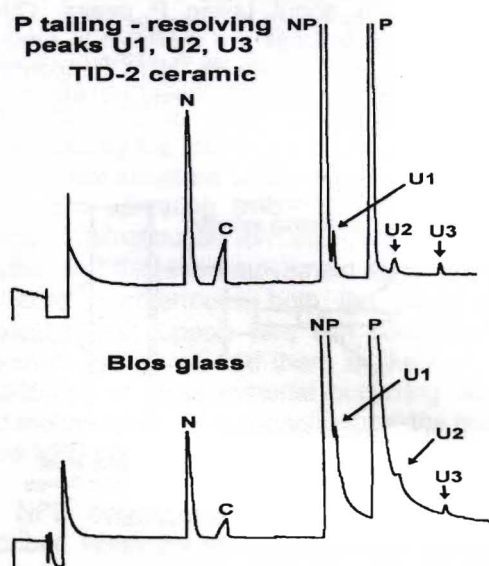


- 1.) **ELIMINATE NPD PHOSPHORUS PEAK TAILING WITH A BLACK CERAMIC ION SOURCE (BEAD) FROM DET.**
- 2.) **DIFFERENCES BETWEEN CERAMIC AND GLASS NPD ION SOURCES.**
- 3.) **SCIENCE OF THE NPD.**
- 4.) **LIFETIME CONSIDERATIONS FOR NPD ION SOURCES.**

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

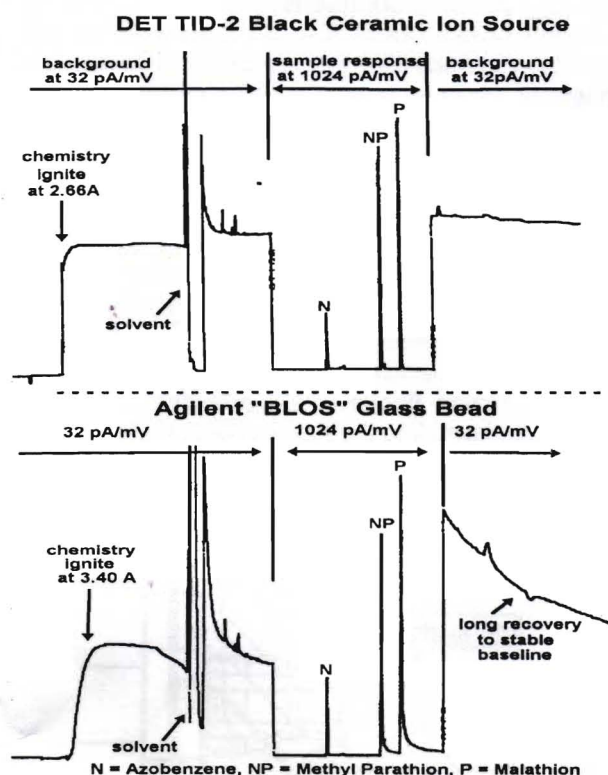
Years ago, Phosphorus peak tailing was a well known characteristic of NP detectors. In 1997, DET announced the development of a durable NPD ion source with a Black Ceramic coating specifically formulated to eliminate the P tailing, while still maintaining excellent P detectivity (e.g., 70 fgP/sec). That 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 reintroduced 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.

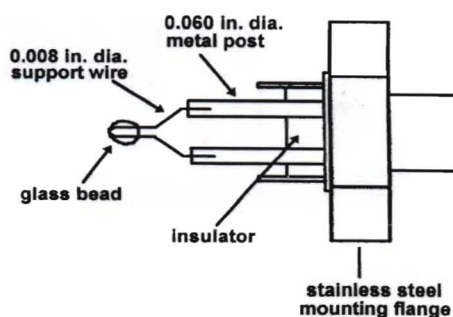
In contrast, the ceramics and additive chemicals used in DET ion sources are all chosen to withstand temperatures in excess of 1000°C, so that a wide range of operating conditions are allowed without destroying the ion source. Also, the method of forming ceramic ion sources allows an almost limitless 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.

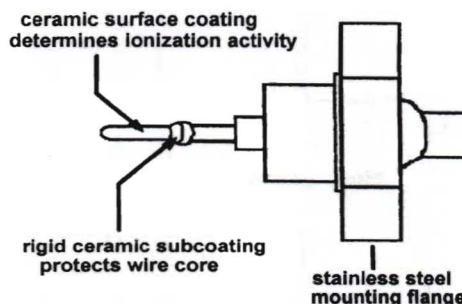
As indicated in Figure 1, the Bloss NPD ion source consists of a small glass bead attached to a loop of bare supporting wire that also is the means of electrically heating the bead. The supporting wire is a very small diameter that can easily be bent out of shape with the slightest touch. Also, the glass 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 Blos Glass Bead.

In a Blos 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 Blos 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 Blos 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 Blos power produced almost the same magnitude baseline change as a 10 millivolt change in the DET TID-2 power. Clearly, the Blos bead demands much better power supply stability.

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

2 pA full scale

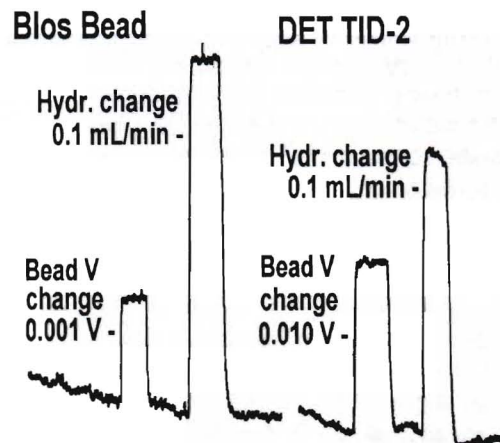


Figure 3. Baseline changes when Ion Source Heating (i.e., Bead Voltage) and Hydrogen flow were changed by incremental amounts. Comparison of Blos glass bead and a DET TID-2 (Black Ceramic) ion source.

## 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 Blos 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 Blos 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

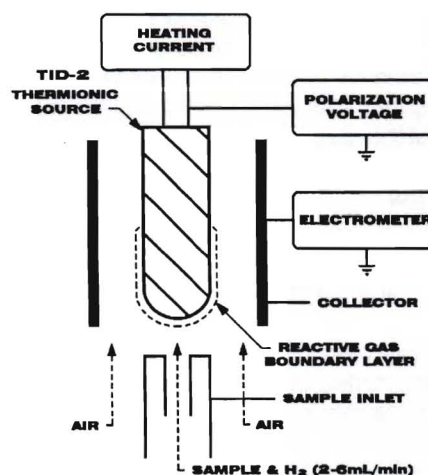


Figure 4. Schematic illustration of an NPD configuration.

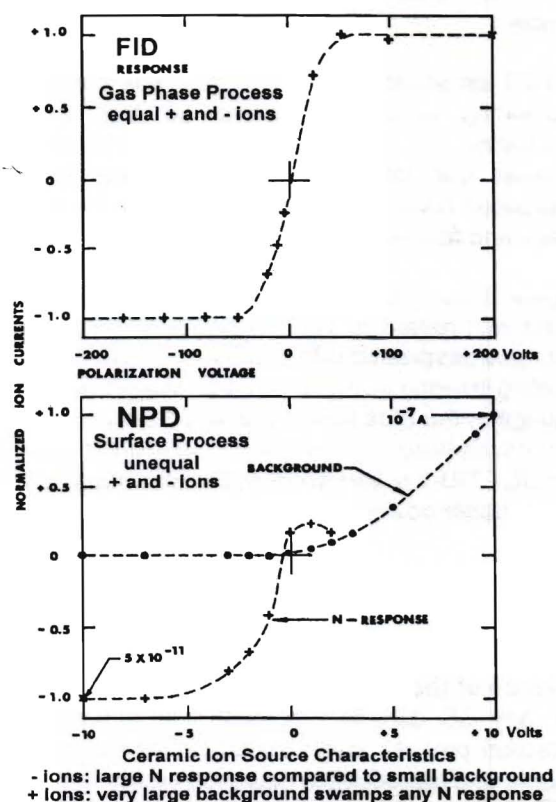
figure, NP selectivity turns on when the ion source is heated sufficiently to ignite the Hydrogen-Air detector gases. An important NPD parameter is that the Hydrogen is maintained at a low enough flow that the ignited chemistry does not flash back and form a self-sustained flame at the Hydrogen/sample 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

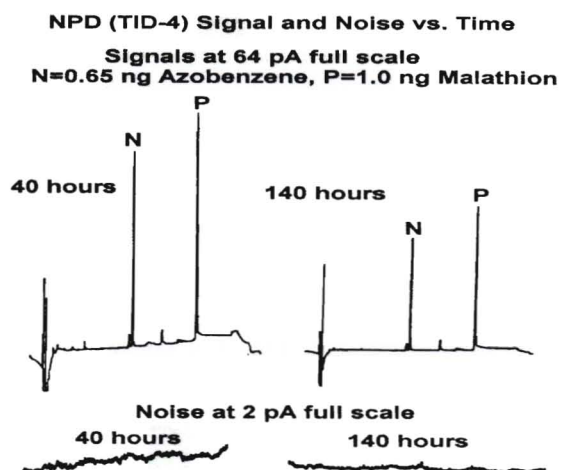


background signal. However, that procedure keeps heating the ion source hotter and hotter, and operating life is greatly shortened. Longest ion source operating life is achieved by leaving the heating current close to that magnitude just needed to ignite the boundary layer chemistry. Chemistry ignition 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.

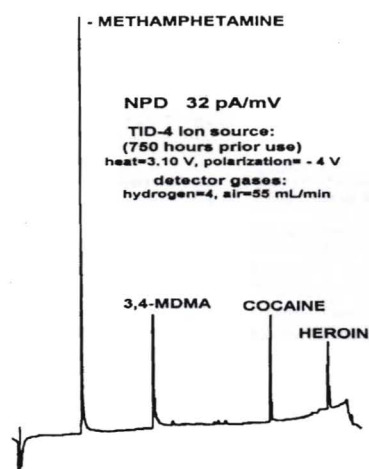
To account for any NPD response decay, use of an internal standard reference compound is usually recommended for the NPD. As an NPD ion source is used for long times, increases in Hydrogen flow and ion source heat can also be used periodically to get larger signals for extended time. DET'S TID-2 and 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.

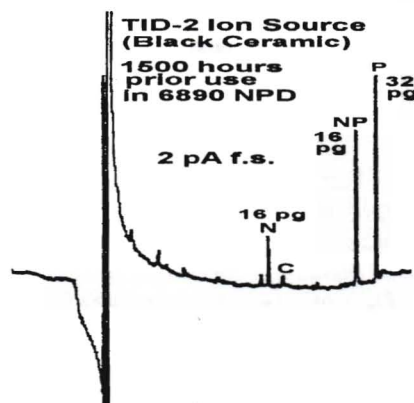


**Figure 6.** Absolute magnitudes of both signals and noise decrease with NPD operating time, but signal-to-noise (i.e., detectivity) remains more constant.

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.

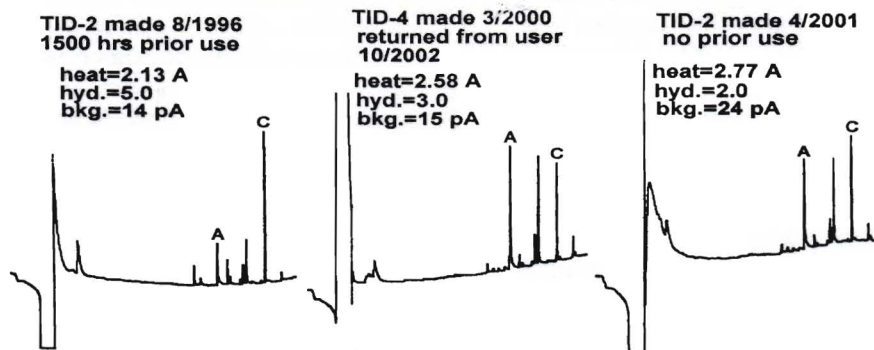


**Figure 7.** DET TID-4 White Ceramic ion source used 750 hours prior to these data. Signals 4.4 times less than when new, noise 5.5 times less, signal-to-noise 20% better than new.

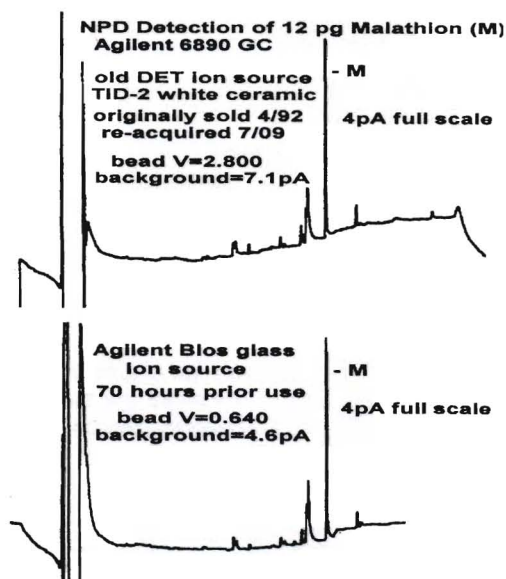


**Figure 8.** DET TID-2 Black Ceramic ion source used 1500 hours prior to these data. Still sharp P peaks, good selectivity of N and P vs. C, and low picogram sensitivity. N=Azobenzene, NP=Methyl Parathion, P=Malathion C=32,000 pg n-Heptadecane.

**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



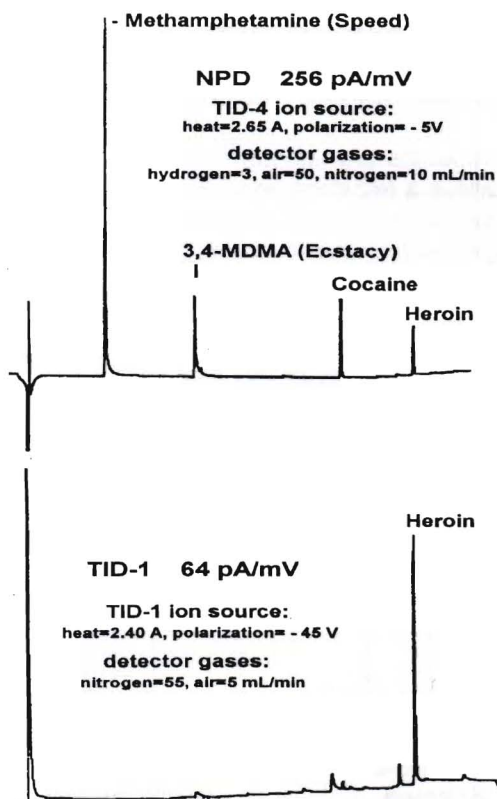
**Figure 9.** Demonstration that DET ceramic ion sources have unlimited shelf life.



**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.



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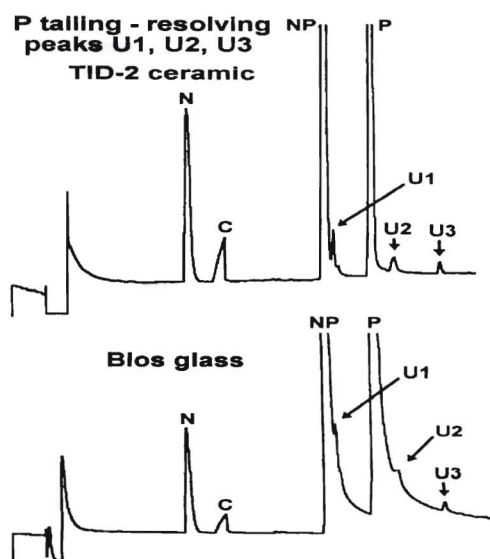


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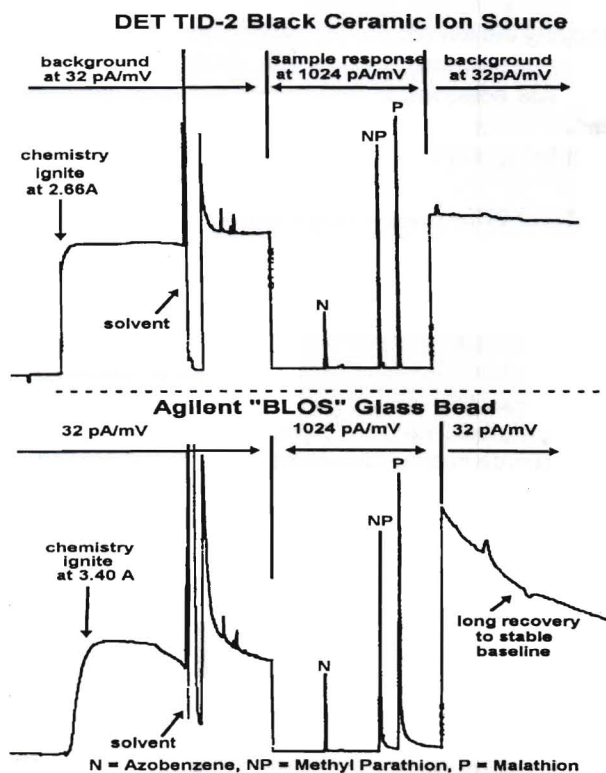


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# DET

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.