# DET
innovations in chemical detection

**DET**ector Engineering & Technology, inc.
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# OPTIMUM NPD CONFIGURATION

## Cylindrical Shaped Ion Source Positioned on Axis of Collector Cylinder

**(this configuration used in Agilent 6890/7890, Thermo 1300, and all DET Retrofit NPD Equipment)**

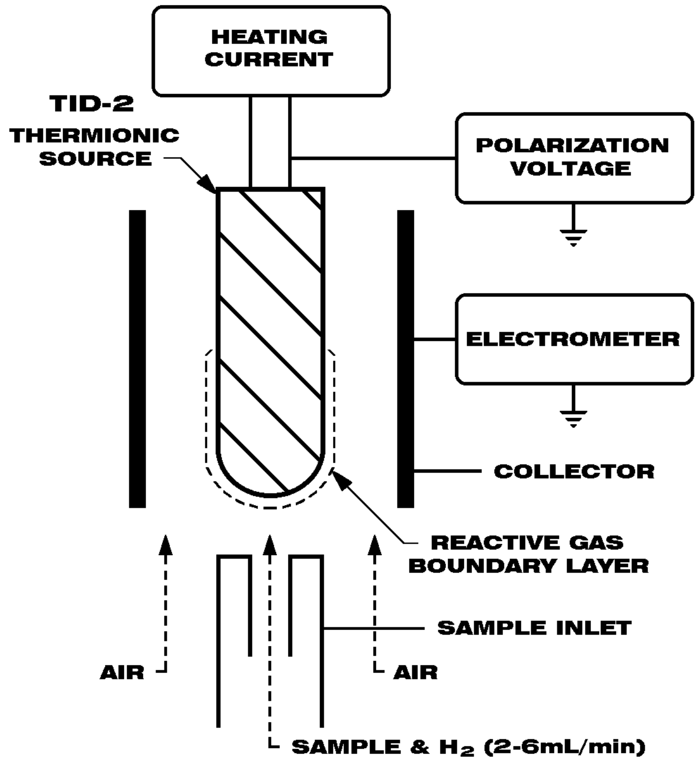
## DET NP Ion Sources:

### TID-2 (Black Ceramic - best for non-tailing P peaks)

### TID-4 (White Ceramic - best for largest possible N response)

**Wire core in the Ion Source is heated with electrical current & polarized at a negative voltage with respect to the Collector electrode - negative ion signal current is measured with Electrometer.**

**Concentric cylinder geometry provides streamlined flow for detector gases, radial electric field for efficient collection of ions, and top access mounting of ion source for easy replacement with minimal instrument downtime.**




**NECESSARY CONDITIONS REQUIRED FOR NP DETECTION:**
**1. Ion Source must be heated enough (600 - 800°C) to ignite the Hydrogen - Air detector gases;**
**2. Hydrogen flow must be low enough (2 - 6 mL/min) so the ignited chemistry stays as a boundary layer around the hot ion source.**

**DETECTION PRINCIPLE: Sample decomposed in ignited ion source boundary layer chemistry. Electronegative N and P decomposition products extract negative charge from the hot ion source surface.**

**After NP chemistry ignition, absolute magnitudes of sample response and background signal can be varied over a wide range by variations in ion source heating current and/or Hydrogen flow. NPD performance is best indicated by considering the ratio of sample response to background signal rather than considering just the absolute magnitude of sample response. On most GC instruments, NPD detector noise is typically about 0.1 % of the background signal magnitude, so the ratio of sample response to background effectively indicates NPD signal-to-noise for the amount of sample injected. Longest ion source lifetime is achieved by maintaining ion source heating current just slightly above the minimum value required to achieve Hydrogen-Air ignition.**

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**TYPICAL CHARACTERISTICS OF STATE OF THE ART NPD EQUIPMENT:**
**1. NPD Electrometer has a basic noise level of 0.01 pA or less;**
**2. Detector noise = Electrometer noise when detector background signal is 10 pA or less;**
**3. For detector backgrounds greater than 10 pA, stability of the ion source heating current and the detector gas flow controls are such that detector noise is about 0.1 % of the magnitude of the background signal.**

**DETERMINING A TYPICAL NPD PERFORMANCE SPECIFICATION:**
**1. Calculate the Ratio of Sample Peak Height to Background (S/B) with both measured in same units (e.g., pA);**
**2. Determine the Signal to Noise S/N = 1000 x S/B for the analyzed Sample Weight (W) measured in pg;**
**3. Determine the Peak Width (PW) in seconds by dividing Peak Area by Peak Height;**
**4. Calculate the Sample Weight (MDL) that would give a response = 2 times the noise level.**

**MDL = 2 x W x 0.001/(S/B) x 1/PW in pg/sec units.**

**Typical final test MDL values for new TID-2 (Black Ceramic) ion sources:**
**Azobenzene (15.37% N), W = 2000, S/B = 4.7, PW = 1.8**
**MDL = 0.47 pg/sec, (x 15.37% = 0.072 pg N/sec)**

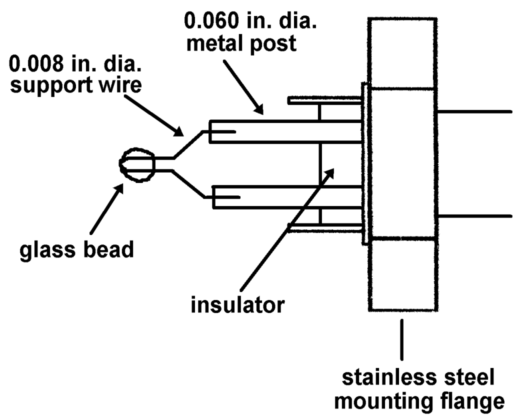
**Malathion (9.38% P), W=4000, S/B = 10.9, PW = 2.1**
**MDL = 0.17 pg/sec, (x 9.38% = 0.016pg P/sec)**

**TID-4 (White Ceramic) ion source has 2 to 3 times lower MDL for N, but P compounds tend to have more tailing than a TID-2 ion source.**

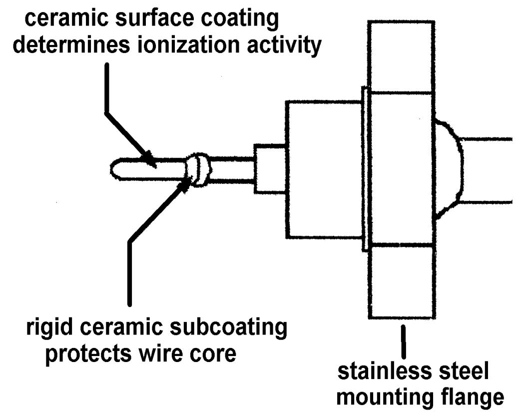
**With ion source aging, N response tends to decay more rapidly than P response.**

**A new ion source typically has a background (B) in the range of 40 - 60 pA. DET recommends allowing the background to decrease with time to about the 10 pA level before adjusting Hydrogen flow or ion source heating current to maintain the background in the 10 - 15 pA level. If heating current and Hydrogen flow remain at constant values, the sample response and background get more and more stable with operating time. When heating current and Hydrogen flow are increased, the rate of decay in sample response will also increase. Therefore, a procedure such as Agilent's "Adjust Offset" where heating current is automatically increased to maintain some prescribed background level, is counter-productive because the NP response decays faster and faster as the ion source temperature is increased further and further. This leads to much faster degradation of the ion source lifetime. To preserve ion source lifetime whenever the NPD is not being used for a significant period of time (e.g., overnight), turn off the NP chemistry by setting the ion source heating current to Off or to a level below that which is needed to sustain the ignited chemistry.**

# COMPARISON OF ION SOURCES FOR AGILENT NPD

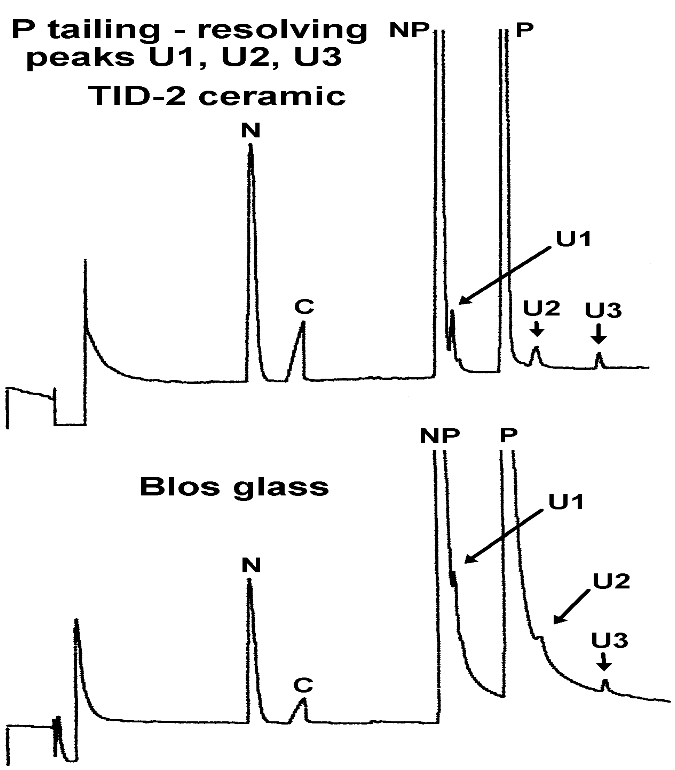



Blos Bead for Agilent NPD




DET Ion Source Construction
(fits Agilent & DET structures)

**Blos NP ion source is a small Glass Bead deposited on the end of a loop of bare support wire. DET ion source is a more rigid cylindrical structure comprised of layers of ceramic materials coated over an inner wire core. NP detection requires ion source temperatures in the range of 600 - 800$^{o}$ C to ignite the Hydrogen-Air chemistry. At those temperatures, the Blos Glass is in a softened physical state, as evidenced by migration of the glass mass away from the tip of the heating wire with operating time. By comparison, DET Ceramics remain solid during operation. In operation, a DET NP ion source has an electrical resistance of 1.2 Ohms versus 0.2 Ohms for the Blos Bead. That Blos resistance is close to the resistance of the attached external wiring leads and connectors, so those components get hotter than is the case with DET ion sources.**




## PHOSPHORUS PEAK TAILING

**Tailing of Phosphorus peaks has been a notorious characteristic of many past NP ion sources. DET's Black Ceramic coating is formulated to eliminate P tailing. This allows detection of small peaks eluting right after large peaks, and allows rapid recovery to baseline so that another analysis can be run soon thereafter.**

**All DET ion sources are conditioned and tested prior to shipment, so they are ready for use when installed in an instrument. This means minimum instrument downtime when replacing an ion source. DET ceramics also have unlimited shelf life when stored under ambient conditions.**

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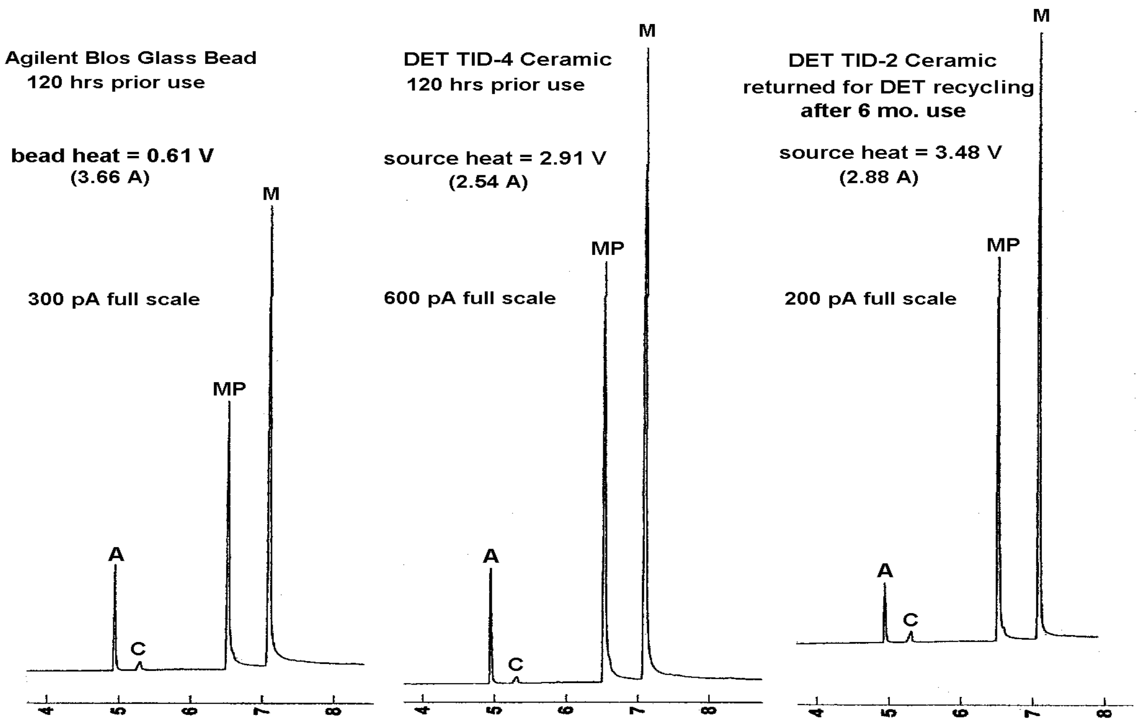
## BASIC INFORMATION FOR BETTER UNDERSTANDING OF THE OPERATION OF ALL NPDs:

**NP selective detection "turns on" when ion source temperature is hot enough (600 - 800°C) to ignite Hydrogen/Air detector gases - low Hydrogen flow (2 - 5mL/min) restricts ignited chemistry to boundary layer about hot ion source - absolute magnitudes of NP signals and noise (related to detector background) can be varied over a wide range by variations in ion source heating power and/or Hydrogen flow - signal to noise (detectivity) should be the measure of NPD performance rather than just absolute signal magnitudes - minimum noise on most NPD equipment is achieved when detector background signal is 10 pA or less - longest operating life of an NP ion source is achieved by leaving the ion source heating power at the magnitude level just required to ignite the Hydrogen/Air chemistry - when ion source heating power left at its original ignition level, NP response gets more and more stable with continued operating time - increases in source heating power and/or Hydrogen flow to recover decayed sample response will result in sample response decaying at an even faster rate.**

## RESPONSE COMPARISON OF AGED ION SOURCES IN AN AGILENT NPD

**Hydrogen=3.0, Air=60, Nitrogen makeup=10 mL/min, Source Heat adjusted to give 10 pA background**
**Sample: A=0.8ng Azobenzene, C=1600ng Heptadecane, MP=0.8ng Methyl Parathion, M=1.6ng Malathion**




**Different Aging Environments: Blos - repetitive injections of this test sample; TID-4 - miscellaneous drug, food, and beverage samples; TID-2 - undefined end user's applications.**

**NP (A, M) SIGNAL TO BACKGROUND (B) RATIOS**

**Blos: A/B = 3.6, M/B = 15; TID-4: A/B = 8.1, M/B = 42; TID-2: A/B = 1.3, M/B = 13**

**ORIGINAL FINAL TEST RATIOS**

**Blos: not available; TID-4: A/B = 16, M/B = 16; TID-2: A/B = 3.9; M/B = 11**

**Changes with aging: TID-4: A/B decrease by 2, M/B increase by 3; TID-2: A/B decrease by 3, M/B no change**

**Other Observations: TID - 2 still exhibits less tailing of P peaks; TID - 2 still provides useful NP data even though returned for recycling; TID-4 provides large response to P as well as N, although P peaks tail more than TID-2.**

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# OPTIMUM ION SOURCE POWER FOR NPD & OTHER MODES

**Background:**
DET's family of ceramic coated ion sources require electronics that heat the ion source by supplying electrical current through the source's wire core, and that polarize the ion source at a negative voltage with respect to a surrounding ion current collector electrode.

**Electrical Heating:**
DET ion sources are compatible with heating by NPD electronics already existing on the GC (Agilent, Thermo, Varian, SRI Instruments, etc.). Some GC models provide this heating using a Constant Voltage power supply while others provide a Constant Current power supply. Constant Current is inherently more stable because the current flowing through the ion source wire core is not dependent on the electrical resistance of the cabling connecting the ion source and the power supply. With Constant Current power, cabling between source and power supply can be many feet long, whereas Constant Voltage requires the shortest possible separation between ion source and power supply. For GC models like Agilent 6890/7890 which have Constant Voltage NPD electronics, DET has available a stand-alone Current Supply which provides the more stable Constant Current heating.

**Ion Source to Collector Polarization Considerations:**
The polarization voltage causes ions formed at the ion source surface to move to the collector electrode. The magnitude of the polarization voltage required for optimum ion collection depends on whether the detector equipment is being used for NP selectivity, or other modes of selective detection.

**NP Selectivity:** For the case of NP detection, consideration must be given to the difference between negative NP ions originating from a surface process at the ion source versus interfering Hydrocarbon ions originating from a gas phase process in the ignited chemical boundary layer of the ion source. Gas phase ionization of Hydrocarbons generates both positive and negatively charged species, and a relatively low polarization allows these Hydrocarbon ions to recombine before reaching the collector. Therefore, for optimum NP to Hydrocarbon selectivity, most NPDs use a polarization voltage in the range of - 4 to - 5 V.

**TID Modes of Selective Detection:**
TID refers to a Thermionic Surface Ionization process involving direct impact of electronegative heteroatom sample compounds with a catalytic ion source surface, with no intervening gas phase chemistry. For this case, the higher the polarization voltage the bigger the ion current signal. Hence, signal to noise enhancement of a factor of 10 or more can be obtained by using a polarization of - 45 V or more instead of the - 4 or - 5 V which is optimum for NPD. Currently, Thermo is the only GC manufacturer with NPD electronics providing a selection of polarization from - 2 to - 100 V for optimum detection in all possible modes of selectivity using the same basic equipment. For other GC models like the Agilent 6890/7890, the stand-alone DET Current Supply can be used to access selectable polarizations of - 5, - 15, or - 45 Volts.

**Versatile Stand-Alone DET Current Supply:**
Stand-alone DET Current Supply can be used to power any DET Ion Source used on a wide variety of GC models (e.g., Agilent 6890/7890, Varian/Bruker/Scion, HP 5890, SRI Instruments, etc.), or used in stand-alone non-GC screening and monitoring applications.
**Features:** Constant Current Heating, 0 to 4.000 Amps; Polarization, switch selectable - 5, - 15, or - 45 V;
Red/Green front panel indicator of Ion Source open circuit.
**Part: 001-901-01, Price: $2244.** (January 2016)

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## STAND-ALONE DET CURRENT SUPPLY

**Provides Constant Current heating and polarization voltage for powering DET's ceramic ion sources used in GC detectors, stand-alone transducers, or other applications requiring conversion of chemical compounds into measurable ion species (e.g., ion sources for mass spectrometers or ion mobility spectrometers). The electrical resistance of DET ion sources typically ranges from 0.7 Ohms when cold to 1.1 – 1.3 Ohms at operating temperature.**


**Thumbwheel set of ion source heating current (0 to 4.000 Amps) in 1 mA steps; Red/Green Status Light indicates open circuit or OK in ion source wiring – gives an immediate troubleshooting diagnosis in case of burnout of ion source wire core.**


**Switch selection of – 5, - 15, - 45 Volt ion source polarization (bias); – 5 V optimum for NP detection, higher polarizations provide 10 times better signal-to-noise for other detection. Twinex connectors on module & accompanying 4 foot long cable provide compatibility for powering ion sources on Agilent, Thermo, Varian/Bruker, and all DET NPD/TID equipment. Dimensions: 5 ½ inches high, 6 inches wide, 10 ½ inches deep.**

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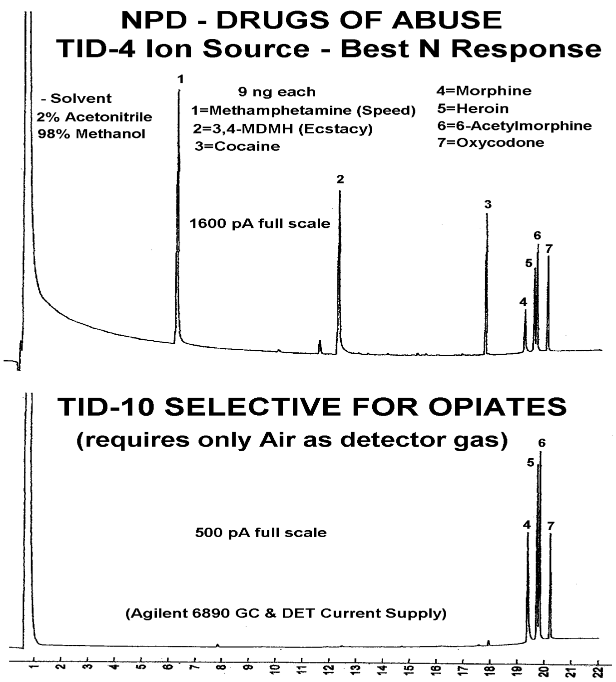
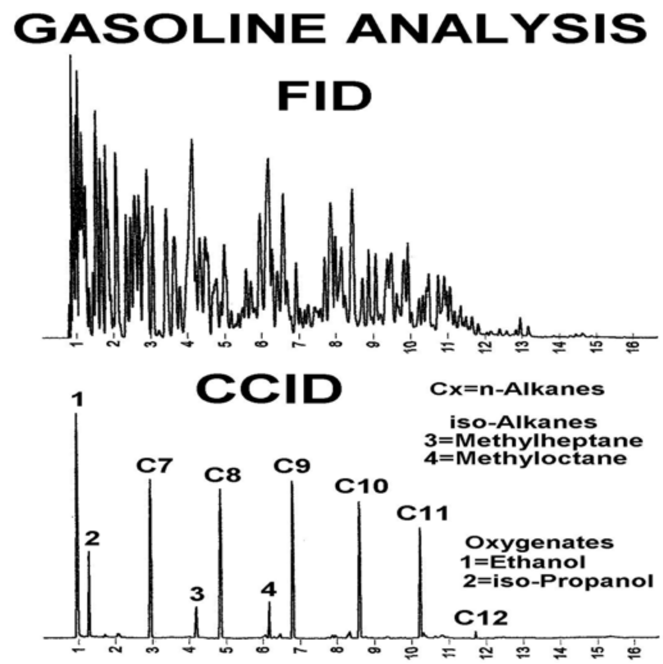
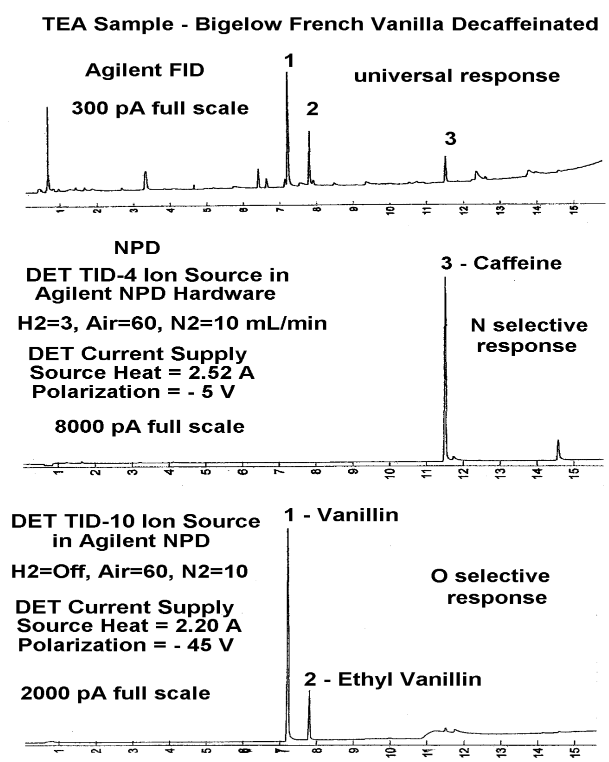
## TID-10 Thermionic Surface Ionization - $N_2$ or Air Gas - Selective for Oxygenates
## TID-10 Catalytic Combustion Ionization - Air or $O_2$ Gas - Selective for $CH_2$ Chains



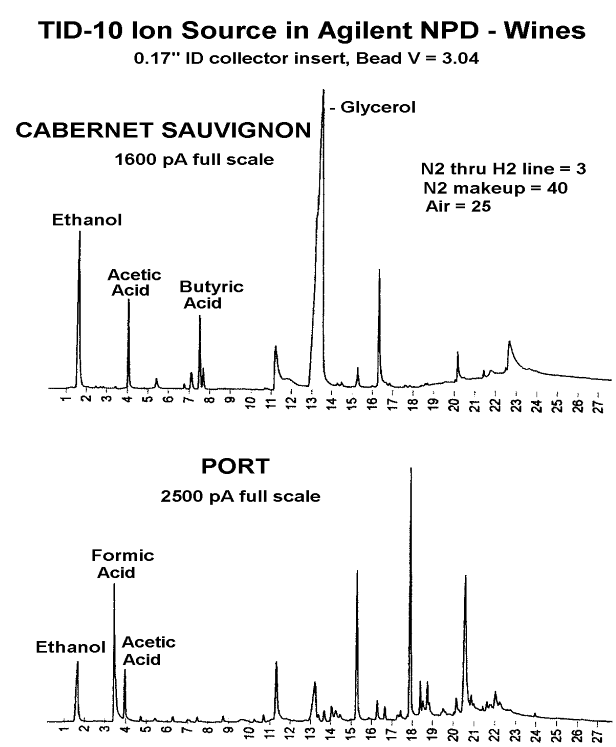

**NPD detects all N drugs, TID-10 detects Opiates**




**Simplified chromatographic fingerprints of fuels**




**Selective detection of food flavor/fragrance compounds**




**Large responses to Volatile Acids**

# CERAMIC COATED THERMIONIC ION SOURCES by DET
# Improved NPD Performance - - Extended Detection Modes

## THERMIONIC IONIZATION SOURCES (BEADS) - - - - - - - - - - - - - - - - - $495. each

Durable 0.062 inch diameter cylindrical ceramic structures molded about a heater wire core, and mounted on a hexagonal shaped stainless steel flange. Different ceramic additives provide a family of ion source types having different work functions for the emission of electrical charge, and different catalytic and ionizing activities. DET sources are all pre-tested for response before shipment, and are interchangeable in Agilent 6890/7890 NPD assemblies, in all DET detector assemblies, and in the Thermo 1300 NPD assembly. Standard electrical connection is a Twinex type compatible with Agilent and Thermo NPD electronics, Varian TSD electronics, as well as a stand-alone DET Current Supply. Unlike the Blos glass NPD bead, DET ceramics will not soften or melt at operating temperatures typical of NP detection. (Ion Sources are also available in a ¼ inch tube mounting, or with bare metal leads instead of the Twinex.)

**TID-10 (010-910-00)** - selective response to **Oygenates** (especially **Phenols**, **Carboxylic Acids**, and **Glycols**), **Nitro-compounds**, **some Halogenates**, **Pyrrole functional group**, and other electronegative functionalities - operates at 400 - 600$^o$C in inert ($N_2$) or oxidizing (air, $O_2$) gas environments – best signal-to-noise when polarized at -45 Volts or higher as available from a DET Current Supply or Thermo NPD electronics - femtogram detection for compounds like Methyl Parathion, 4-Nitrophenol, Pentachlorophenol, Heptachlor, 2,4-Dinitrotoluene, TNT when powered at high polarization – TID-10 is also the key element used in the **Catalytic Combustion Ionization (CCID)** mode which is selective to compounds containing **chains of Methylene ($CH_2$) groups** in Petroleum Hydrocarbons, FAMEs, or Triglycerides with no response to Aromatic or Cyclo-Hydrocarbons and with discrimination between compounds containing saturate vs. unsaturated Carbon bonds. Also, **TID-9 (010-909-00)** & **TID-11 (010-911-00)** for lower & higher concentrations of TID-10 type ceramic catalyst formula.

**TID-2 (010-902-00) - NPD** - selective response to **N,P compounds** - Black Ceramic coating has long life and minimal tailing of phosphorus compounds - operates at 600 - 800$^o$C in a dilute $H_2$ in air gas environment - low picogram detection for NP compounds - lower cost alternative to Agilent NP sources.

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

**TID-3 (010-903-00)** - Selective response to **Volatile Halogenates** - more uniform response to halogenates than TID-1 - operates at 600 - 800$^o$C in inert ($N_2$) or oxidizing (air, $O_2$) gas environments - low picogram detection for Trihalomethanes with minimal peak tailing and greater response for Br versus Cl – best sensitivity when polarized at -45 Volt or higher.

**TID-5 (010-905-00)** - **Halogen selective** detection - more uniform response than TID-3 - operates at same temperatures and gas environment conditions as TID-2, but with a polarization voltage of -45 V or higher – also provides exceptional **selectivity for Br and I versus Cl** when configured with a stoichiometric mixture of Hydrogen and Air (e.g., $H_2$ = 5, Air = 12.5, $N_2$ makeup = 30 mL/min).

**TID-6 (010-906-00) - P selective detection with suppressed N** response - uses much higher Hydrogen, Air, and Nitrogen flows than the TID-2 and TID-4 NPD modes, and uses a detector structure with an internal upstream restrictor to prevent flashback to a self sustaining flame (e.g., $H_2$ = 20, Air = 200, $N_2$ makeup = 100 mL/min).

**TID-7 (010-907-00)** - Green Ceramic for **Halogenated Pesticides, PCBs** - operates in $N_2$, Air, or $O_2$ - best sensitivity when polarized at –45 V or higher.

**CFID (020-901-00)** – High work function for operation downstream of a flame in a **Remote FID** detection mode which is selective to **compounds containing P, Pb, Sn, or Si atoms**. Selectivity improved by using a Hydrogen-Methane fueled flame.

**FID Probe (020-902-00)** – Uncoated Pt alloy wire used for **Universal Detection** in **FID** or **HWCID** (Hot Wire Combustion Ionization) mode.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**January 2016**

## DET RETROFIT NPD/TID/CCID/FID HARDWARE FOR DIFFERENT GC MODELS

DET retrofit hardware is easily mounted onto an existing NPD or FID base, and uses the existing heater and pneumatics controls connected to that base. All DET retrofits consist of a tower structure featuring a common concentric cylinder geometry that positions an electrically-heated ion source in the center of a collector electrode, with top access for easy interchange of ion sources. Mounting on the bottom of the tower is custom designed to be compatible with the detector base on the GC being retrofitted. DET hardware is compatible with all DET ion source elements so that NPD, TID, CCID, and FID modes of detection can be accommodated with the same equipment.

**THERMO TRACE ULTRA GC (part 010-860-55, price $2340).** Replaces the Thermo NPD hardware which has a side mounted ion source, with a more optimum concentric cylinder geometry and a top mounted ion source. Hardware includes a ceramic tipped jet. Any DET ion source priced at **$495** each can be accommodated. Hardware is fully compatible with Thermo NPD electronics, and the combination provides the most versatile NPD, TID, CCID, FID equipment currently available. Tandem TID hardware is also available for 2 simultaneous signals from one sample, as well as Remote FID hardware for added selectivity of P, Pb, Sn, Si compounds.

**VARIAN/BRUKER/SCION GC MODELS (part 010-860-20, price $2100).** Replaces the Varian/Bruker/Scion TSD/NPD hardware which has a side mounted NP bead, with a more optimum concentric cylinder geometry and a top mounted ion source. Hardware includes a ceramic tipped jet that seals into the detector base with a standard stainless steel ferrule rather than the crushable Vespel/Graphite ferrule required by a Varian/Bruker/Scion jet. Varian retrofits can use any standard DET ion source priced at $495, and these can be powered with Varian TSD electronics. Bruker/Scion retrofits require custom low resistance ion sources priced at $700 in order to be powered by Bruker/Scion TSD/NPD electronics. Signal-to-noise for TID, CCID, FID modes can be substantially improved by powering ion sources with a stand-alone DET Current Supply described below. For Bruker/Scion GCs, powering ion sources with the DET Current Supply requires use of a simulated bead ($175) to avoid Bruker/Scion "bead open circuit" sensing, although the DET supply then allows DET's lower price ($495) standard ion sources to be used. Tandem TID and Remote FID hardware assemblies are also available.

**SRI INSTRUMENTS GC MODELS (part 050-864-98, price $2340).** Replaces the SRI NPD/FID hardware with a more optimum concentric cylinder geometry and an end mounted ion source. Hardware includes a ceramic tipped jet. Ion sources used with this hardware have bare wire terminations **(priced at $460),** and any type DET ion source can be accommodated. SRI's existing NPD or FID electronics can be used to power the ion sources and measure signals.

### AGILENT 6890/7890 NPD MODELS

All DET ion sources are compatible with mounting into existing Agilent 6890/7890 NPD hardware. Agilent electronics suffice for NPD operation, but substantial improvement for TID and CCID modes of detection is achieved by substituting a stand-alone DET Current Supply to power ion sources with a higher polarization voltage. DET also recommends replacing the small orifice Agilent NPD jet with a wide bore jet as described below.

**DETECTOR CURRENT SUPPLY (part 001-901-01, 115Vac) - - - - - - - - - - - - - - - - - - $2244. each**

Stand-alone module provides heating current and a selection of -5, -15, or -45 V polarization voltages for DET thermionic sources or the Agilent NP source. Recommended for use in place of the Bead Voltage supply on the Agilent NPD because it provides more stable Constant Current heating power for thermionic sources versus the Constant Voltage power provided by the Bead Voltage supply. Also, for modes of detection other than NP, the higher polarizations available from the DET supply provide as much as a factor of 10 improvement in signal-to-noise versus the fixed low polarization available from the Agilent supply. The DET supply also includes a green/red status light to immediately indicate that the source has burned out or the source power cable is not properly connected.

**WIDE BORE JET & COLUMN SPACING KIT**

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

**(010-886-13) -** column spacer & 64 mm long jet for Agilent's adaptable fitting NPD base - **$ 190. each**

**(010-887-13)** – column spacer & 43 mm long jet for Agilent's dedicated capillary base - - **$ 250. each**