

# DET REPORT

NO.57 AUGUST 2008

- 1.) REALIZING THE FULL DETECTION CAPABILITY OF AGILENT 6890/7890 NPD EQUIPMENT.
- 2.) DET NPD/TID EQUIPMENT FOR RETROFIT ON VARIAN GC MODELS.
- 3.) TANDEM THERMIONIC DETECTION ON AN SRI 8610 GC  
1 GC COLUMN EFFLUENT - 2 SIMULTANEOUS DETECTOR SIGNALS (TID-1/NPD, NPD/TID-1, AND OTHER COMBINATIONS).
- 4.) TID-1 DETECTION OF 1,4-BUTANEDIOL COATING ON "AQUA-DOTS" CHILDREN'S TOY.

## 1.) REALIZING THE FULL DETECTION CAPABILITY OF AGILENT 6890/7890 NPD EQUIPMENT.

In addition to its use for NP detection, the basic equipment comprising an Agilent 6890/7890 NPD can be easily and inexpensively adapted to other modes such as selective detection of Oxygenates, Halogenates, and other functional groups. This is a result of recognizing that NP detection is just one member of a family of detectors that operate according to the principles of thermionic surface ionization. In such detectors, there are 4 operating parameters that determine selectivity and sensitivity. These are the chemical composition of the coating used for the ionizing surface; the temperature of the ionizing surface; the composition of the gas environment about the ionizing surface; and the magnitude of polarization between the ionizing surface and a surrounding collector electrode. Changes in detector selectivity can be realized through permutations of these 4 parameters. This report reviews how that is accomplished using the 6890/7890 NPD equipment.

The design features of 6890/7890 NPD equipment that make it well suited to multiple detection uses are as follows:

1.) The NPD hardware configuration is an optimum concentric cylinder design in which a cylindrical ion source is located on the axis of a surrounding collector cylinder. (See Figure 1.) This geometry provides a streamlined gas flow through the detector volume, and a radial electric field for efficient collection of ions formed at the ion source surface.

THERMIONIC IONIZATION DETECTOR DESIGN  
(CONCENTRIC CYLINDER GEOMETRY)

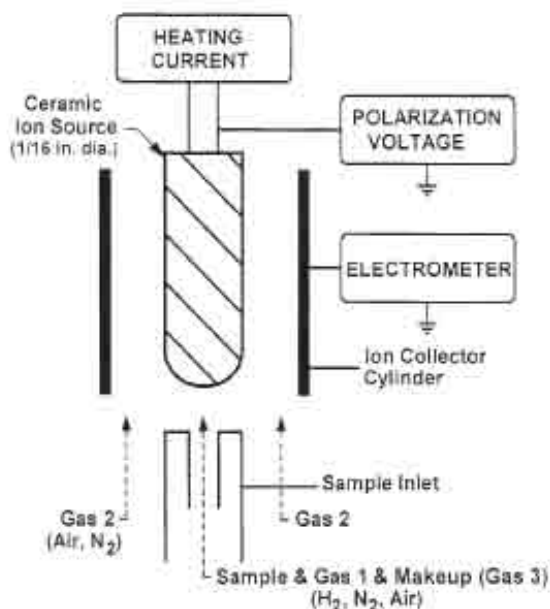


Figure 1. Schematic of the concentric cylinder geometry used in Agilent 6890/7890 NPD equipment. The type of ceramic ion source; composition of detector gases 1, 2, and 3; and magnitudes of heating current and polarization voltage determine the type of selective detector response.

# DET REPORT

NO.57 AUGUST 2008

2.) The Agilent hardware was originally designed to accommodate the hexagonal shaped mounting flange which is standard on DET ion sources, so there are available for use any of the different ceramic coating formulations developed by DET over the past 25 years.

3.) The Agilent equipment has 3 separate gas inlets that can be used to supply gases of different composition to the detector structure.

4.) The 6890/7890 NPD electrometer provides a state-of-the-art low noise amplifier capable of measuring the very small levels of negative ion signal currents emanating from thermionic detectors.

We have used 6890 NPD equipment for years to generate final test chromatograms of ceramic ion sources manufactured at DET. One modification we made to the original equipment was to replace the small orifice jet with a wide bore jet (Agilent part 18789-80070) so fused silica columns of 0.53mm diameter or less could be inserted clear through the jet to a termination closer to the ion source. With this simple change, effluent from the GC is dispensed into the flowing gas stream of the detector rather than into the jet interior where samples are susceptible to degradation from interaction with the hot jet metal. This also eliminates the need to ever have to replace the jet due to contamination of the orifice from column bleed or complex sample matrices. To facilitate positioning the column end, DET has available a spacing kit (part 010-885-13, price \$95). Also available is a short wide bore jet (part 010-419-13, price \$135) with a 48 mm length to fit Agilent's dedicated capillary NPD base weldment.

Although the 6890/7890 NPD Bead Voltage can be used to power the ion sources in all modes of detection, optimum performance is better realized by substituting a stand-alone DET Current Supply (part 001-901-01, price \$1760) for the Bead Voltage supply. There are 2 reasons for this:

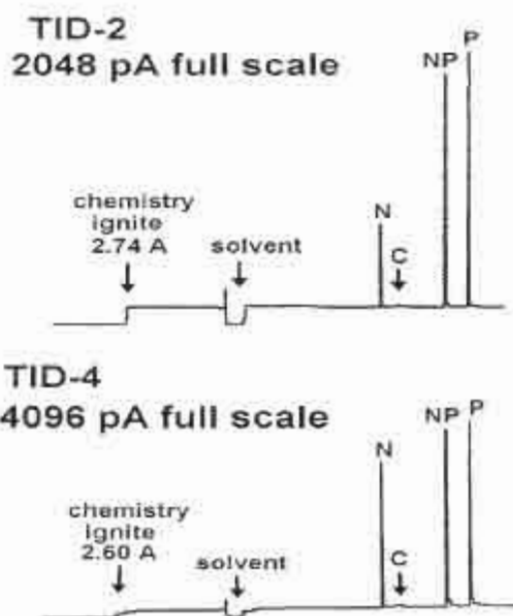
1.) The DET supply provides a Constant Current type heating for the ion source versus the Constant Voltage type heating provided by the Agilent Bead Voltage supply. Constant Current operation ensures that the electrical current flowing through the ion source's wire core is not dependent on the resistance of lead wires attached to the ion source, and this is the most stable means of heating ion sources.

2.) The DET supply also provides a selection of - 5, -15, or -45 Volt polarizations for the ion sources versus a fixed - 4 V provided by the Agilent Bead

Voltage supply. Whereas - 4 or -5 V work well for NP detection, the higher polarizations provide much better signal to noise for detection modes other than NP.

**Optimum NP Detection.** For NP detection, Gas 1 in Figure 1 is normally a low flow of Hydrogen (e.g., 3 mL/min), Gas 2 is Air (e.g., 50 mL/min), and Gas 3 Makeup is Nitrogen (e.g., 10 mL/min). The necessary and sufficient condition for turn on of NP response is that the ion source must be heated enough to ignite the Hydrogen-Air mixture. This ignition forms a chemically reactive boundary layer that surrounds the ion source, and it is indicated by a sudden increase in the detector background signal. The NP chemistry is maintained as long as sufficient heating current is continuously supplied to the ion source.

## DET NP ION SOURCES



**Figure 2.** DET ion sources in Agilent 6890 NPD with ion source power supplied by DET Current Supply. Sample is Varian part 82-005048-04. N=2ng Azobenzene, C= 4000ng n-Heptadecane, NP=2ng Methyl Parathion, P=4ng Malathion, solvent is iso-Octane. Both chromatograms illustrate sudden increase in background signal as ion source heating current was raised to point of NP chemistry ignition. TID-4 exhibits more tailing of P peaks with operating time.

# DET REPORT

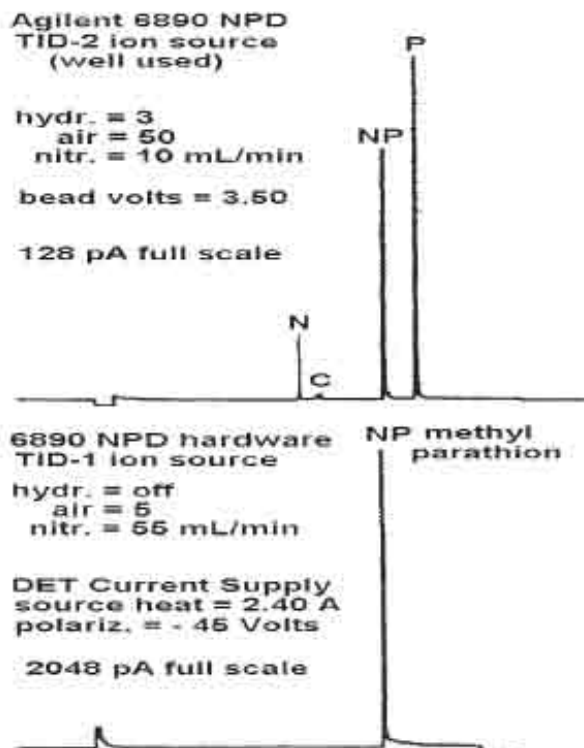
NO.57 AUGUST 2008

NPD versions first described over 30 years ago used ion sources comprised of alkali-glass material that operated in a "softened state". These glass based ion sources were limited in operating conditions because of concern for exceeding the melting point of the glass. By contrast, the ceramic ion source technology pioneered by DET eliminates this structural melting problem, and at the same time allows wide variations in the chemical composition of the source coating to optimize the source's ionizing characteristics. For example, to provide the very best performance for all kinds of NP applications, DET developed 2 different types of NP ion sources. For applications requiring P and/or both P and N detection (e.g., pesticides), a TID-2 type source coating (Black Ceramic) was specifically formulated to provide sharp, non-tailing peaks for P compounds. Alternatively, for applications requiring detection of only N compounds (e.g., drugs of abuse, explosives), a TID-4 type source coating (White Ceramic) was formulated to provide the best possible N response without concern for tailing of P compounds. Figure 2 shows a comparison of TID-2 and TID-4 responses in typical final tests of these 2 source types. Note that the TID-4 chromatogram is displayed at a full scale sensitivity which is twice that of the TID-2 chromatogram.

**TID-1 Ion Source and Selective Detection of Nitro Compounds, Oxygenates, Some Halogenates, Pyrrole vs. Pyridine compounds, and CH<sub>2</sub> Functional Groups in High Concentrations of Linear Chain Hydrocarbons.** Converting a 6890/7890 NPD to a TID-1 mode of detection involves changes in all 4 of the parameters mentioned earlier. The NP ion source is replaced by a TID-1 type ion source which has a lower work function for emission of electrical charge; the ion source is operated at a lower temperature (i.e., 400 - 600°C) than an NP source (i.e., 600 - 800°C); the detector gas environment is Nitrogen or Air versus the Ignited Hydrogen-Air of the NPD, and the optimum polarization is - 45 V versus -4 or -5 V for the NPD.

TID-1 detection represents surface ionization in its purist form in the sense that there is no intervening gas phase chemistry as exists in the NPD. Instead, samples directly impact the hot TID-1 surface and form negative ions that move off through the surrounding gas to be measured at the collector electrode.

Unlike the NPD which responds to most N or P compounds, TID-1 detection is much more dependent on the detailed molecular structure of the compound. Figure 3 shows a comparison of NPD and TID-1 chromatograms for the same test sample used in Figure 2. Whereas NPDs are widely specified for Organophosphorus pesticide analyses, it is clear from Figure 3 that if the requirement is the specific detection of Methyl Parathion, then TID-1 ionization provides much better selectivity and sensitivity, and it is easier to implement because it does not require any Hydrogen. TID-1 selectivity to Methyl Parathion is due to the NO<sub>2</sub> functional group located in a para location relative to other functionalities in that molecule. TID-1 ionization similarly provides exceptional selectivity and sensitivity to other Nitro pesticides, explosives like TNT and 2,4-Dinitrotoluene, and environmental pollutants like 4-Nitrophenol.



**Figure 3.** TID-1 and NPD chromatograms of the same sample as Figure 2. TID-2 (NPD) ion source was a well used source returned to DET for recycling, but it still exhibited excellent NP selectivity v.s. C, and a sharp P peak. TID-1 selectivity to Methyl Parathion was due to the NO<sub>2</sub> functional group in that molecule.

# DET REPORT

NO.57 AUGUST 2008

Perhaps the most important detection capability of TID-1 ionization is its selectivity for a wide range of Oxygenated compounds. A signature chromatogram that demonstrates this selectivity versus Hydrocarbons is the analysis of Ethanol in Gasoline as shown in Figure 4. This analysis was performed with TID-1 modified Agilent 6890 NPD equipment, and a single Nitrogen gas used for both GC carrier and detector gas.

Other unique detection capabilities of TID-1 ionization have been described in previous reports from DET (e.g., Library of TID-1 Chromatograms, March 2008). Some notable examples are the selective detection of certain Halogenated compounds like Heptachlor and Chlordane; selective detection of Pyrrole versus Pyridine based compounds; and selectivity for the number of CH<sub>2</sub> functional groups in high concentrations of Hydrocarbons.

**TID-3 Ion Source and Selective Detection of Halogenates.** The TID-3 mode of detection is similar to the TID-1 mode in that it uses a detector gas environment of Nitrogen or Air, and has optimum sensitivity with a polarization of -45 V. However, the TID-3 ion source is designed to operate at a surface temperature more comparable to that of an NP source instead of the lower TID-1 surface

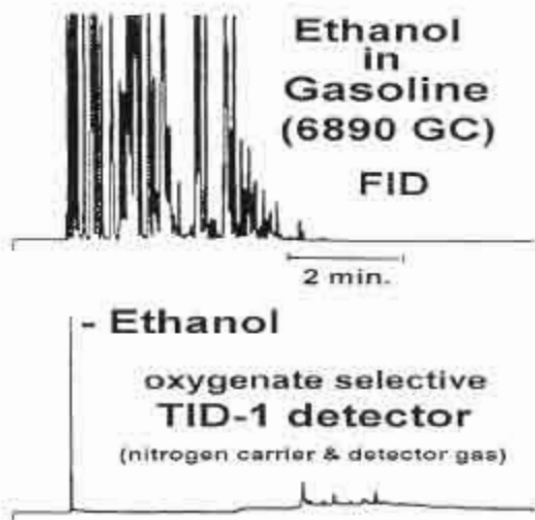


Figure 4. 0.2µL injection of commercial gasoline sample. TID-1 powered by a stand-alone DET Current Supply.

temperature. TID-3 was developed to eliminate severe peak tailing problems that occurred when TID-1 detection was attempted for halogenated volatiles like Trihalomethanes. Figure 5 illustrates the selectivity of TID-3 detection.

Like TID-1, TID-3 thermionic ionization is a surface catalyzed negative ionization process involving direct impact of samples with the hot ion source. It detects volatile Halogenates like Trihalomethanes with a sensitivity of 1 pg/sec, a selectivity of 100,000:1 vs. Hydrocarbons, and a linear response exceeding a range of 10,000 in sample weight. Unlike other halogen detectors, TID-3 response to Br is significantly more than Cl, and the detector gases do not need to be an ultrahigh purity quality. TID-3 and all ceramic coated DET ion sources have excellent shelf lives so that they can be reliably re-used after long periods of inactivity, and they do not need storage in desiccators.

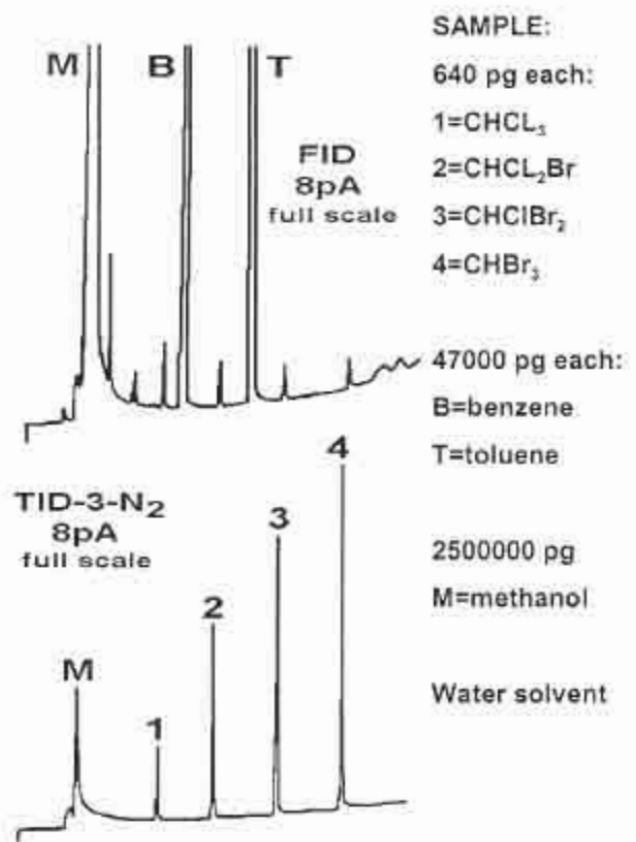


Figure 5. Comparison of FID vs. TID-3.

# DET REPORT

NO.57 AUGUST 2008

**TID-5 Ion Source and Selective Detection of Br and I Compounds versus other Halogenates.** A TID-5 ceramic ion source has a higher work function for the emission of electrical charge than any of the other ion sources in this report. The TID-5 source operates with -45 V polarization at temperatures comparable to those of an NPD, and in a dilute Hydrogen - Air gas environment. Two versions of selective detection are possible depending on the relative magnitudes of the Hydrogen and Air flows. These are illustrated in Figure 6 in analyses of a mixture of substituted benzene compounds. In one version, the gas flows are similar to those commonly used for NP detection, and TID-5 ionization in Figure 6 detected the Cl, Br and N compounds in the sample mixture. In the second more unique version, the Hydrogen and Air flows were a stoichiometric ratio supplemented by a large flow of Nitrogen, and the TID-5 ionization responded primarily to just the Br compound with selectivity versus the Cl and N constituents.

**Summary.** The combination of Agilent 6890/7890 NPD equipment, DET ceramic ion sources, and a stand-alone DET Current Supply allows the same basic equipment to be used for multiple modes of selective detection. Changes from one mode to another are easy and inexpensive.

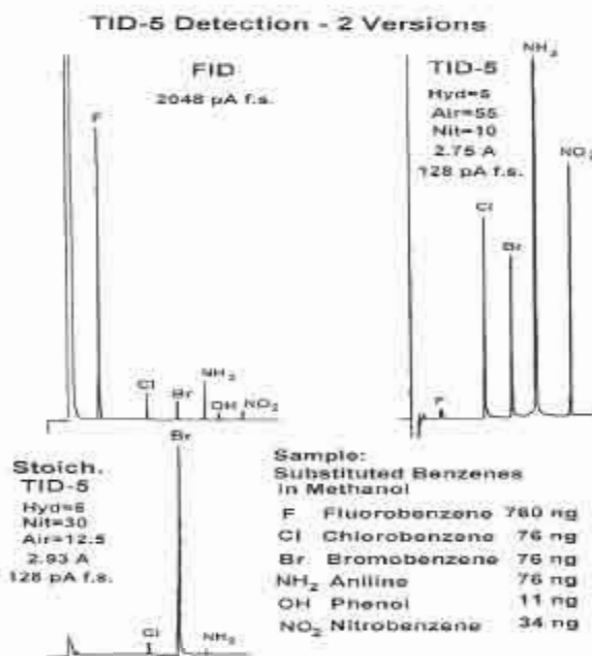


Figure 6. For the stoichiometric gas flows, Air was supplied through the detector makeup gas line, and the Nitrogen was supplied through the detector "Air" line.

## 2.) DET NPD/TID EQUIPMENT FOR RETROFIT ON VARIAN GC MODELS.

In order to use DET's ceramic ion sources on Varian GC models, DET has an entire tower structure that mounts onto Varian's FID or TSD detector base. (TSD is Varian's nomenclature for an NPD.) The DET tower provides an optimum concentric cylinder configuration that was depicted in Figure 1, and it can accommodate the same style DET ion sources as used with the Agilent 6890/7890 GC. Hence, different modes of selective detection are possible in addition to NP detection. Varian's pneumatics controls suffice for detector gases, and Varian's TSD electronic modules are compatible with powering the DET ion sources and measuring detector signals. However, for optimum response in modes other than NPD, a stand-alone DET Current Supply is recommended for powering the ion sources because it provides a selection of higher polarizations than the Varian power supply.

Figure 7 compares Varian's TSD response versus response from DET's TID-2 type ion source in a DET tower on the Varian GC. Both the TSD bead and the TID-2 ion source are fabricated from ceramic materials, and both were newly acquired for the Figure 7 data. The P response of the TID-2 source clearly demonstrated the improvement in peak tailing achieved with that coating.

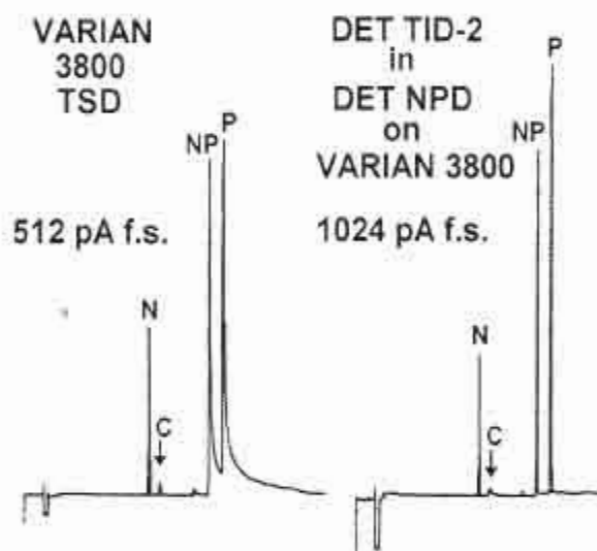


Figure 7. Same sample as Figure 2. Varian TSD electronics used for both chromatograms. TSD bead heat=3.10 A. TID-2 source heat=2.95 A.

# DET REPORT

NO. 57 AUGUST 2008

formulation. For the TSD data, Varian's recommended flows of Hydrogen = 4 and Air = 175 mL/min were used, while the TID-2 data were generated with Hydrogen = 3 and Air = 60 mL/min.

The price difference between ion sources is \$1086 for Varian's TSD bead versus \$310 for DET's TID-2 source. Hence, the initial cost of converting from Varian's TSD tower structure to DET's tower (part 010-860-20, price \$1550) can soon be recovered by

savings in the cost of replacement sources.

DET's tower for Varian GC models is about half the size of Varian's TSD tower, and the mounting allows rotation of the tower body so the signal probe arm can be positioned to avoid adjacent structures. The DET hardware also includes a ceramic lined jet that seals into Varian's detector base with a stainless steel ferrule instead of the crushable Graphite or Vespel ferrule used with Varian jets.

## 3.) TANDEM THERMIONIC DETECTION ON AN SRI 8610 GC 1 GC COLUMN EFFLUENT - 2 SIMULTANEOUS DETECTOR SIGNALS (TID-1/NPD, NPD/TID-1, AND OTHER COMBINATIONS).

Tandem TID detection refers to a series combination of two different types of thermionic detectors such that a single column effluent passes through both and produces 2 simultaneous signals. Figure 8 shows a schematic illustration of tandem equipment as it was recently fit onto an SRI 8610 GC. Each detection stage is an optimum concentric cylinder configuration, and each has an independent ion source, ion source power supply, and electrometer amplifier. As shown in Figure 8, there are provisions for adding 3 different detector gases so the gas environments in the 2 stages can also be different.

The SRI GC equipment used in this work was equipped with an on-column injector, 2 FID detector bases, 2 electrometer amplifiers, and multichannel

data acquisition. Connection to a laptop computer provided column temperature and carrier gas pressure programming capability, as well as data system processing of the signals. The SRI equipment included a built-in Air compressor that was used to provide detector Air flow where that was required. For improved injector to column and column to detector seals, we replaced SRI's fittings with Agilent parts G1532-80540 (TCD capillary column adaptor), 5181-8830 (column nut), and 5080-8773 (1.0 mm ID Graphite ferrule for 0.53 mm column). The Hydrogen line to one of the detector bases included restrictor tubing normally used to provide low flows for an NPD,

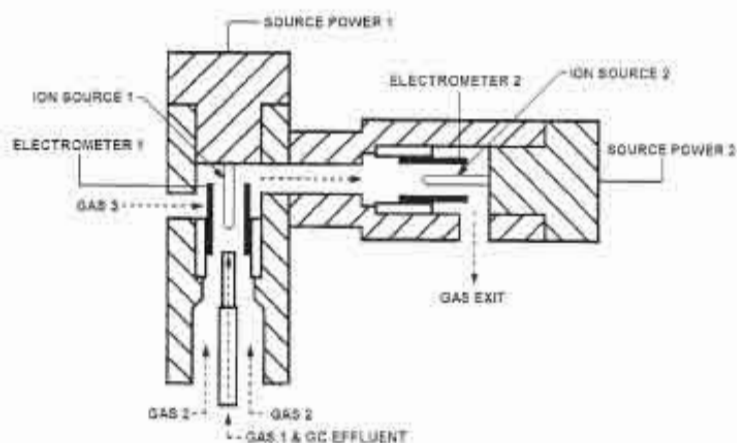


Figure 8. Schematic of Tandem TID equipment.

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

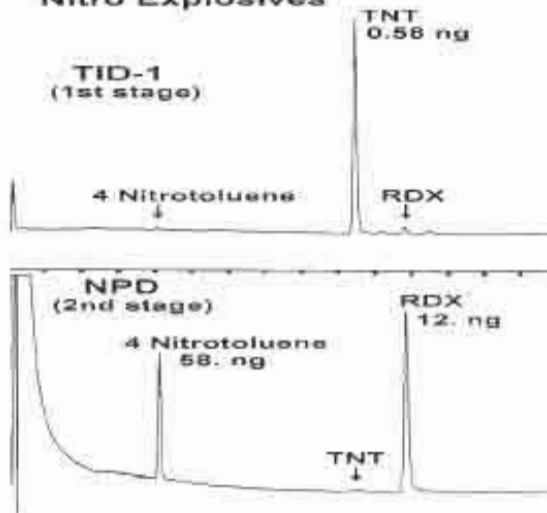


Figure 9. 6m x 0.53mm x 1.5µm Rtx-TNT, 50-200°C at 10°C/min, He carrier program 3-6psi at 0.2psi/min. Gas 1=H<sub>2</sub> (8psi), Gas 2 & 3=Air (2psi). TID-1 heat=2.55A, polar.= - 45V; NPD (TID-4) heat=3.05A, polar.= - 5V.

# DET REPORT

NO.57 AUGUST 2008

while the Air lines to both detector bases included restrictor tubing also normally used for an NPD.

DET tandem hardware included a ceramic tipped jet that mounted into the SRI FID base, and 2 tower bodies constructed of 3/4 inch hexagonal stainless steel with 1/8 inch Swage inlets. The first stage tower mounted onto the jet, and included two 1/16 inch gas inlets for Gases 2 and 3. The second stage tower mounted onto the exit of the first tower. Both towers used the same type ion sources as Agilent 6890/7890 NPD equipment, and 2 stand-alone DET Current Supplies were used to power the ion sources.

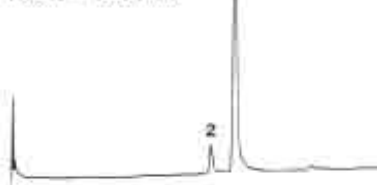
Figure 9 shows a TID-1/NPD tandem combination applied to an analysis of Nitro explosives. TID-1 detection provided exceptional sensitivity for the TNT component of the sample, while the NPD with a TID-4 ion source provided more universal detection of all the N-compounds in the sample.

NPD (1st stage) heat = 3.30 A

1=Mevinphos  
2=Trifluralin  
3=Simazine  
4=Chlorpyrifos



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



TID-1 (2nd stage)  
heat = 2.57 A  
1st stage heat  
at 2.30 A - no  
NP chemistry

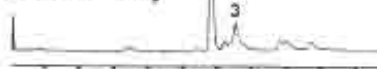


Figure 10. 15m x 0.53mm x 1.5µm DB5, 100 -250°C at 10°C/min, He carrier 15 -22.2psi at 0.4psi/min. Gases 1, 2, and 3 same as Figure 9. NPD (TID-2) polarization = - 5 V, TID-1 polarization = - 45V. Bottom chromatogram was 2<sup>nd</sup> stage signal with NP chemistry of 1<sup>st</sup> stage turned off.

Usually, the first stage of a tandem detector is non-destructive to the sample. However, it is possible to use a destructive first stage to produce decomposition products that are then better detected in the second stage. Figure 10 illustrates this for NPD/TID-1 analysis of a pesticide mixture. Note that when the NP chemistry of the first stage was turned off by reducing the ion source heating current in that stage, the selectivity of TID-1 detection in the second stage changed.

Figure 11 provides an illustration of first stage sample decomposition in an FID, followed by second stage selective detection of the Halogenated decomposition products. FID response in Figure 11 was achieved by using a Bare Wire Probe (DET part 020-902-00, price \$195) in the first stage instead of a ceramic coated ion source. The bare wire was heated to ignite a self-sustaining flame at the ceramic jet tip. Then the heating current was reduced to zero, and the probe acted as the polarizer for ion collection.

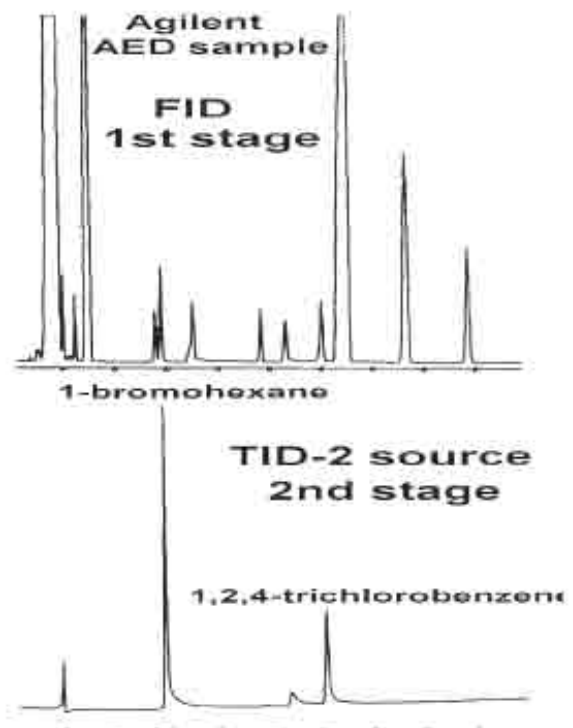


Figure 11. 1.0µL injection of Agilent test sample for Atomic Emission Detector (AED). Same column as Figure 10. 50 - 250°C at 10°C/min, He carrier 5 -13psi at 0.4psi/min. Gas 1=H<sub>2</sub> (30psi), Gas 2 & 3=Air (5psi). Bare wire ignitor/polarizer used in FID stage, TID-2 source heat=3.30A, polariz.= - 45 V, TID-2 in downstream flame effluent responds to Br and Cl components of the sample.

# DET REPORT

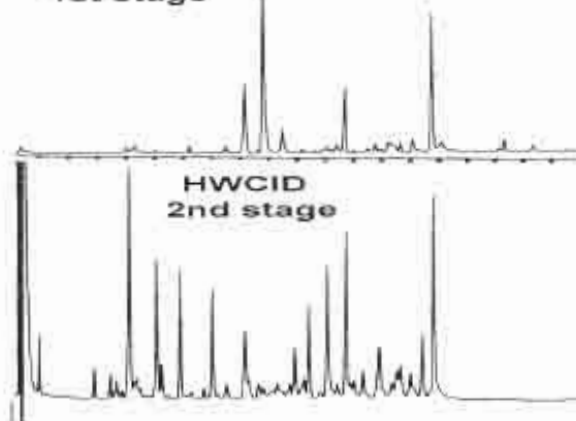
NO.57 AUGUST 2008

Figure 12 shows a combination of TID-1 first stage detection followed by Hot Wire Combustion Ionization Detection (HWCID) using the bare wire probe mentioned in Figure 11. HWCID provides universal detection like an FID, but it maintains the ignited Hydrogen - Air chemistry adjacent to a continuously heated wire instead of in a self - sustaining flame.

When considering that each stage of Tandem TID equipment can have a number of different ionizing elements installed, and there are numerous gas flow mixtures that can be used, then it is clear that there are many other signal combinations beyond those described here. Previous DET reports have also described Tandem TID detection on Varian and Agilent GC systems. On Varian GC models, Varian's TSD electronic modules can be used for signal measurement and for some ion source power. For Agilent GC models, DET Tandem TID hardware fits onto the Agilent FID base, and requires stand-alone electronics for both ion source power and signal measurement.

Poison Eau de Cologne

TID-1  
1st stage



HWCID  
2nd stage

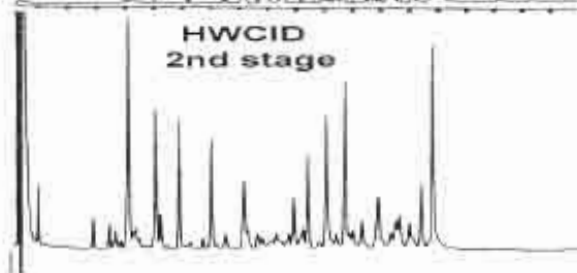


Figure 12. 0.5µL injection. Same column and program as Figure 11. Gas 1=H<sub>2</sub> (21psi), gas 2=N<sub>2</sub> (100mL/min from auxiliary flow module), gas 3=Air (5psi). TID-1 source heat=2.50 A, bare wire heat in HWCID = 3.00A.

## 4.) TID-1 DETECTION OF 1,4-BUTANEDIOL COATING ON "AQUA-DOTS" CHILDREN'S TOY.

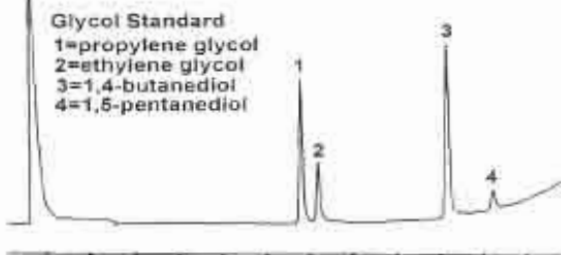
Earlier this year there was an application note by Andrew Tipler on the Perkin Elmer web site describing a GC/MS method for screening Glycols in the coating of small beads used in a children's toy called "Aqua-Dots". In the latter months of 2007, there was widespread publicity concerning this toy due to concern that the coating could convert to the date rape drug GHB if children put the beads in their mouths. Tipler pointed out that the problem was associated with the compound 1,4-Butanediol in the coating instead of the safer 1,5-Pentanediol.

Since TID-1 surface ionization has a good response to Glycols, and since a DET employee brought in a sample of their child's "Aqua-Dot" beads, an evaluation was undertaken following the simple Methanol extraction described by Tipler. For this analysis, an SRI 8610 GC fitted with a DET detector structure and TID-1 ion source was used. A single Nitrogen supply sufficed for both the GC carrier and detector gases.

Figure 13 shows a comparison of data obtained from the "Aqua-Dot" bead extract versus retention times for various Glycols. It was clear that our Aqua-Dot bead sample had the 1,4-Butanediol compound rather than the 1,5-Pentanediol. This was a good example of how the Oxygenate selectivity of TID-1 detection can be used in a very simple analysis system.

TID-1 on SRI 8610 GC  
nitrogen carrier & detector gas

Glycol Standard  
1=propylene glycol  
2=ethylene glycol  
3=1,4-butanediol  
4=1,5-pentanediol



Methanol Extract  
of  
"Aqua Dot"

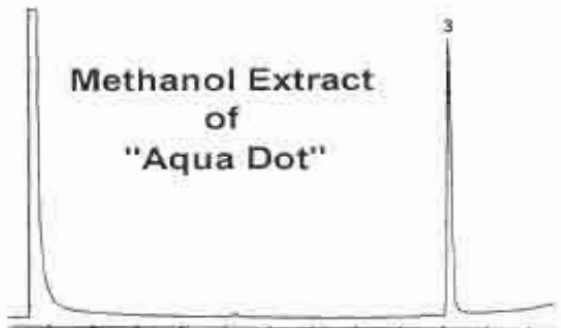


Figure 13. 15m x 0.53mm x 1.2µm EC-Wax (Alltech), temperature programmed 50 - 180°C at 10°C/min, with Nitrogen carrier gas programmed at 6 - 11.2psi at 0.4psi/min.