.**

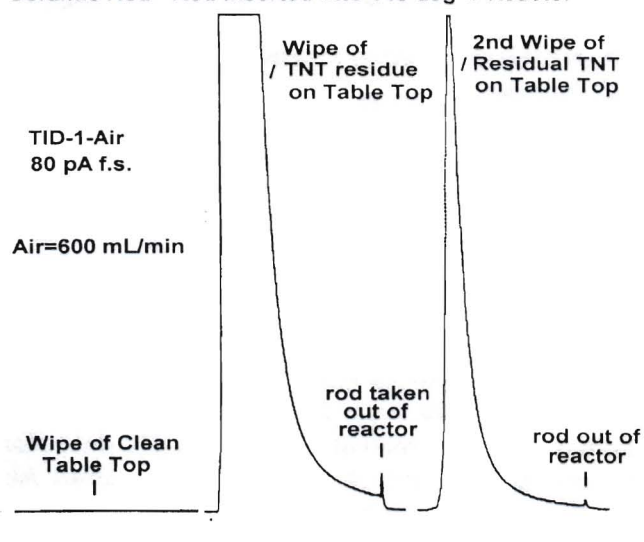
## Reactor Thermionic Ionization Analysis (RTIA)

selective TID/NPD transducer screening of vapors evolved from  
**THERMAL DESORPTION/OXIDATION**  
 of nonvolatile liquid residues or solid sample constituents

**Background:** Thermal desorption continues to be an increasingly popular means of preparing real world samples for subsequent analysis by gas chromatography. Among the many different types of GC detectors, TID and NPD detectors have the distinctive characteristic that they can provide chemical species selectivity using Air as the primary detector gas. Consequently, these detectors are well suited to non-GC chemical screening applications where the gas environment is simply ambient Air drawn through a TID/NPD transducer by a sampling pump. In an **RTIA** configuration, such a transducer is preceded by a heated reactor chamber into which are inserted solid samples packed into a glass tube or liquid sample residues on a ceramic rod. The TID or NPD transducer provides selective responses to vapors evolved from thermal desorption and/or oxidation of the samples. At low reactor temperatures, thermal desorption usually accounts for most detected signals, while at high temperatures oxidative sample decomposition products often provide large signals. Good examples of the oxidative detection processes are large TID-1 signals from oxidation of sugars and proteins. For TID-1 and TID-3 thermionic detection, only Air is required as the operating gas, while for NPD a small flow of Hydrogen has to also be introduced into the incoming Air.



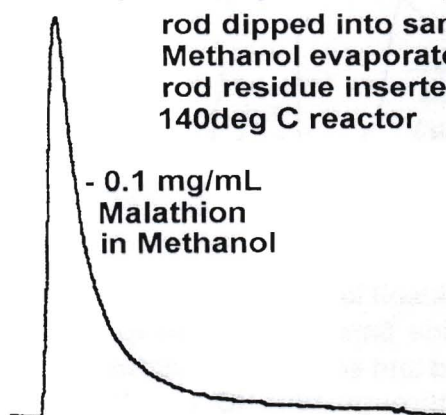
i-Propanol Wipe Transfer of Surface Residue to 1/16 in. Ceramic Rod - Rod inserted into 140 deg C Reactor



Malathion Residue on Quartz Rod

NPD, 160 pA f.s., Hydr.=4.3, Air=200

rod dipped into sample -  
 Methanol evaporated -  
 rod residue inserted into  
 140deg C reactor

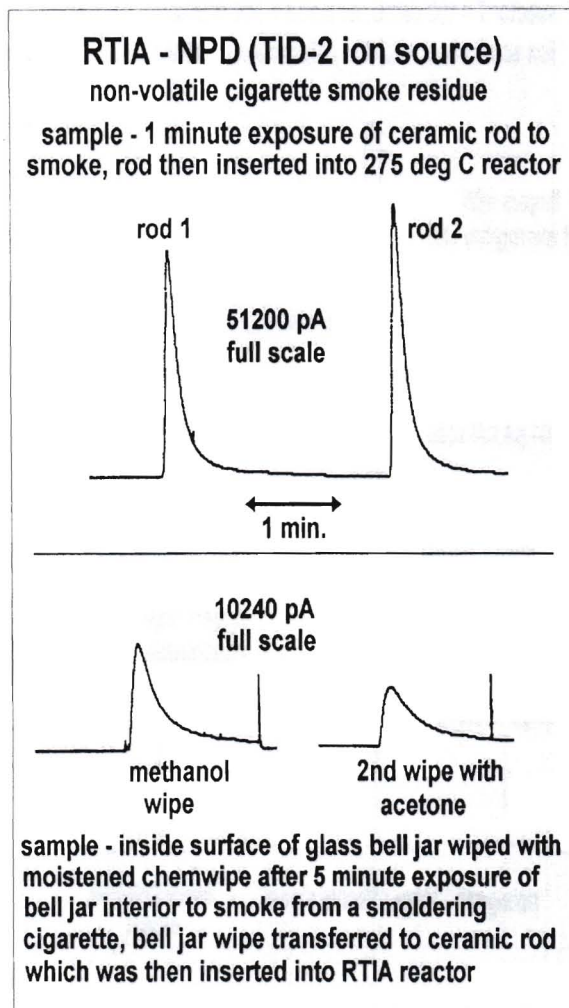
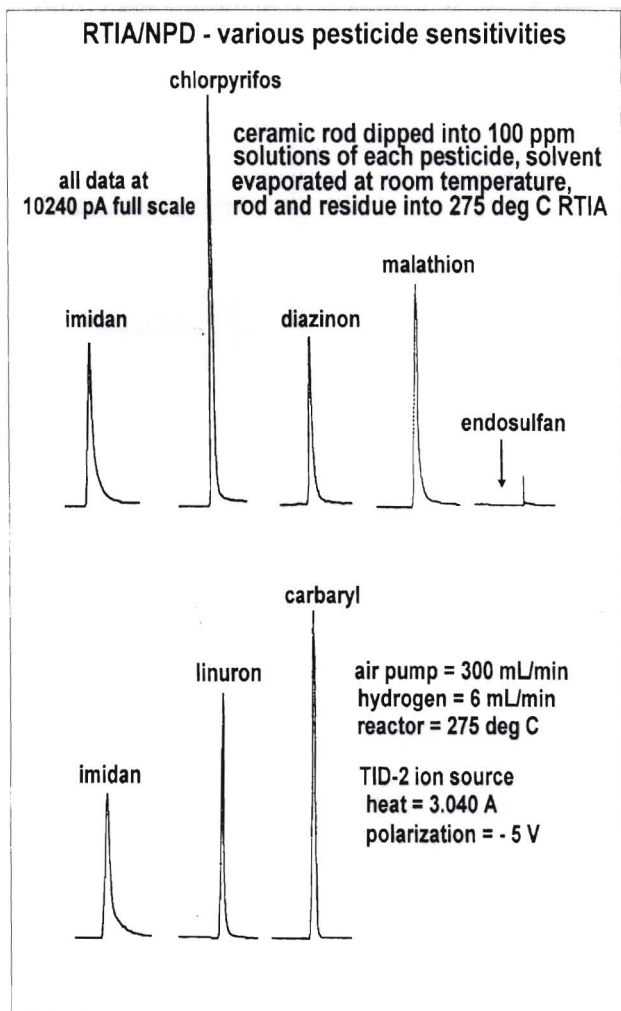


dried TNT residue on a table top wiped with an iso-propanol pad and transferred to ceramic rod.

small quartz rod dipped into a 0.1mg/mL solution of Malathion in Methanol.



## Different Methods of Acquiring Non-Volatile Sample Residues on a Ceramic Rod for Subsequent Selective Screening by the RTIA Method

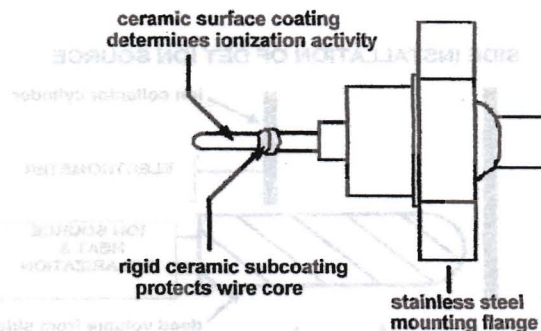


Tip of 1/16 inch diameter ceramic rod dipped into solution of non-volatile pesticides in a volatile solvent like Methanol. Solvent evaporated, then rod inserted into RTIA reactor for detection of selected vapors with a Nitrogen-Phosphorus Detector. RTIA/NPD detected N and P pesticide residues, but not Endosulfan which contained lots of Cl and no N or P. An NPD is commonly used as a GC detector, and these data illustrate its use in detecting Linuron and Carbaryl which normally are not analyzed using a GC method.

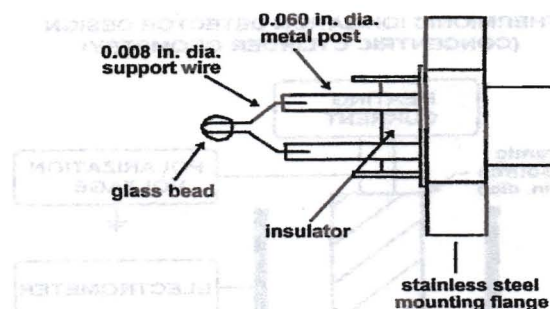
**“Third Hand Smoke”. RTIA/NPD detection of non-volatile residues deposited on surfaces exposed to Second Hand Smoke. Top data illustrate signals from smoke residues deposited directly onto tips of 2 ceramic rods. Bottom data illustrate Methanol and Acetone wipes of a surface exposed to Second Hand Smoke, with the wipes subsequently transferred to the tip of a ceramic rod. For surfaces that can tolerate it, Acetone is a more effective wipe than Methanol for removing non-volatile residues.**



## NPD ION SOURCES (BEADS) USED IN AGILENT NPDS COMPARISON OF CERAMIC VERSUS GLASS CONSTRUCTION



**DET Ion Source Construction**  
 (fits Agilent & DET structures)



**Blox Bead for Agilent NPD**

### CERAMIC

- 1.) 1/16 inch diameter ceramic materials coated over an internal wire core.
- 2.) Ceramic ion sources remain a rigid solid surface at the 600 - 800°C temperatures required for NP detection.
- 3.) Additives in the ceramics withstand temperatures in excess of 1000°C so ion sources can be used with a wide variety of operating conditions without danger of melting.
- 4.) Ceramic sublayer coating completely covers the wire core of the ion source and protects it from corrosion from additives in the surface coating or from corrosive sample matrices. Sublayer additives are chosen to enhance the hardness and electrical conductance of that ceramic coating.
- 5.) Additives in the ceramic surface layer determine the ionizing and catalytic activity of the ion source. Many different surface coatings are possible to optimize NP response characteristics as well as provide other modes of thermionic ionization detection such as selectivity for Oxygenates and Halogenates.
- 6.) In operation, electrical resistance of the ion source wire core is 1.2 Ohms which ensures that heating power is mainly dissipated in the ion source rather than in the electrical lead wires and connectors.
- 7.) Physical size of the ion source minimizes sensitivity to gas flow changes in the detector.

### GLASS

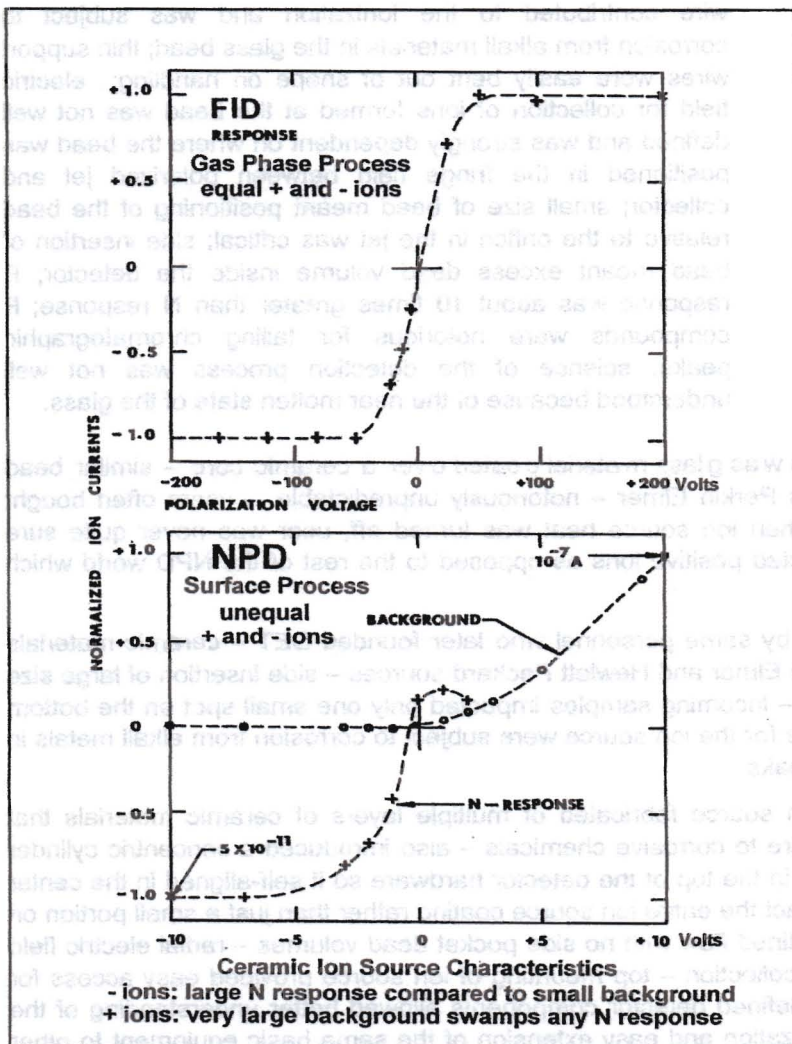
- 1.) Approximately 0.040 inch diameter glass bead deposited on the loop end of 0.008 inch diameter support wire.
- 2.) Glass bead is in a softened state at the temperatures required for NP detection. Microscopic examination of used beads often reveals internal bubbles and/or particulate growths on the surface. Some volatilization of bead material is also likely with vaporized material depositing on colder surfaces downstream.
- 3.) Detector operating conditions must be carefully controlled to avoid melting the glass.
- 4.) Thin support wire is easily bent out of shape by the slightest touch.
- 5.) Thin support wire is exposed to corrosion from additives in the glass as well as from corrosive sample matrices.
- 6.) Exposed support wire contributes some ionization in addition to the glass bead. Tailing of Phosphorus peaks is a characteristic of the NP responses.
- 7.) In operation, electrical resistance of the ion source is 0.19 Ohms which means that ion source heating power heats lead wires and connectors in addition to the ion source, and the temperature of the ion source is extremely sensitive to the stability of the heating power supply.
- 8.) Small physical size of the glass bead means the bead is very sensitive to fluctuations in gas flows, and positioning the bead relative to the incoming sample orifice is critical.



**AGILENT 6890 & 7890 NPD** – adopted same concentric cylinder geometry as DET – 3 types of NP ion sources are available – Black Ceramic supplied by DET, White Ceramic made by Agilent (old formula originally licensed from DET), and “Blos” glass bead similar to the Perkin Elmer bead except it is inserted in the concentric cylinder geometry like that of DET.

**THERMO SCIENTIFIC TRACE GC** – uses ceramic ion sources manufactured by DET, but side insertion of the ion source is similar to the Varian configuration and has more dead volume than the concentric cylinder geometry.

## IDENTIFICATION OF THE NPD OPERATING MECHANISM AS A SURFACE IONIZATION PROCESS



The accompanying graph was an important milestone in the evolution of understanding the NPD operating mechanism. The data in the graph compared ion currents measured for representative samples using an FID versus an NPD with a Ceramic Ion Source.

As is well known, the ionization in an FID is a Gas Phase process that produces equal numbers of positive and negative ions. That is clearly shown by the symmetry in the FID data as ion currents were measured versus negative and positive polarization voltages.

In contrast to the FID, ion current data measured with the NPD demonstrated that the ceramic ion source was a prolific emitter of large magnitudes of positive ion background with increasing positive polarizations, but a negligible emitter of background current at negative polarizations. At the same time, there was a significant ion current response to the test N compound at negative polarizations while any response at positive polarizations was swamped by the high background. The unsymmetrical NPD data clearly indicated that the response mechanism in that detector was a surface ionization process rather than a gas phase process. From the recognition of the NPD mechanism as a surface process, it was then possible to proceed on to identify other surfaces and other detector gas environments that produced other modes of selective detection. The ceramic fabrication technology facilitated this expansion to other modes by not being limited by ion source melting constraints.



Ionization Detector (FID). A main difference between an NPD and an FID is that the NPD requires much lower flows of Hydrogen and Air, so detector pneumatics controls must be capable of controlling these low flows. Also unlike an FID, an NPD does not involve a self-sustained flame burning at a jet structure, so any NPD jet structure serves only as a means of routing the GC column, sample, and detector gases into the detection volume.

5. NPD/TID electronics include a power supply that electrically heats and polarizes the ion source, and an electrometer to measure signals. All DET ion sources produce negatively charged ions so the ion source is polarized at a negative voltage relative to the collector, and the electrometer measures negative rather than positive ion current.

A power supply that provides controlled levels of Constant Current to heat the ion source is preferred to a power supply that provides controlled levels of Constant Voltage. With Constant Voltage power, the magnitude of heating current through the ion source's wire core depends on the resistance of the wire core plus all the electrical leads and connectors to the ion source. Conversely, a Constant Current supply provides the same heating current irrespective of these resistances. As the electrical resistance of the ion source increases slightly with thermal equilibration and age, Constant Voltage power produces an undesirable decrease in heating current and a corresponding decrease in detector response that is purely caused by the electronic power means rather than by a loss in ionizing activity of the ion source's surface.

The polarizing voltage applied to the ion source produces an electric field that causes ions formed at the ion source surface to migrate to the collector electrode. In an optimum concentric cylinder detector configuration, the internal diameter of the collector cylinder is normally 0.25 to 0.30 inches, and an optimum polarization for NP detection is in the range of 3 to 5 Volts. Higher polarizations for the NP mode generally result in decreases in signal to noise and in selectivity. For other modes of detection, higher polarizations in the range of 50 to 100 Volts can produce improved signal to noise by as much as a factor of 10.

Currently, the NPD electronics on a Thermo Scientific Trace GC provide the most versatility for all modes of NPD/TID detection. Thermo's power supply provides Constant Current heating in the range of 1.000 to 3.500 Amps settable in increments of 0.001 Amps; negative polarization voltages settable in the range of 1 to 99 Volts; capability of turning ion source heating current On/Off as a timed event; and readout indication of an open circuit in the source wiring. A limitation of NPD electronics such as those built into Thermo and Agilent GCs is that the NPD power electronics are subject to thermal gradients inside the instrument package corresponding to when the GC oven cools, and that can cause excessive upsets and wander noise in the detector baseline. Specifications for a stand-alone DET Current Supply include constant heating currents in the range of 0.000 to 4.000 Amps settable in 0.001 Amp increments; switch selection of - 5, - 15, or - 45 Volt polarizations, and a Status Light warning indication of an open circuit in the source wiring.



## TID-2-H<sub>2</sub>/AIR & TID-4-H<sub>2</sub>/AIR

### Equipment:

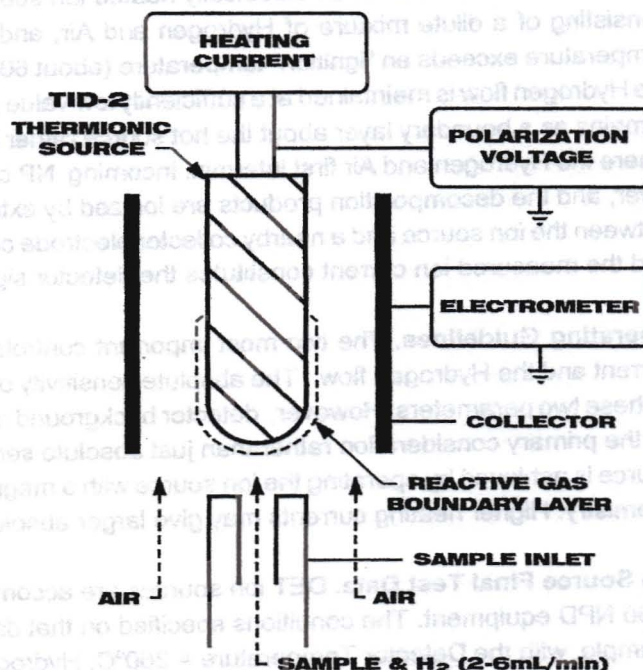
This detection mode uses a TID-2 or TID-4 type thermionic source mounted in a concentric cylinder geometry relative to a collector electrode. The detector gases are a low H<sub>2</sub> flow (2 - 6mL/min) and a flow of air (50mL/min). The source is heated by a constant current supply and is polarized at -5 Volts with respect to the collector. During operation, the surface temperature of the source is in the range of 600 - 800°C which produces a visible orange glow.

### Principle:

This mode uses a thermionic surface of moderate work function operated in a dilute H<sub>2</sub>/air environment. High selectivity is obtained for organic compounds containing N or P atoms. The NP selectivity turns on abruptly when the temperature of the source exceeds an "ignition" point (about 600°C) for the H<sub>2</sub>/air mixture. This "ignition" of H<sub>2</sub> and O<sub>2</sub> in the detector gases creates a hot, chemically reactive gas boundary layer containing radical species such as H, O, and OH in the immediate vicinity of the source. Sample compounds impact this boundary layer and are decomposed. Samples containing N or P atoms form decomposition products which are electronegative and which are converted to gas phase negative ions by the extraction of electrons from the thermionic surface.

### Response:

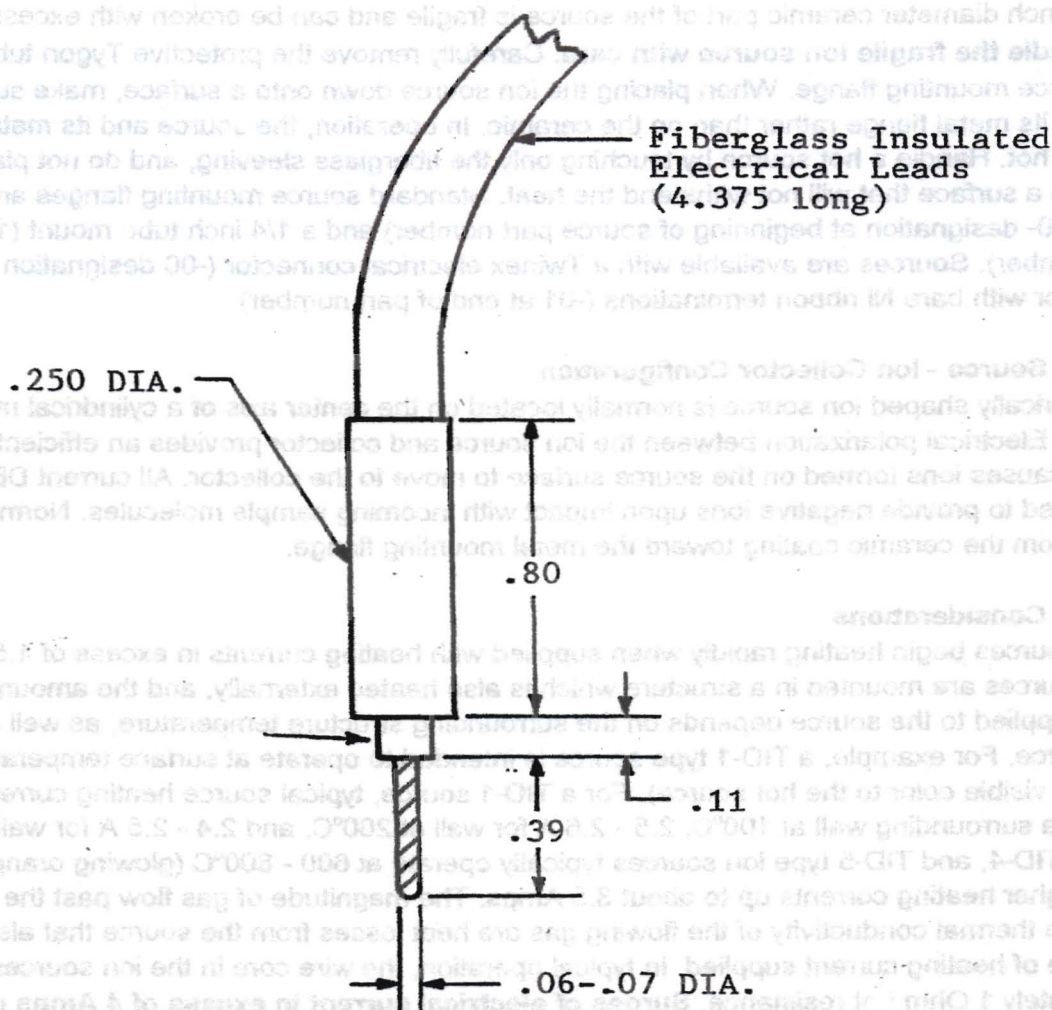
The existence of a chemically reactive boundary layer is an essential requirement for responses to a wide range of N or P compounds. Unlike an FID, there is not sufficient H<sub>2</sub> supplied to sustain the "flame like" boundary layer when the heating current to the thermionic source is turned off. The two most important controls are the source heating current and the H<sub>2</sub> flow. The thermionic source is normally operated at a heating current just sufficient to give "ignition" of



the boundary layer. For organic compounds containing N or P atoms, the detection limit is 0.07pg N(P)/sec, the selectivity versus hydrocarbons is 10<sup>5</sup>gC/gN(P).

NP detectors from different manufacturers vary widely in performance. The ceramic coatings on DET thermionic sources are formulated to provide long term responses. The TID-2 type source is recommended for applications requiring both N and/or P detection, and features minimal tailing of P compounds. The TID-4 type source is recommended for applications requiring only N detection, and represents our best possible N response. All DET sources are tested chromatographically before shipment. Also, a cost-saving recycling service is available for depleted sources.

### $\frac{3}{4}$ " TUBE MOUNT



**NOTE:** All dimensions in inches.



## CUSTOM APPLICATIONS OF DET THERMIONIC SOURCES

### General Construction of the Ion Sources

All DET Thermionic Sources have a fine wire core covered by layers of ceramic material. The outermost ceramic surface coating determines the ionizing characteristics (i.e., TID-1, TID-2, etc. type of ion source). The 1/16 inch diameter ceramic part of the source is fragile and can be broken with excess transverse force. **Handle the fragile ion source with care.** Carefully remove the protective Tygon tubing from the metal source mounting flange. When placing the ion source down onto a surface, make sure the source is resting on its metal flange rather than on the ceramic. In operation, the source and its metal mounting flange get hot. Handle a hot source by touching only the fiberglass sleeving, and do not place a hot source down onto a surface that will not withstand the heat. Standard source mounting flanges are a hexagonal mount (010- designation at beginning of source part number) and a 1/4 inch tube mount (110- designation in part number). Sources are available with a Twinex electrical connector (-00 designation at end of part number), or with bare Ni ribbon terminations (-01 at end of part number).

### Usual Ion Source - Ion Collector Configuration

The cylindrically shaped ion source is normally located on the center axis of a cylindrical metal collector electrode. Electrical polarization between the ion source and collector provides an efficient radial electrical field that causes ions formed on the source surface to move to the collector. All current DET ion sources are intended to provide negative ions upon impact with incoming sample molecules. Normal gas flows are directed from the ceramic coating toward the metal mounting flange.

### Electrical Considerations

The ion sources begin heating rapidly when supplied with heating currents in excess of 1.5 Amps. Usually, the ion sources are mounted in a structure which is also heated externally, and the amount of electrical current supplied to the source depends on the surrounding structure temperature, as well as on the type of ion source. For example, a TID-1 type source is intended to operate at surface temperatures of 400 - 600°C (no visible color to the hot source). For a TID-1 source, typical source heating currents are 2.6 - 2.7 Amps for a surrounding wall at 100°C, 2.5 - 2.6 A for wall at 200°C, and 2.4 - 2.5 A for wall at 300°C. TID-2, TID-3, TID-4, and TID-5 type ion sources typically operate at 600 - 800°C (glowing orange color), and require higher heating currents up to about 3.5 Amps. The magnitude of gas flow past the ion source, as well as the thermal conductivity of the flowing gas are heat losses from the source that also affect the magnitude of heating current supplied. In typical operation, the wire core in the ion sources has approximately 1 Ohm hot resistance. **Surges of electrical current in excess of 4 Amps can burn out the heater wire core.** In addition to the electrical heating current, power to the sources usually also includes polarizing the heater wire core at a negative voltage relative to the collector electrode. Current DET electronics provide polarizations of -45 Volts for TID-1, TID-3, and TID-5 type sources, and -5 V for TID-2 and TID-4 sources. Higher polarizations up to 100 or 200 Volts would probably further improve the detection limits for TID-1, TID-3, and TID-5 sources.

### Typical Gas Environments for the Ion Sources

TID-1 and TID-3 ion sources are intended for operation in gas environments of N<sub>2</sub>, Air, or O<sub>2</sub>, while TID-2, TID-4, and TID-5 sources usually operate in an environment consisting of a dilute mixture of H<sub>2</sub> in Air, where the mixture ratio is not sufficient to support ignition of a self sustaining flame. TID-1 sources have been used in total gas flows ranging from 20 to 1000 mL/min in magnitude.

whether the chemistry could be reignited again - collected positive ions as opposed to the rest of the NPD world which collected negative ions.

**VARIAN** - first ceramic ion source developed in 1978 by same personnel who later founded DET - ceramic materials eliminated the softening and melting limitations of Perkin Elmer and Hewlett Packard sources - side insertion of large size ion source resulted in excessive detector dead volume - incoming samples impacted only one small spot on the bottom surface of the ion source - exposed metal support posts for the ion source were subject to corrosion from alkali metals in the ceramic coating - excessive tailing of Phosphorus peaks.

**DET** - introduced in 1982 - a cylindrically shaped ion source fabricated of multiple layers of ceramic materials that completely protected the heating wire core from exposure to corrosive chemicals - also introduced a concentric cylinder NPD configuration in which the ion source was installed in the top of the detector hardware so it self-aligned in the center of the collector electrode - incoming samples could impact the entire ion source coating rather than just a small portion on one side - detector geometry provided optimum stream-lined flow with no side pocket dead volumes - radial electric field between ion source and collector provided efficient ion collection - top mounting of ion source provided easy access for installation/removal of replacement ion sources - well defined detector components allowed better understanding of the general operating mechanism of thermionic surface ionization and easy extension of the same basic equipment to other modes of detection - ceramic coating technology allowed development of many different coating formulations without concern for ion source melting - a Black Ceramic ion source eliminated Phosphorus tailing, while a White Ceramic ion source provided the best possible Nitrogen response.