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1.) SELECTIVE DETECTION OF BISPHENOL A AT LOW PICOGRAM LEVELS WITH TID-1 SURFACE IONIZATION.

2.) UNIQUE CONSTRUCTION OF DET CERAMIC ION SOURCES FOR NPD AND OTHER MODES OF THERMIONIC DETECTION.

3.) OPTIMUM THERMIONIC DETECTOR CONFIGURATION USED IN DET AND AGILENT 6890/7890 NPD EQUIPMENT.

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1.) SELECTIVE DETECTION OF BISPHENOL A AT LOW PICOGRAM LEVELS WITH TID-1 SURFACE IONIZATION.

Bisphenol A (BPA) is a chemical compound that has received much attention recently in both public and scientific media (eg., Chemical and Engineering News, April 28, 2008, page 11). This toxic compound is a ubiquitous contaminant found in baby bottles and other drink bottles made from polycarbonate material. Although there remains uncertainty regarding whether the level of BPA found poses a threat to human health, bottle manufacturers, vendors, and government officials are all taking steps to reduce public exposure to this compound.

Past experience with TID-1 thermionic surface ionization has demonstrated that Phenols are a class of Oxygenated compounds that are especially well detected with excellent selectivity versus Hydrocarbons. Accordingly, BPA is a good candidate for TID-1 detection because it contains t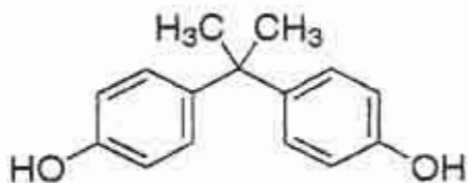wo Phenol functional groups. This method of GC detection is relatively simple. It uses NPD-like detector equipment, and features a low work function ceramic ionizing surface operated in a detector gas environment of Nitrogen. Incoming samples impact the heated ionizing surface; negative ions are formed by extraction of electrons from the surface; and a prevailing polarization voltage moves the ions through the gas phase to a surrounding collector electrode. Unlike an
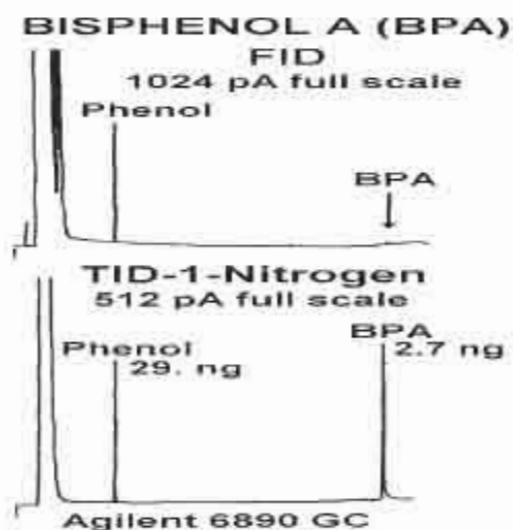

Figure 1. Molecular structure of Bisphenol A.

Figure 2. Comparison of FID and TID-1 chromatograms for a sample mixture containing 29 ng Phenol and 2.7 ng BPA in a Methanol solvent.

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NPD which detects all organically bound N or P compounds with similar signal magnitudes, TID-1 detection often exhibits large differences in response depending on the detailed molecular structure of the analyte molecule.

Figure 2 shows a comparison of FID and TID-1 chromatograms for a mixture containing Phenol and BPA in a Methanol solvent, with the BPA concentration being approximately 10 times less than that of Phenol. At the sensitivity displayed, the FID provided a large Phenol peak, but only a barely visible signal for the BPA. In contrast, the TID-1 detector provided large peaks for both the Phenol and BPA constituents.

The data in Figure 2 were generated using an Agilent 6890 GC. Chromatographic conditions were as follows: 30m x 0.32mm x 0.25µm HP-5ms column; He carrier = 3 mL/min; program = 60°C - 1 min, 60 - 110°C at 7°C/min, 110 - 250°C at 13°C/min, 250°C -1 min; Injector = 250°C; and detector = 280°C. For the TID-1 data, the Agilent 6890 NPD structure was used with a TID-1 ceramic ion source and with detector gas flows of Nitrogen makeup = 55 mL/min, and Air = 5 mL/min. The ion source was heated with a stand-alone DET Current Supply providing a constant heating current of 2.450 A, and a polarization voltage of - 45 V. Signals were measured with the 6890 NPD electrometer.

As shown in Figure 2, the TID-1 response to BPA was exceptionally large. The noise level of this mode of detection was comparable to just the noise of the 6890
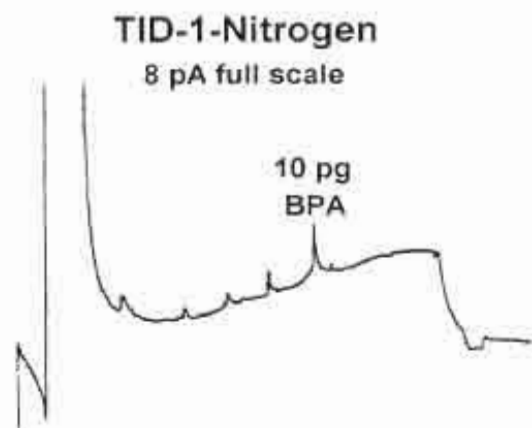
NPD electrometer, and the 2.7 ng peak for BPA had a signal to noise ratio of 13000:1. This translates into a BPA detectivity in the sub- picogram range. Figure 3 shows TID-1 detection of 10 pg of BPA. In this illustration, impurities in the Methanol solvent constituted the detectivity limitation rather than noise in the system.

For the data in Figures 2 and 3, a stand-alone DET Current Supply module was used to power the ion source rather than the 6890 NPD Bead Voltage supply on the GC. This was because the DET module could provide a selection of a higher polarization of -45 V versus the fixed -4 V available from the 6890 supply. Whereas the lower polarization is optimum for an NPD, the higher polarization produces much larger signal magnitudes for the TID-1 mode of detection. For comparison with Figure 2, Figure 4 shows chromatograms of that same sample generated using the 6890 NPD Bead Voltage instead of the DET supply. Signal to noise for the 2.680 V BPA data in Figure 4 was 940:1, which was 14 times lower than the Figure 2 data that were generated with the higher polarization.

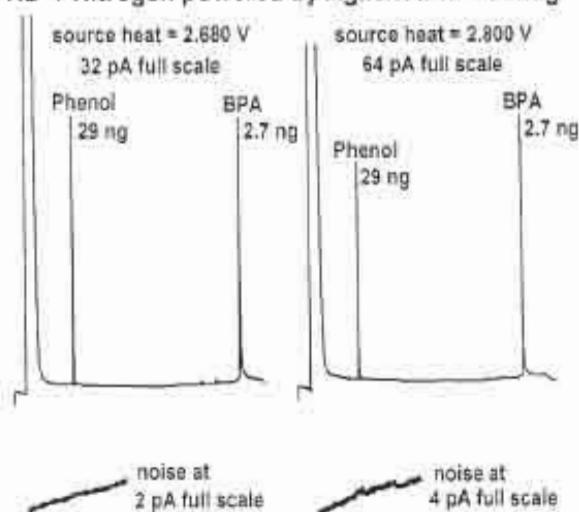### TID-1-Nitrogen powered by Agilent Bead Voltage

Figure 4. Same sample and chromatographic conditions as Figure 2 except the Agilent 6890 NPD Bead Voltage supply was used to heat and polarize the TID-1 ion source at -4 V rather than the - 45 V polarization available from the DET Current Supply used for Figure 2..

TID-1-Nitrogen
8 pA full scale

Figure 3. Same column and carrier as Figure 2. 150 - 250°C at 8°C/min.

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Another means of increasing the absolute magnitude of TID-1 signals is to increase the temperature of the ion source by applying higher heating power. Figure 4 compares signals and noise for 6890 Bead Voltages of 2.680 V and 2.800V. It is clear from this comparison that the higher heating power also increases the detector noise, so that there is no net gain in signal to noise (i.e., signal to noise for 2.800 V was only 460:1
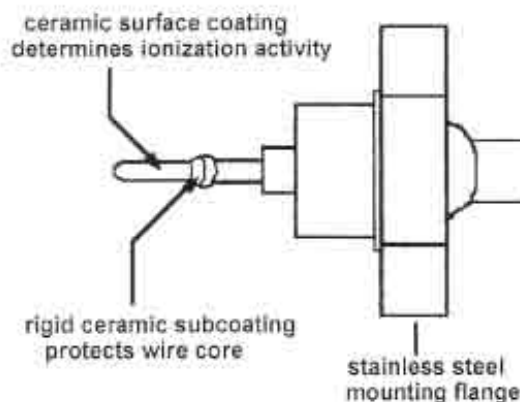
compared to 940:1 for 2.680 V). In our experience with TID-1detection, optimum detectivity and selectivity is usually achieved with the ion source heated just enough to produce a detector noise level comparable to that of the signal measuring electrometer (e.g., 6890 NPD electrometer noise displayed with the 2.680 V chromatogram of Figure 4). This corresponds to a detector background signal of 10 pA or less.

2.) UNIQUE CONSTRUCTION OF DET CERAMIC ION SOURCES FOR NPD AND OTHER MODES OF THERMIONIC DETECTION

Fabrication of a TID-1 ion source like that of the preceding section is possible because of the unique construction of DET ceramic sources. DET ion sources originated years ago when it was recognized that the operating mechanism of NP detectors was a surface process, and that NP detection was just one possible member of an entire family of selective detectors operating according to surface ionization principles.

For NP detection, a necessary condition is that the ion source must be heated to a temperature in the range of 600 - 800°C in order to ignite a chemically reactive Hydrogen-Air boundary layer about the hot source. For NPDs where the ion source consisted of a glass type bead formed onto a bare Platinum wire, the required ignition temperature was close to the softening point of the glass, and this was a significant limitation on the operating parameters for these beads. To overcome this limitation, DET chose to develop NP and other ion sources out of higher temperature ceramic materials which were more robust and could withstand a much wider range of operating conditions. In addition to the NPD operating temperature consideration, ceramic ion sources have proven to be more reliable to manufacture because coatings are formed from room temperature slurries rather than having to go through a molten stage.

Figure 5 illustrates the multilayered structure of DET ion sources. As with all NP ion sources, DET sources have a wire core that allows the ionizing surface to be electrically heated to temperatures considerably higher than the surrounding detector structure. A unique feature of DET ion sources is that the wire core is completely covered by a sub-layer ceramic coating in order to eliminate any extraneous ionization from exposed wire material, and to protect the wire from corrosion from additives in the active surface coating

ceramic surface coating determines ionization activity

rigid ceramic subcoating protects wire core

stainless steel mounting flange

DET Ion Source Construction (fits Agilent & DET structures)

Figure 5. Illustration of the construction of DET ion sources that fit Agilent 6890/7890 NPD equipment and all DET detector structures. Stainless steel mounting flange that is depicted is a 3/4 inch hexagonal design. Other available mounting flange designs are a 1/4 inch diameter tube which is used in NPD equipment manufactured by Thermo Scientific and SRI Instruments, and a round flange design that fits an older model Finnigan/Tremetrics 9001 NPD structure.

or from complex sample matrices. The sub-layer coating also provides a rigid structural basis for subsequently applying surface coatings of ceramic with widely varying additive formulations. DET ion sources can withstand operation in either vertical or horizontal orientations without concern for sagging support wires as can occur with glass bead/Pt wire type ion sources. Also, DET ion sources have

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sufficient thermal mass to resist surface temperature fluctuations due to minute changes in detector gas flows.

Whereas the sublayer ceramic structure is the same for all DET ion sources, ceramic coatings applied over this sublayer can have a wide range of additives which define the ionizing and/or catalytic activity of the surface. For NP detection, two surface coating formulations have been developed. One is a Black Ceramic (TID-2 type) which was designed specifically to minimize Phosphorus compound peak tailing which had been a characteristic of many past NPD detectors. For applications where there never is concern for P peak shape (i.e., analyses of only N compounds), DET developed a White Ceramic surface (TID-4 type) that produces the largest possible N response. The TID-1 type ion source which has already been discussed, produces selectivity for many Oxygenates, and exceptional detectivity for Nitro compounds like TNT, 2,4-Dinitrotoluene, Methyl Parathion, and 4-Nitrophenol. Whereas, the NPD TID-2 and TID-4 ion sources are designed to operate with Hydrogen and Air as the detector gases, TID-1 is designed to operate in either Nitrogen or Air. Other DET ion sources that have been identified include the following:
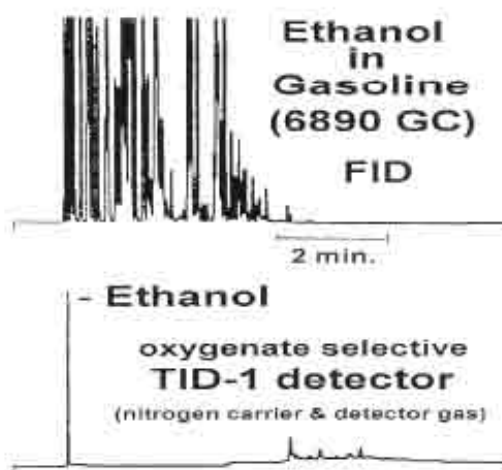
TID-3 type for operation in Nitrogen or Air to provide non-tailing peaks for Volatile Halogenates such as Trihalomethanes;

TID-5 type for operation in a stoichiometric mix of Hydrogen and Air to provide selectivity for Br and I compounds versus other Halogenates;
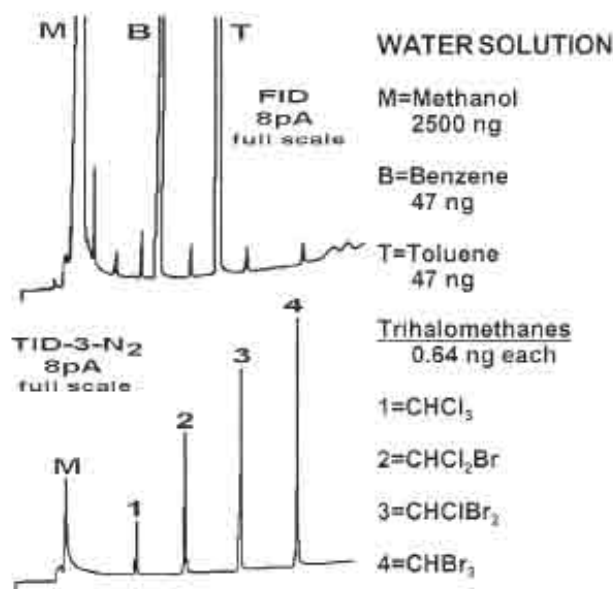
TID-6 for operation in a pre-mixed high flow of H_2/Air and a detector tower structure identified by PTID nomenclature (Phosphorus Thermionic Ionization Detector) to provide selectivity and very high ionization efficiency for Phosphorus;

CFID for operation in the moisture saturated downstream effluent of a self-sustained flame and with a detector configuration described by Remote FID nomenclature to provide selectivity to Pb, Sn, P, or Si compounds.

Figures 6 - 11 demonstrate the versatility of ceramic ion sources by showing different coating formulations operated in various detector gas environments.

Ethanol in Gasoline (6890 GC) FID

2 min.

Ethanol

oxygenate selective TID-1 detector

(nitrogen carrier & detector gas)

Figure 6. This is a signature chromatogram that demonstrates how a selective detector can greatly simplify a chemical analysis. Detection of Ethanol in gasoline requires just a single Nitrogen supply for carrier and detector gases, and the analysis can be done in a short time because there is no need to chromatographically resolve the many Hydrocarbon components.
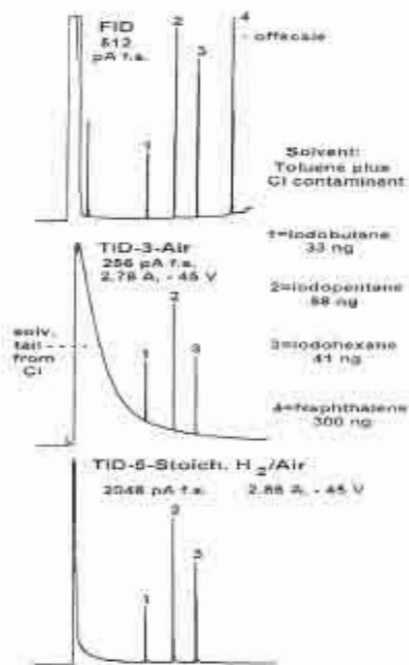

WATER SOLUTION

FID 8pA full scale

M=Methanol 2500 ng

B=Benzene 47 ng

T=Toluene 47 ng

TID-3-N$_2$ 8pA full scale

Trihalomethanes 0.64 ng each

1=$CHCl_3$

2=$CHCl_2Br$

3=$CHClBr_2$

4=$CHBr_3$

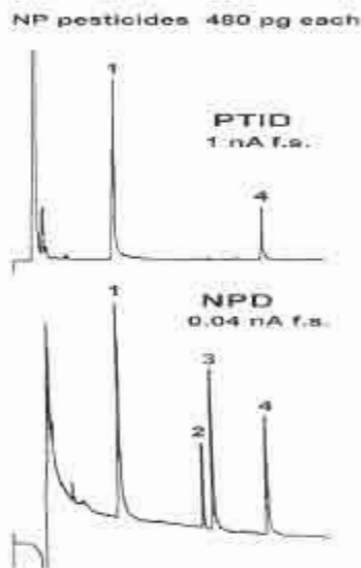Figure 7. TID-3 ion source in a Nitrogen detector gas environment.

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Figure 8. TID-3 and TID-5 sources in Agilent 6890 NPD hardware and powered with DET Current Supply. Detector gas for TID-3 was 55 mL/min Air. Detector gases for TID-5 were H_2=5, Air=12.5, N_2=30 mL/min.

NP pesticides 480 pg each

Figure 9. Mevinphos (1), Trifluralin (2), Simazine (3), and Methyl Parathion (4). DET PTID detector mounted on Agilent 6890 FID base. DET Current Supply and Keithley Electrometer used for detector electronics. **PTID:** TID-6 ion source heat = 3.20 A, polarization = - 45 V, H_2=30, Air=300 mL/min. **NPD:** TID-2 source heat=3.25 A, polarization = - 5 V, H_2=4, Air=70 mL/min.

Sn SPIKE IN GASOLINE
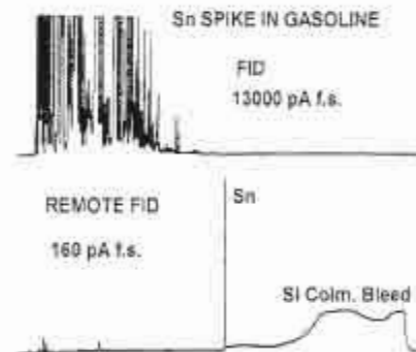
Figure 10. Gasoline spiked with 12 ppm Tetrabutyltin. DET Remote FID tower mounted on Agilent 6890 FID base with DET Current Supply and Keithley Electrometer electronics. Remote FID tower positions a CFID type source and collector electrode several centimeters downstream of a flame. Long lived Sn ions survive to reach the collector while Hydrocarbon ions dissipate by gas phase recombination. Flame gases were H_2=20, CH_4 through makeup gas line = 5.5, and Air=170 mL/min.
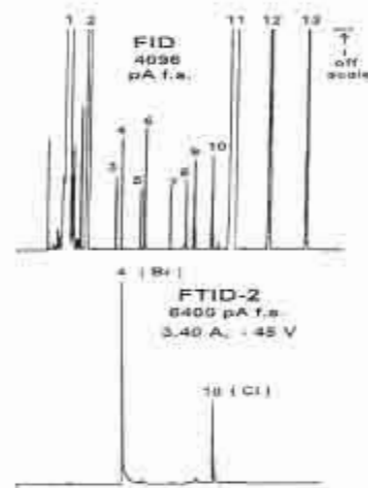
Figure 11. Same Remote FID tower as Figure 10 but with a TID-2 ion source normally used in the NPD now operating in the moist downstream effluent of a flame. Flame gases were 20 mL/min of a Hydrogen-20% Methane gas mixture, and 200 mL/min Air. Agilent AED test sample #2: 1=i-C_8 solvent; 2=4.04% n-C_9; 3=0.07% 4-fluoroanisole; 4=0.07% 1-bromohexane; 5=0.05% tetraethylorthosilicate; 6=0.05% n–decane (perdeuterated); 7= 0.07% nitrobenzene; 8=0.06% triethyl phosphate; 9=0.05% tert-butyl disulfide; 10=0.08% 1,2,4-trichlorobenzene, 11=4.3% n-C_{12}; 12=0.43% n-C_{13}; 13=0.13% n-C_{14}. FTID-2 selectively detects just the Halogenated components.

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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,
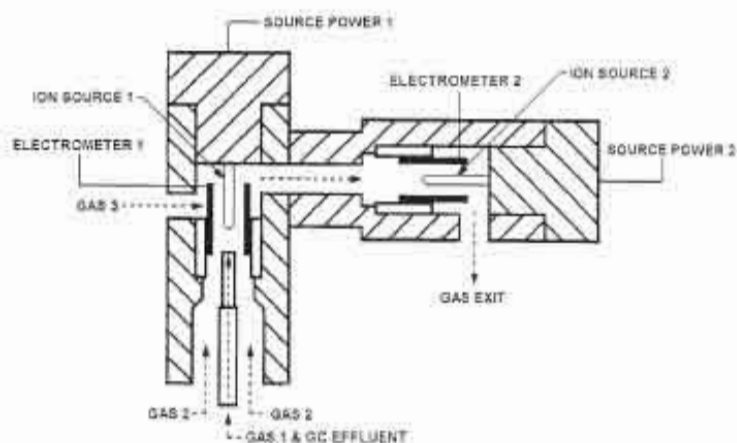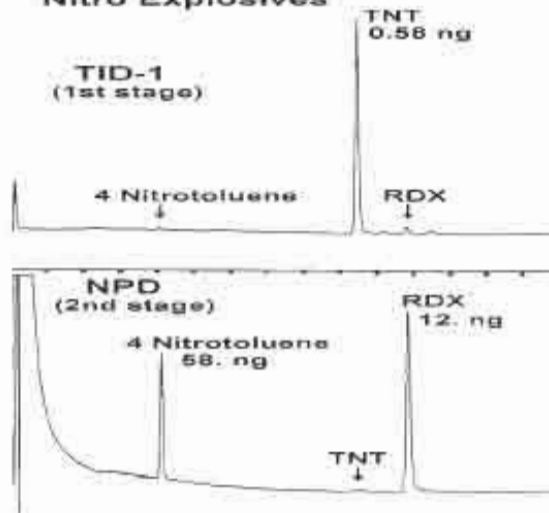

Figure 8. Schematic of Tandem TID equipment.

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=H₂ (6psi), Gas 2 & 3=Air (2psi). TID-1 heat=2.55A, polar.= - 45V; NPD (TID-4) heat=3.05A, polar.= - 5V.
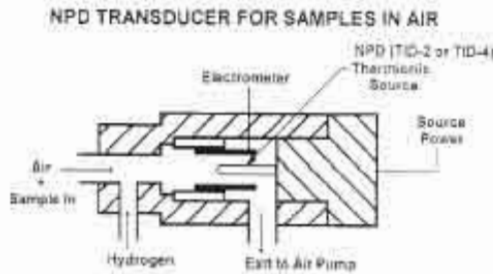
NPD TRANSDUCER FOR SAMPLES IN AIR

Figure 14. No external heat, but body of NP transducer self-heats by radiation from hot ion source.
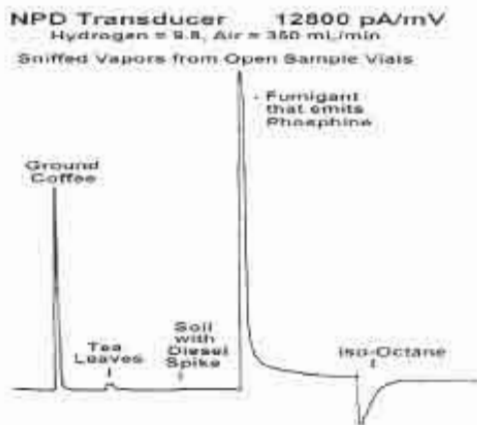

Figure 15. NP detection of sniffed vapors. Large concentration of iso-Octane vapors caused a negative dip in the detector baseline.
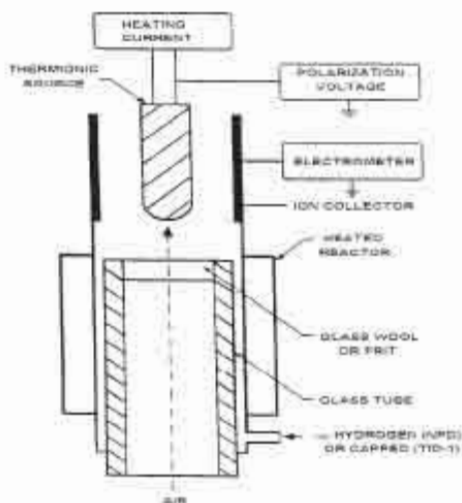

Figure 16. Thermionic transducer preceded by a heated inlet reactor. Sample pump pulls ambient Air through transducer.

Malathion Residue on Quartz Rod
NPD, 160 pA f.s., Hydr.=4.3, Air=200

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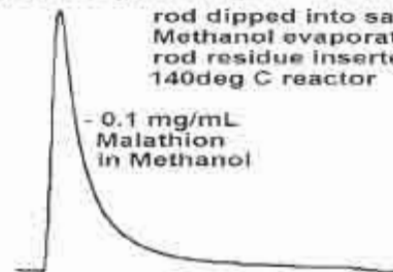Methanol evaporated -
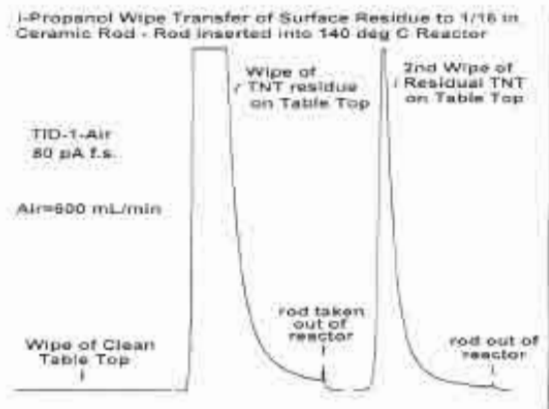rod residue inserted into
140deg C reactor

- 0.1 mg/mL
Malathion
in Methanol

Figure 17. NPD detection of Malathion residue.

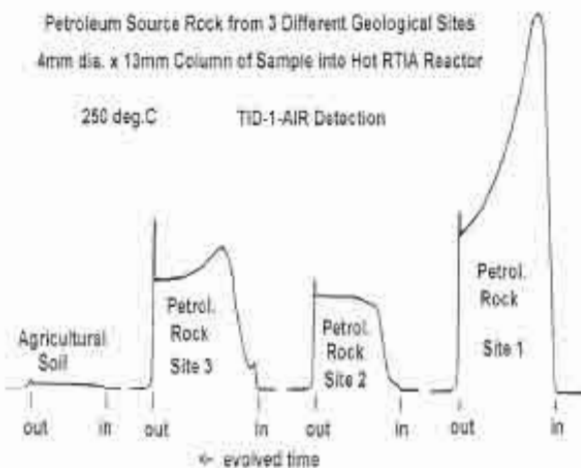Figure 18. Exceptional TID-1 sensitivity to TNT.

Figure 19. Soil/crushed rock samples inserted into glass tube, and tube then inserted into hot reactor preceding a TID-1 transducer. Ambient Air pulled through sample and transducer.

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4.) RECYCLE USED CERAMIC ION SOURCES FROM THE AGILENT 6890/7890 NPD.

As long term users of NP ion sources, we are very much aware that depleted quantities of this consumable component eventually accumulate in the laboratory. Instead of discarding these parts into commercial trash, an alternative is to return them to DET for salvaging of materials used in their manufacture. This recycling program applies to ceramic ion sources used in the Agilent 6 890/7890 NPD or in DET NPD/TID detector structures, and includes ion sources originally manufactured by either Agilent or DET. Among the component pieces of returned ion sources, we are able to re-use the Twinex electrical connector and machined Aluminum collector holder. These 2 parts can be attached to an otherwise new source wiring, mounting flange, and ceramic ionization surface, and the resulting recycled assembly is available at a reduced price of $280 versus $310 for an entirely new ion source. Recycled ion sources are available w ith a ny o f t he d ifferent c eramic c oatings developed by DET, irrespective of what the original coating was on the depleted source returned to DET.

A most important benefit of DET's recycling program is that we have been able to examine thousands of ion sources to determine how they hold up after extensive use by many different types of customers, and in many different types of applications. This information has been an invaluable aid to determining ways to improve the quality of DET manufactured ion sources, as well as a guide to identifying better ceramic coating formulations.

One of the most interesting findings is that end users have a wide range of criteria for determining when to replace an NPD ion source. A broken source ceramic, or burned out wire core, or ionizing surface covered by Silicon Dioxide or other material from a complex sample matrix or derivatizing reagent are obvious reasons to replace the ion source. However, the majority of returned sources still are capable providing good NP selectivity with reasonably good signal-to-noise, although the absolute magnitudes of signal, background, and noise may be as much as 10 times less than when the ion source was new. Figure 20 shows data from a TID-4 ion source that was returned after extensive use. The signal to noise with this TID-4 source was still good enough to provide femtogram detectivity for Nicotine.

As a ceramic ion source ages and its sample response tends to decrease, one way of recovering lost response is to increase the surface temperature by increasing the heating power to the source. However, this can often be counterproductive because it causes the response to decay at an even faster rate. In the case of NP ion sources, an additional means of increasing sample response is to increase the flow rate of Hydrogen supplied to the detector. Figure 21 shows data from a TID-2 ion source that had been operated for 1500 hours in the Agilent 6890 NPD. By increasing the Hydrogen flow from 3 to 4 mL/min, and by increasing the heating power above that minimum needed to ignite the H_2 - Air chemistry, it was possible to still obtain good selectivity, low picogram detectivity, and sharp peaks from this well used ion source.
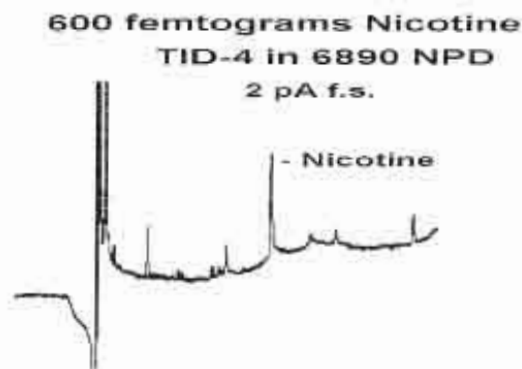
600 femtograms Nicotine
TID-4 in 6890 NPD
2 pA f.s.

- Nicotine

Figure 20.

TID-2 Ion Source
(Black Ceramic)
1500 hours prior use in 6890 NPD
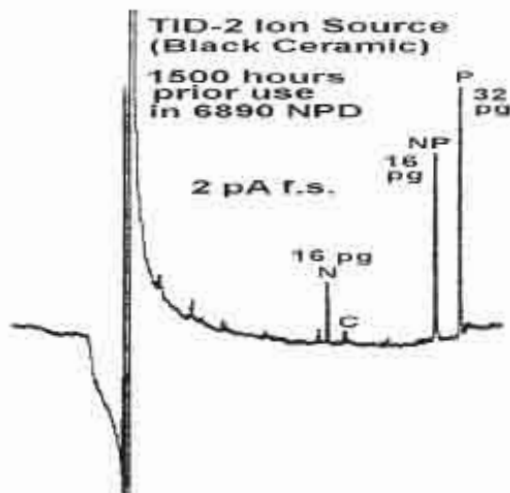
P 32 pg

NP 16 pg

2 pA f.s.

16 pg N

C

Figure 21. N = azobenzene, C = n–heptadecane (32 ng), NP = methyl parathion, P = malathion.