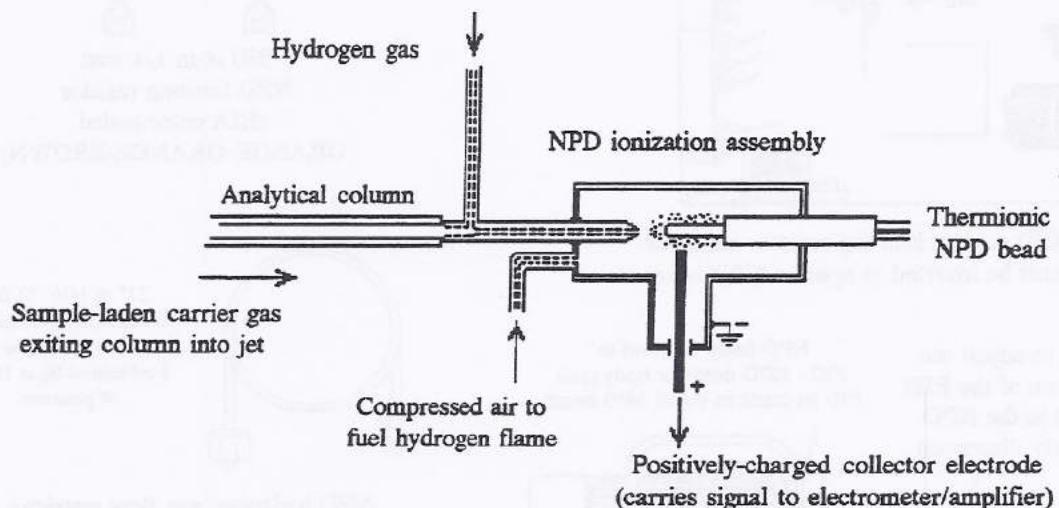
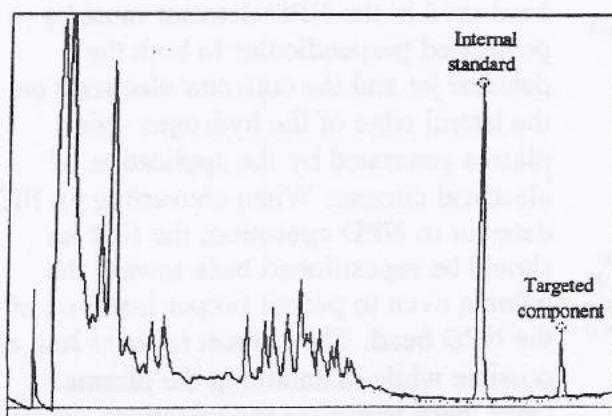


The Nitrogen / Phosphorus Detector, or NPD, as it is commonly referred to, is specified for the analysis of organic compounds containing nitrogen and/or phosphorus. The NPD detector is ideal for the analysis of pesticides and herbicides such as Parathion®, which contains nitrogen, phosphorus and sulfur. Minimum detectable quantities are in the 10 picogram range for this compound.

In principle, when organic compounds containing either nitrogen or phosphorus are introduced into a hydrogen plasma induced around a salt, charged particles or ions are generated, either by thermal ionization or oxidation. In the case of the NPD detector, ionization occurs as each sample component is eluted into the hydrogen plasma glowing around the NPD bead which is located directly at the exit of the analytical column. Ions freed in the plasma are then collected by a positively-charged collector electrode immediately adjacent to the gas plasma, and the electrical current produced by the passing of each component is carried to the electrometer/amplifier for processing and routing to the data system. The SRI NPD design exhibits extremely linear response.



BASIC NITROGEN/PHOSPHORUS DETECTOR DIAGRAM

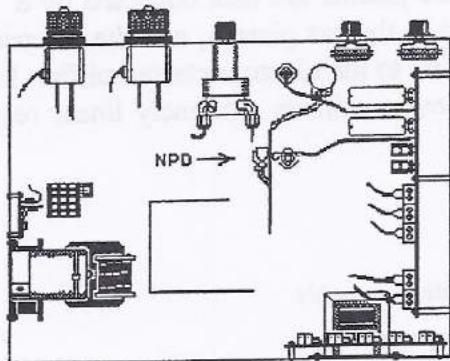


5 ppm concentration of target component in nitrogen

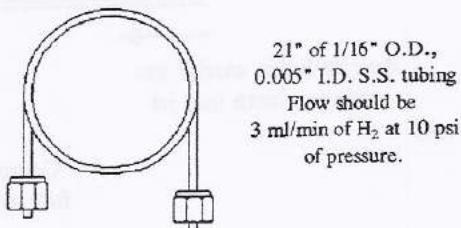
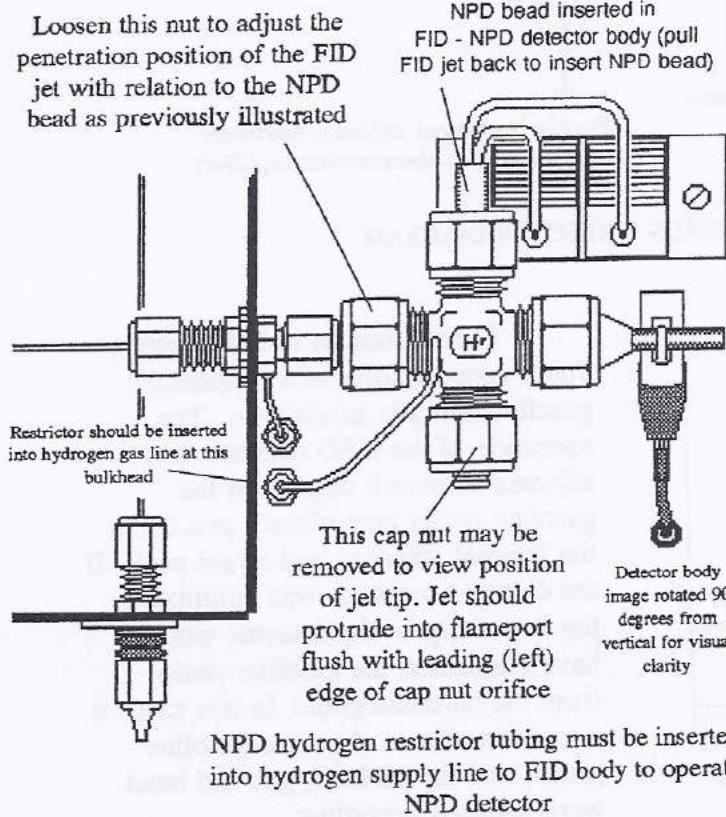
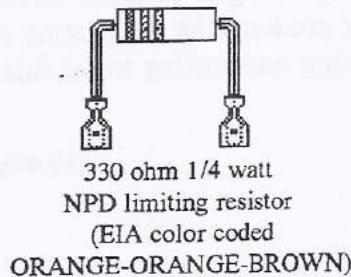
The illustration at left shows a 5ppm concentration of a proprietary gasoline additive in nitrogen. The operation of the NPD detector was adjusted to permit display of the gasoline peaks immediately preceding the internal standard and target peak. If the detector response was optimized, the selectivity of the detector would have eliminated the gasoline peaks from the chromatogram. In this case, it was desireable to show the gasoline peaks, and the NPD H<sub>2</sub> gas and bead were adjusted according.

The majority of gas chromatographs manufactured by SRI Instruments that offer the Nitrogen-Phosphorus Detector option are equipped with a flame ionization detector as standard equipment. The Nitrogen-Phosphorus Detector is configured for use by a conversion (hardware modification) to the FID system in the field. The modification of the FID detector is minimal and may be performed in a matter of minutes. Reversion back to the standard FID detector configuration may be performed as needed without any major interruption to the throughput of analyses through the chromatograph.

In some specific cases, the gas chromatograph is equipped with a permanent configuration of the nitrogen-phosphorus detector (NPD). On such models, the hardware modifications indicated on this page are not applicable, as the detector is already configured and not convertible.

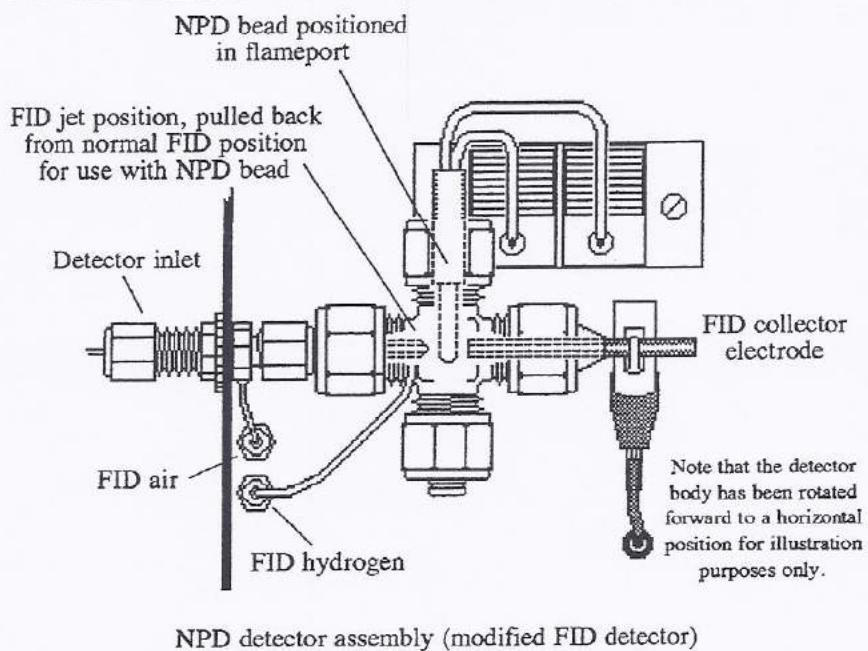


Location of NPD current limiting resistor inside of GC chassis (must be inserted to operate NPD bead).



NPD hydrogen gas flow restrictor  
(for reducing hydrogen gas flow  
to proper level for NPD operation)

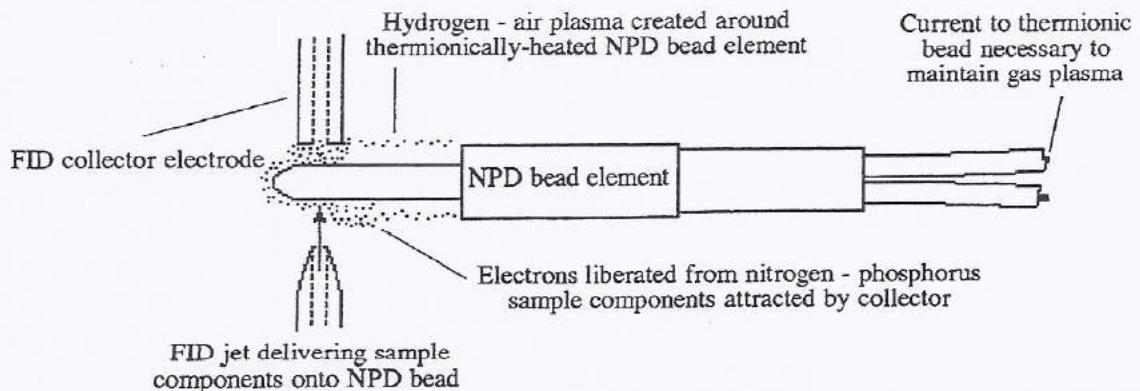
The thermionically-heated alkali bead used in the NPD detector must be positioned perpendicular to both the detector jet and the collector electrode on the lateral edge of the hydrogen - air plasma generated by the application of electrical current. When converting an FID detector to NPD operation, the FID jet should be repositioned back toward the column oven to permit proper insertion of the NPD bead. The current is set as low as possible while maintaining the plasma. Once these hardware modifications are in place as indicated, adjust the NPD detector as instructed on the previous page.



The SRI design FID detector converts quickly into a nitrogen - phosphorus detector by the simple replacement of the FID ignitor element with the electrically-heated thermionic NPD bead element. The hydrogen flow is then manually reduced to between 1 and 7 ml. per minute by the installation of a flow restrictor prior to the FID detector hydrogen bulkhead fitting (between 1 and 3 ml. per minute is optimum). With the heated NPD bead installed directly in the carrier gas flow exiting the FID jet orifice, the sample components are directed toward the area of the bead, where any molecule

containing a nitrogen or phosphorus group is prompted to release an electron in the hydrogen-air plasma generated by the bead. The liberated electron is attracted to the charged collector electrode and it creates a current that is delivered to the FID electrometer for processing. Note that the FID jet should be relocated (pulled away) from the NPD bead and collector electrode, as illustrated, for proper operation. Return the FID jet to its original position when returning to FID operation.

The nitrogen - phosphorus bead is extremely selective, providing 10,000 times higher response to nitrogen - phosphorus compounds than to hydrocarbons. When using the NPD detection method, nitrogen is the carrier gas of preference although helium carrier gas may be used. The bead must be operated with the minimum current required to maintain the hydrogen-air plasma. If more current than necessary is applied, the detector will show greater sensitivity, but the life and subsequent sensitivity of the NPD bead will be greatly reduced. The NPD should only be operated with the 330 ohm NPD current-limiting resistor in place in the circuit. AT NO TIME should the NPD voltage be operated above 4.4 volts. Nitrogen - phosphorus compounds increase the current in the plasma as they collide with the surface of the thermionic heated alkali metal bead.

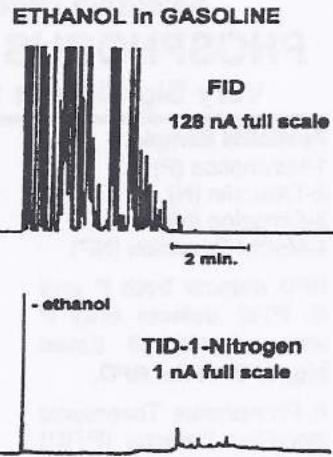


In order to operate the NPD detector, verify that the hydrogen flow rate is in the vicinity of 3 ml per minute by using a bubble flow meter capable of accurate measurement in that range. The hydrogen flow rate is normally maintained at 20 to 25 ml per minute. The air flow must be adjusted to approximately 80 ml per minute. This is much lower than the 250 - 300 ml per minute flow rate that is typically used for flame ionization detector operation.

## Oxygenate Selective Detection for GC ETHANOL in GASOLINE

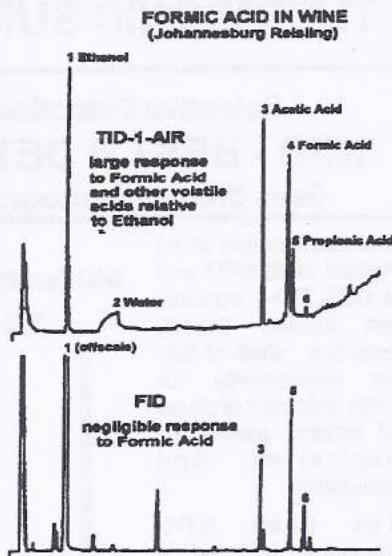
Negative Ionization on a ceramic TID-1 surface detects Oxygenates with good selectivity vs. Hydrocarbons.

TID - 1 detection provides a simple analysis for the Ethanol additive in gasoline. Only a single gas supply (Nitrogen) suffices for both GC carrier and detector gases. Short analysis times can be used because Ethanol is easily detected amidst many overlapping Hydrocarbon components. TID-1 also detects Phenols, Glycols, and other Oxygenated compounds.



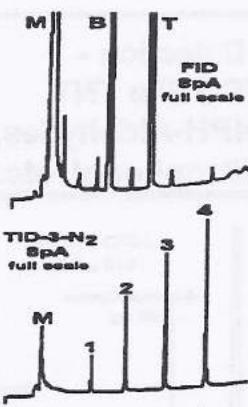
## Oxygenate Selective Detection for GC CARBOXYLIC ACIDS

TID-1 surface ionization with an Air detector gas gives big signals for Carboxylic Acids relative to other Oxygenates like Alcohols. TID-1 detection includes Formic Acid which is not detected by an FID. TID-1 detection is also non-destructive so component aromas can be sensed at the detector exit.  $H_2O$  is also detectable to ppm levels



## Selective Detection for GC TRIHALOMETHANES

TID-3 surface catalyzed negative ionization process



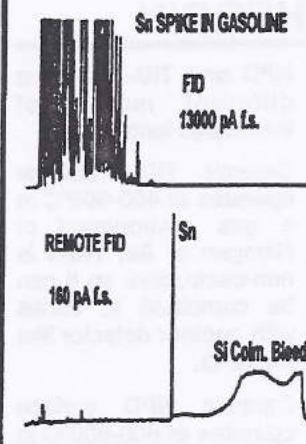
Volatile HALOGENATES detected with a sensitivity of 1 pg/sec, selectivity of 100,000:1 vs. hydrocarbons, and linear response exceeding a range of 10,000 in sample weight.

Unlike other halogen detectors, TID-3 response to Br is significantly more than Cl. Detector gas may be Nitrogen or Air with no requirement for ultra high purity. This detector is much easier and less costly to operate and maintain than an Electrolytic Conductivity Detector.

### Sample analyzed:

640 pg each: 1= $CHCl_3$ , 2= $CHCl_2Br$  3= $CHClBr_2$ , 4= $CHBr_3$   
47,000 pg each: B=benzene T=toluene  
2,500,000 pg: M=methanol Solvent: water

## Pb – Sn – P – Si (Lead, Tin, Phosphorus, Silicon) selective detection with a DET innovation Organically-Fueled Remote FID



A polarizer and ion collector located several centimeters downstream of a flame jet detect long-lived ion species that originate in a flame fueled by  $H_2$  -  $CH_4$  - Air. Ionization from Hydrocarbon combustion at the jet dissipates before reaching the downstream collector.

Detectivity of 1 pg/sec for Pb, Sn, P with a selectivity of 500,000:1 versus Carbon.

Sample:  
12 ppm tetrabutyltin in gasoline

# DETector Engineering & Technology, Inc.

486 North Wiget Lane, Walnut Creek, CA 94598 USA

ph: 925-937-4203, fx: 925-937-7581, [www.det-gc.com](http://www.det-gc.com)

# CHEMICAL DETECTION by DET

featuring novel applications of the principles of  
THERMIONIC SURFACE IONIZATION and FLAME IONIZATION

## Selective Detection for GC NPD - BEST N DETECTIVITY (less than 70 femtograms N/sec)

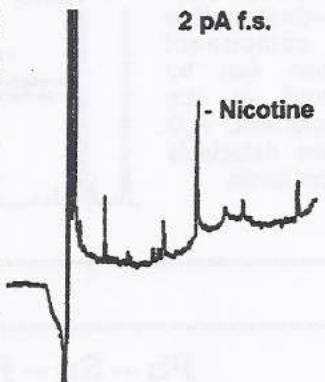
The combination of an Agilent 6890 NPD and a DET TID-4 ceramic ion source (bead) provides state-of-the-art N-selectivity for trace detection of drugs of abuse, pesticides, explosives, and pollutants.

The 6890 NPD hardware features a concentric cylinder ion source - collector electrode geometry for stream-lined gas flow and efficient ion collection. Similar DET equipment is available for HP5890, Varian 3400-3800, and SRI 8610 GC models.

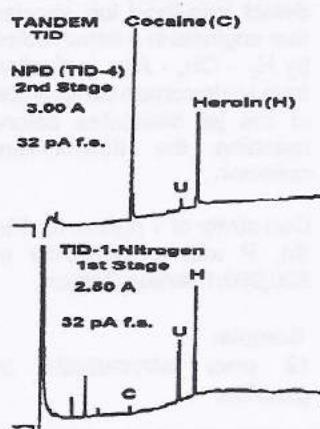
600 femtograms Nicotine  
TID-4 in 6890 NPD

2 pA f.s.

- Nicotine



## Tandem Thermionic Detection for GC COCAINE - HEROIN



NPD and TID-1 are two different modes of thermionic ionization.

Ceramic TID-1 surface operates at 400-600°C in a gas environment of Nitrogen or Air. TID-1 is non-destructive so it can be combined in series with another detector like the NPD.

Ceramic NPD surface operates at 600-800°C in an ignited, dilute mix of Hydrogen in Air.

Sample analyzed: NPD detects both Cocaine (C) and Heroin (H). TID-1 detects Heroin and Heroin impurity (U). Tandem combination gives simultaneous TID-1 and NPD signals for each sample injection.

## Selective Detection for GC PHOSPHORUS COMPOUNDS Very Big Signals with a New PTID

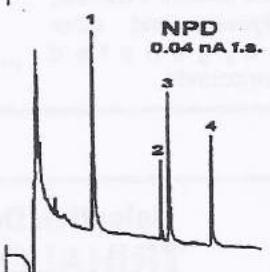
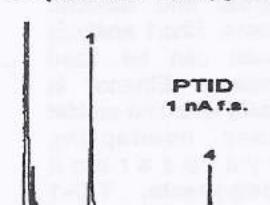
### Pesticide Sample:

- 1-Mevinphos (P)
- 2-Trifluralin (N)
- 3-Simazine (N)
- 4-Methyl Parathion (NP)

NPD detects both P and N. PTID detects only P with signals 10 times bigger than the NPD.

A Phosphorus Thermionic Ionization Detector (PTID) combines surface ionization principles with high flows of Hydrogen and Air for P/C selectivity of 100,000:1, P/N selectivity of 100:1, detectivity of 70 fg P/sec, and a dynamic response range more than 100,000.

NP pesticides 480 pg each

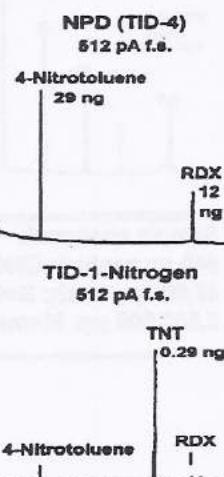


## - Femtogram GC Detection - NITRO-COMPOUNDS like TNT, 2,4-Dinitrotoluene, DNPH-Aldehydes, Methyl Parathion, 4-Nitrophenol, etc.

Unique TID-1 surface ionization provides better selectivity than ECD and NPD, and needs only Air or N<sub>2</sub> as the detector gas with no requirement for high purity.

TID-1 detection is an inexpensive modification of Agilent 6890 NPD equipment. DET NPD/TID-1 equipment is also available to fit HP 5890, Varian 3400-3800, and SRI 8610 GC models.

**EXPLOSIVES Sample:** NPD has a big response to RDX and 4-Nitrotoluene. TID-1 has a much larger response to TNT.



**DETector Engineering & Technology, inc.**

Invited Paper

# Recent Advances in Thermionic Ionization Detection for Gas Chromatography

P.L. Patterson

Detector Engineering & Technology, Inc., 2212 Brampton Road, Walnut Creek, California 94598

## Abstract

Thermionic ionization detectors are most widely used for the specific detection of nitrogen-phosphorus compounds in gas chromatography. The operating mechanism of these detectors is a surface ionization process in which the key parameters are the work function of the thermionic emission surface, the temperature of the thermionic surface, and the composition of the gas environment in the immediate vicinity of the thermionic surface. By systematic variations of each of these three key parameters, the technique of thermionic ionization detection has been greatly expanded to encompass a number of different modes of response, all of which use similar detector hardware and electronic components.

process was operative, it was possible to identify three key operating parameters which control the ionization produced. These parameters are: the electronic work function of the thermionic emission surface which is determined by the chemical composition of the surface; the temperature of the thermionic surface; and the chemical composition of the gas environment immediately surrounding the thermionic surface.

The identification of these parameters has led to a clearer understanding of the complex chemistry active in NP detection, and has provided an important guide for expanding the applications of thermionic ionization techniques. Through systematic variations in each of the key parameters, many different modes of detector response have been achieved (3-6). Hence, the technique of thermionic ionization detection now correctly refers to a number of GC detector responses which are related through the use of many common hardware and electronic components. This article reviews the present state of development of the members of this unique group of detectors.

## Introduction

Thermionic ionization detectors (TID) are best known in gas chromatography (GC) for their application to the specific detection of nitrogen (N) or phosphorus (P) compounds. All modern TIDs are essentially derivations of a basic design first described by Kolb and Bischoff (1) in 1974. The main component in this type of detector is an electrically-heated thermionic emission source in the form of a bead or cylinder which is usually composed of an alkali-metal compound impregnating a glass or ceramic matrix. In the TID, the thermionic source is positioned so that sample compounds may impinge upon its surface, and any ionization produced is measured by an adjacent collector electrode. Kolb and Bischoff were the first to report that a thermionic source comprised of a Rb-silicate glass bead produced very specific NP responses when the bead was operated at high temperatures in a gas environment of dilute H<sub>2</sub> in air.

Since the original work of Kolb and Bischoff, there have been continuing developments in NP detectors, with much emphasis on improved methods of construction and composition of the thermionic emission sources. The most important development, however, has been the recognition in recent years that the operation mechanism of a TID is a surface ionization process (2) rather than the gas phase ionization process originally proposed by Kolb et al. (1,3). Once it was clear that a surface ionization

## Types of Thermionic Emission Sources

All commercially available TIDs use thermionic emission sources formed according to one of the following four general methods:

- (A) homogeneous alkali-glass bead formed on a loop of bare platinum wire (1);
- (B) alkali salt activator coated on a ceramic cylinder core containing an embedded heater coil (7);
- (C) homogeneous alkali-ceramic bead formed on a coil of nichrome heater wire (2,8,9);
- (D) multiple layers of cylindrically-shaped ceramic coatings, with a non-corrosive, electrically-conducting sub-layer of Ni-ceramic completely covering a loop of nichrome wire, and a surface layer comprised of alkali and/or other additives in a ceramic matrix (5,10).

Thermionic sources representing all four categories cited above have been used in NP detectors available from different manufacturers. Generally, those sources formed from ceramic materials provide greater flexibility for varying the chemical composition of the source. This is because the ceramic compositions are formulated and coated from a slurry at room temperature (9), whereas the glass compositions are formed in

a process that proceeds through a molten glass state (11).

The detailed chemical compositions of thermionic emission sources are usually regarded as confidential proprietary information by the manufacturer. Since the first alkali-glass bead reported by Kolb and Bischoff used Rb as the alkali compound, there existed for many years a belief that Rb was an essential component for optimum NP responses. However, in recent years, NP detectors with state-of-the-art performance specifications have been reported in which Cs rather than Rb is used as the alkali component (5). Also, another recent report (12) has described an NP detector which uses a LaB<sub>6</sub>/SiO<sub>2</sub> bead and no alkali additive. In accordance with a mechanism of surface ionization prevailing in the TID, the most important characteristic of the thermionic emission surface is its electronic work function (i.e., the amount of energy required to emit a unit of electrical charge from the surface). Alkali-metal compounds have been especially successful additives because they lower the work function of the glass or ceramic matrix, thereby facilitating the emission of charged particles from the heated thermionic surface. The mathematical relationships between work function, surface temperature, and thermionic emission current have been discussed (2,12).

The development of multiple-layered, ceramic-coated thermionic emission sources has allowed examination of coatings of many different chemical compositions without the risk of materials in the surface layer corroding the heater wire. In the search for expanded applications for thermionic ionization techniques, the basic task is to define a specific match of a thermionic source type with an operating gas environment and a range of operating source temperatures. To date, three different chemical compositions of thermionic sources have been shown (5,6) to have useful applications in differing modes of thermionic detection. These source compositions are shown in Table I. Data obtained using these three types of thermionic emission sources are presented in the following sections.

### Modes of Response

Schematic illustrations of four different versions of thermionic ionization detection equipment are shown in Figures 1 through 4. Common components in each version are as follows: (A) an electrically-heated, thermionic/catalytic source constructed of multiple layers of ceramic coatings; (B) a cylindrical collector electrode surrounding the cylindrically shaped thermionic source; (C) a source power supply that provides heating current to heat the source to typical temperatures of 400° to 800°C, and a bias voltage to polarize the source structure at a negative voltage with respect to the collector;

**Table I. Thermionic Source Surface Layers**

Source type*	Additive	Work function
TID-1	High concentration Cs	Low
TID-2	Low concentration Cs/Sr	Medium
CFID	Nickel	High

\*Nomenclature adopted from Patterson (5).

(D) an electrometer that measures negative ionization currents arriving at the collector electrode.

The TID hardware usually mounts onto an FID-type detector base that is resident on a GC, so that two different detector gases may be supplied in addition to the GC effluent. Therefore, changes in the modes of detector response that correspond to the schematics of Figures 1 through 4 are accomplished by changes in the type of thermionic source, changes in the composition of gases supplied to the detector, or by changes in the operating temperature of the thermionic surface.

Most of the TIDs available commercially function by the collection of negative ionization rather than positive ionization. In the discussion that follows, it will be shown that the concepts of negative ion chemistry provide a logical pattern for correlating the responses of the different modes of thermionic detection.

### TID-1-N<sub>2</sub>: Nitro/electronegative specific response

The simplest mode of thermionic detection is represented by the schematic in Figure 1. In this mode, the low work function thermionic source designated by the TID-1 nomenclature is operated in a detector gas environment of N<sub>2</sub>. Because the detector gases are inert, sample compounds interact directly with the TID-1 surface, which is typically heated to temperatures in the range of 400° to 600°C. The ionization process in this case is direct transfer of negative charge from the TID-1 surface to

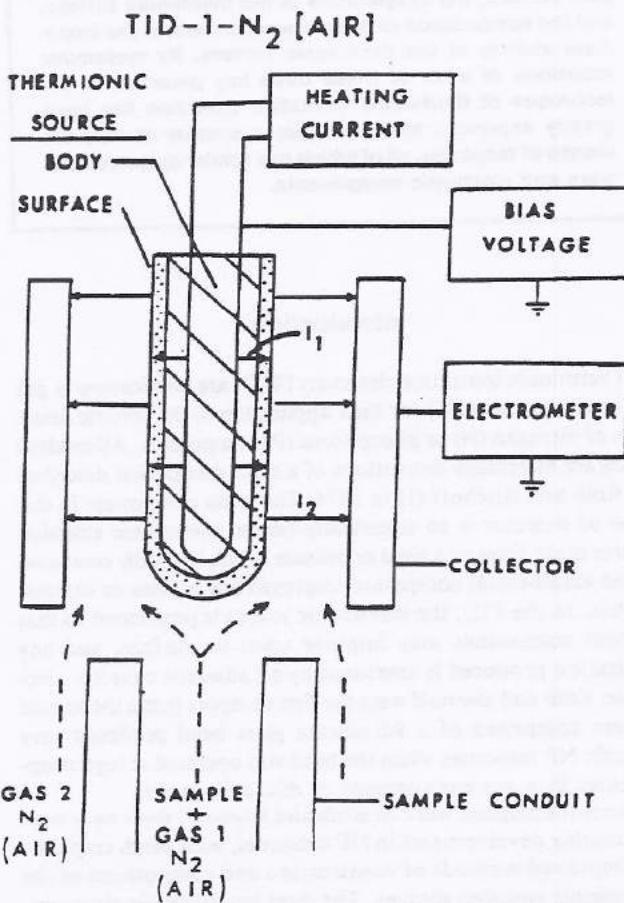


Figure 1. Schematic illustration of the detection configuration for the thermionic ionization modes TID-1-N<sub>2</sub> and TID-1-air. Detector gas 1=FID-H<sub>2</sub> inlet line; detector gas 2=FID-air inlet line.

the sample molecule. Consequently, this mode of response provides exceptionally high specificity and sensitivity to many compounds containing the nitro ( $\text{NO}_2$ ) functional group (5,13), as well as to certain other electronegative compounds (e.g., pentachlorophenol, diazepam, and methaqualone). This mode of detection is very sensitive to the detailed electronegativity of the sample's molecular structure, as has been illustrated by the observation that a larger signal is obtained for the 2,4-isomer of dinitrotoluene in comparison to the 2,6-isomer (5). The TID-1-N<sub>2</sub> mode is superior to a conventional NP detector or an electron capture detector (ECD) for detection of trace level nitro-compounds such as nitro-PAH, nitro-explosives, nitro-pesticides (e.g., parathion, methyl parathion), nitro-drugs, nitro-derivatives. For many nitro-compounds, the specificity vs. hydrocarbons is an astonishing  $10^6$ , and detectivity is in the 0.1- to 1.0-pg range (5).

#### TID-1-air: Halogen/nitro specific response

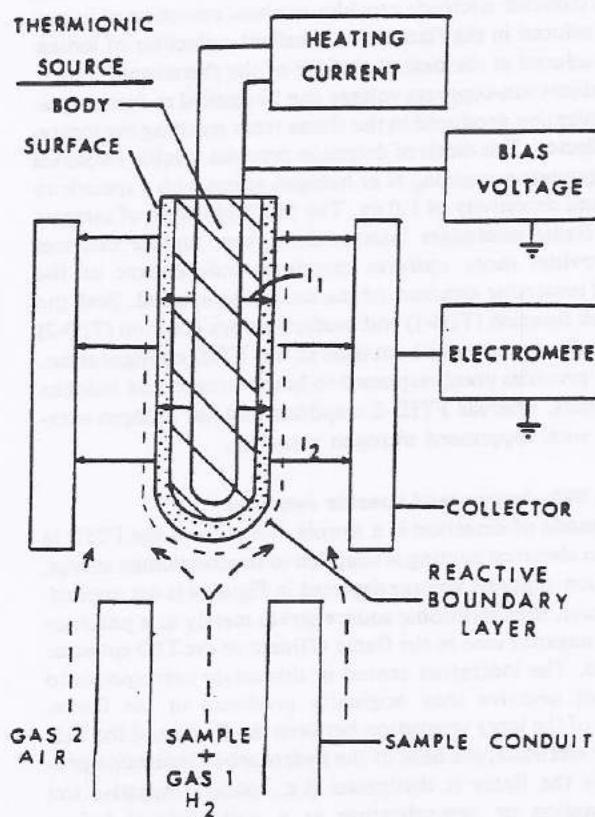
When the TID-1 thermionic source is operated in an oxygen-containing gas environment rather than one of N<sub>2</sub>, specific responses to halogenated compounds are enhanced while responses to nitro-compounds are decreased somewhat (14). The TID-1-air mode of detection is generally not as sensitive as an ECD or Hall detector for chlorinated compounds, but it provides halogen specificity at higher concentrations where ECD and Hall are saturated. Typical specificity is  $10^4$  and detectivity

is 0.1 to 1.0 ng. This is an especially simple mode of detection for ethylene dibromide (EDB) in the headspace vapors of food products.

#### TID-2-H<sub>2</sub>/air: Nitrogen/phosphorus specific response

The schematic illustration of Figure 2 represents the situation that prevails in an NP detection mode. For this mode, H<sub>2</sub> and air gases are supplied to the detector, and a thermionic source of moderate work function (i.e., TID-2) is operated hot enough (600° to 800°C) to cause thermal/chemical decomposition of the H<sub>2</sub> and O<sub>2</sub> gases. A critical parameter in this NP mode is the restriction of the H<sub>2</sub> to low flows (e.g., 3 to 6 ml/min) which are not sufficient to maintain a self-sustaining flame at the sample conduit (i.e., jet structure) depicted in Figure 2. Instead, a flame-like gaseous boundary layer is created in the immediate vicinity of the hot thermionic source. Since this boundary layer is very reactive chemically, sample compounds are decomposed by the active gas phase chemistry, and electronegative products of decomposition are selectively ionized by surface ionization on the thermionic source. N or P compounds are ionized with especially high specificity by this process. An essential condition for the onset of NP detection is that the thermionic source must be hot enough to "ignite" the boundary layer chemistry. Under these conditions, a thermionic source of moderate work function provides the optimum compromise of sample response signal vs. detector background signal. A low work function therm-

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



#### CFID

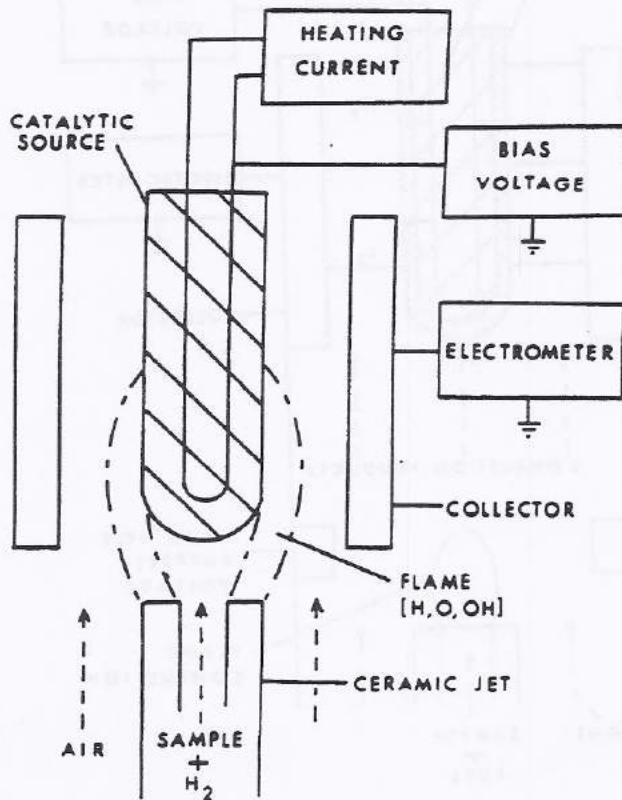


Figure 2. Schematic illustration of the detection configuration for the TID-2-H<sub>2</sub>/air or NP mode of thermionic ionization.

Figure 3. Schematic illustration of the detection configuration for the catalytic flame ionization detector (CFID) mode of response.

ionic source (e.g., TID-1) operated under these conditions would produce an overwhelmingly large background signal. Conversely, a high work function thermionic source (e.g., catalytic flame ionization detection) operated under these conditions would produce smaller NP signals and less specificity than the moderate work function thermionic source. Typical performance specifications for NP detectors are detectivities in the range of 1 to 10 pg, and specificity with respect to hydrocarbons in the range of  $10^4$  to  $10^5$ .

#### CFID: Universal response to all organics

Figure 3 depicts a mode of response achieved when the H<sub>2</sub> flow to the detector is sufficient to produce a true self-sustaining flame burning at the jet structure. This mode of operation has been designated (5) catalytic flame ionization detection (CFID) because of its close similarity to a conventional FID. The CFID is essentially an FID which has been modified by inserting an electrically-heated catalytic source comprised of a Ni-impregnated ceramic into the center of the active flame region. In this detection mode, the catalytic source structure serves the three-fold function of flame ignitor, flame polarizer, and catalytic combustion modifier/thermionic surface ionizer. In the CFID, two types of ionization processes are active: gas phase ioniza-

tion processes identical to those which occur in a conventional FID, and surface ionization processes at the catalytic source structure which especially enhance the ionization efficiency of many heteroatom compounds (especially halogenated and phosphorus compounds).

Like a conventional FID, the magnitude of the gas phase ionization is determined primarily by the magnitudes of H<sub>2</sub> and air flows and the size of the jet orifice, so that additional electrical heating of the CFID source has little effect on the gas phase ionization. However, the magnitudes of ionization produced by surface processes at the CFID source is strongly dependent on the electrical heating of the source. Hence, in many cases, response factors for heteroatom compounds can be enhanced to be comparable to hydrocarbons by a judicious selection of source heating current. For this CFID mode of detection, the thermionic/catalytic source of highest work function is most suitable because the flame heat would otherwise cause an excessive thermionic emission background signal. The CFID provides detectivities in the 10- to 100-pg range for most organic compounds.

#### FTID: Nitrogen/halogen specific response

Figure 4 depicts a further detection mode in which the thermionic source and collector electrode structure are positioned well downstream of the active region of a self-sustaining flame. The basic concept (6) of this flame thermionic ionization detection (FTID) mode is to burn sample compounds in a self-sustaining H<sub>2</sub>/air flame at a flame jet, and to selectively re-ionize electronegative combustion products by means of the thermionic ionization components located downstream. In the FTID, a large physical separation between the flame and the thermionic source/collector electrode provides minimal collection of ionization produced in the flame, but excellent collection of ionization produced at the heated surface of the thermionic source. An auxiliary ion-suppress voltage can be applied to further prevent ionization produced in the flame from reaching the ionization collector. This mode of detection provides specific responses to compounds containing N or halogen atoms with a specificity of  $10^3$  and detectivity of 1.0 ng. The precombustion of samples in the flame minimizes interferences from sample matrices and provides more uniform responses independent of the original molecular structure of the sample compound. Both the low work function (TID-1) and moderate work function (TID-2) thermionic sources have been used in this FTID configuration. FTID-1 provides good responses to both nitrogen and halogen compounds, whereas FTID-2 responds best for halogen compounds with suppressed nitrogen response.

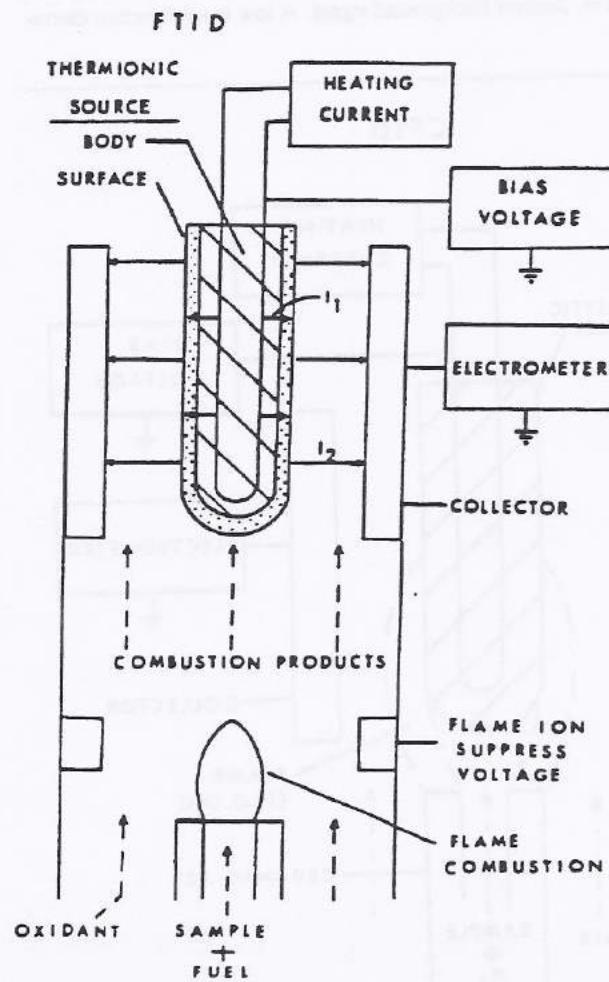


Figure 4. Schematic illustration of the detection configuration for the flame thermionic ionization detector (FTID) mode of response.

#### Remote FID: Organo-lead specific response

This mode of detection is a simple variation of the FTID in which no electrical heating is supplied to the thermionic source, and the ion-suppress voltage depicted in Figure 4 is not applied. In this case, the thermionic source serves merely as a polarizer to drive negative ions in the flame effluent to the TID collector electrode. The ionization sensed in this mode corresponds to long-lived negative ions originally produced in the flame. Because of the large separation between the flame and the TID collector electrode, the bulk of the hydrocarbon ionization produced by the flame is dissipated (i.e., positive-negative ion recombination or neutralization at a wall surface) before reaching the TID collector. However, certain heteroatom compounds appear to combust to negative ion products which are especially stable and long-lived. The outstanding demonstration

of this effect is the specific detection of lead compounds in gasoline. Since the thermionic source is not electrically-heated and is not used as a source of surface ionization, any type of thermionic source may be employed in this mode.

## Experimental

The applications data presented in this report were obtained with equipment previously described (5,6,14). All the data were obtained using a Model 3740 gas chromatograph (Varian Associates) equipped with either a TID/CFID detector assembly (TID-1-N<sub>2</sub>, TID-1-air, TID-2-H<sub>2</sub>/air, and CFID modes) or an FTID/TID detector assembly (FTID and remote FID modes) (Detector Engineering and Technology). The TID-1, TID-2, and CFID thermionic emission sources were also manufactured by Detector Engineering and Technology, as was the Model 4000 detector current supply. Negative ionization signals from the detector were measured using the differential electrometer (Varian) in a negative polarity configuration.

The detector assemblies mounted onto the FID-base on the GC, so that different detector gas environments were implemented by plumbing in the appropriate gas through the two gas lines that normally supply H<sub>2</sub> and air to an FID. Typical gas flows supplied for different modes of detection are detailed in Table II.

All the data presented in this report were obtained using glass columns, 6 ft × ¼ in. × 2 mm i.d., packed with either 3% SP-2250, 3% SP-2100, or 1% SP-1240 DA on 100/120 Supelport (Supelco) or 80/100 Chromosorb 102. The GC carrier gas in all cases was N<sub>2</sub> at a flow rate of 30 ml/min. For complex samples like gasoline, the chromatographic separation was intentionally very poor in order to produce a challenging detector environment to demonstrate specificity of response in the simultaneous presence of many overlapping compounds.

Sample mixtures that were analyzed included a TSD test sample (ng levels of azobenzene, methyl parathion, and malathion) (Varian); Base-Neutral 1 sample (Supelco); phenol mix (Supelco); DCMA PCB mixture (Supelco); and nitroaromatic mixture (Supelco) diluted in reagent-grade benzene. Gasoline, cologne, and diesel fuel samples were analyzed by direct injection of 0.5 to 1.0 µl amounts onto the column. Other samples chromatographed were a 1% v/v each mixture of acetone and carbon tetrachloride in water; and an 11% v/v each mixture of methylene chloride, n-C<sub>10</sub>, benzene, i-C<sub>8</sub>, toluene, n-C<sub>12</sub>, p-Xylene, n-C<sub>10</sub>, and n-C<sub>12</sub>.

**Table II. Typical Gas Flows Supplied for Each Mode of Detection**

Mode	Gas 1	Gas 2
TID-1-N <sub>2</sub>	10 ml/min N <sub>2</sub>	60 ml/min N <sub>2</sub>
TID-1-air	10 ml/min air	60 ml/min air
TID-2-H <sub>2</sub> /air	3 ml/min H <sub>2</sub>	60 ml/min air
CFID	25 ml/min H <sub>2</sub>	200 ml/min air
FTID	20 ml/min H <sub>2</sub>	200 ml/min air
Remote FID	20 ml/min H <sub>2</sub>	200 ml/min air

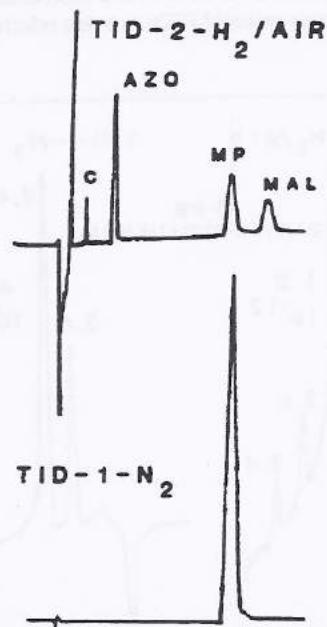
## Applications\*

Specially formulated test samples are often employed to demonstrate the specificity and sensitivity of NP detectors. The data in Figure 5 correspond to such a test sample comprised of 2.2 ng each of azobenzene (N) and methyl parathion (N,P), 4.4 ng of malathion (P), and 4400 ng of n-C<sub>10</sub>, in a solvent of iso-octane. The data illustrate clearly the substantial differences in response between two different modes of thermionic detection, and the very high specificity of the TID-1-N<sub>2</sub> mode for sensing the NO<sub>2</sub> group in methyl parathion. The ionization signals in both chromatograms are very large, indicating detectivities in the pg and sub-pg range.

Figure 6 shows another comparison of the TID-1-N<sub>2</sub> mode vs. the NP mode of detection for a sample consisting of 15 pg amounts of the 2,4- and 2,6-isomers of dinitrotoluene in a relatively impure, reagent grade benzene solvent. For many nitro-compounds, the TID-1-N<sub>2</sub> mode provides substantial improvements in specificity and sensitivity in comparison to an NP mode. However, the NP mode (i.e., TID-2-H<sub>2</sub>/air) provides more universal detection for all N-compounds. In Figure 6, the differing magnitudes of TID-1-N<sub>2</sub> signals for the two dinitrotoluene isomers also demonstrate that the TID-1-N<sub>2</sub> signals are very sensitive to the detailed electronegative character of the sample's molecular structure.

Figure 7 shows the differing responses of six modes of thermionic detection in the analysis of base neutral compounds of concern as water pollutants. The CFID provides universal response to all compounds in this sample with a relatively uniform sensitivity of 0.01 coul/gC. The TID-1-N<sub>2</sub> mode of opera-

\*Data presented are from References 6 and 14.



**Figure 5.** Chromatograms showing two modes of response to a test sample containing a large concentration of a hydrocarbon (C) and trace levels of azobenzene (AZO), methyl parathion (MP), and malathion (MAL). Both chromatograms were recorded at the same sensitivity of  $128 \times 10^{-11}$  amps/mV. Column: SP-2250, isothermal at 210°C.

tion provides very specific responses only to a nitro-compound (2,6-dinitrotoluene) and a chlorinated compound (3,3'-dichlorobenzidine). The lack of significant TID-1-N<sub>2</sub> response to nitrobenzene, bis(2-chloroethyl)ether, bis(2-chloroisopropyl)ether, or 4-bromophenyl-phenyl-ether demonstrates that the TID-1-N<sub>2</sub> response depends on how the electronegative functionalities are bound up in the molecular structure of the sample compound. When the detector gas environment of the TID-1 source is changed from N<sub>2</sub> to O<sub>2</sub>, the TID-1-O<sub>2</sub> mode provides enhanced relative responses to the chlorinated compounds and a diminished relative response to the nitro-compound. The TID-1-O<sub>2</sub> mode continues to provide good discrimination in favor of chlorinated compounds with respect to hydrocarbons, while exhibiting some low level responses to phthalate compounds. The TID-2-H<sub>2</sub>/air mode responds to all the N-compounds, with some small interferences from chlorinated compounds. The FTID-1 mode uses a TID-1 source and provides responses to all the nitrogen and halogen compounds in the sample. The FTID-2 mode uses a TID-2 source which produces responses to the halogenated compounds but suppressed responses to nitrogen compounds in comparison to FTID-1. This set of six chromatograms provides a good illustration of how the detector response can be varied through simple changes in the composition of the detector gas environment.

Figure 8 shows chromatograms of a sample mixture consisting of 75 ng each of 2-chlorophenol, 2-nitrophenol, phenol, 2,4-dimethylphenol, and 2,4 dichlorophenol; 225 ng each of 2,4,6-trichlorophenol, and 2,4-dinitrophenol; and 375 ng each of 4-chloro-*m*-cresol, 4,6-dinitro-*o*-cresol, pentachlorophenol, and 4-nitrophenol. The CFID provides a relatively uniform response of 0.004 coul/gC for all these compounds. (Note: The flame tip orifice for these CFID data was 0.062 in. instead of 0.031 in., which is normally used. The smaller orifice usually provides improved sensitivities of approximately 0.01 coul/gC.)

The CFID data provide a good illustration of a principal difference in the responses of a CFID vs. a conventional FID. It is well known that conventional FIDs provide relatively uniform

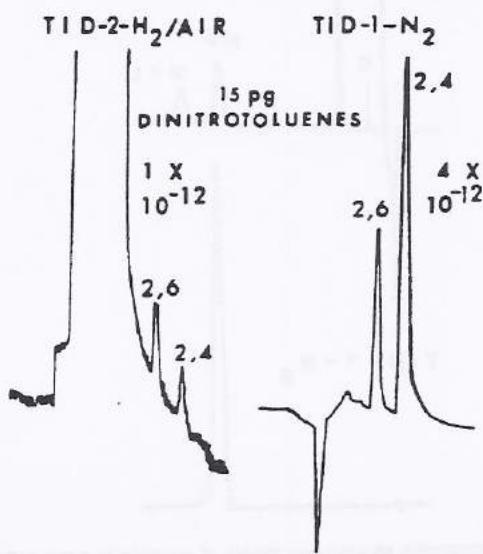


Figure 6. Chromatograms comparing the responses of the TID-1-N<sub>2</sub> mode and the TID-2-H<sub>2</sub>/air (NP) mode to traces of dinitrotoluenes. Column: SP-2100, 160° to 200°C at 10°/min.

response to many hydrocarbon compounds. However, when heteroatoms, such as O, Cl, or P, are present in the sample compounds, the FID response is frequently significantly lower than its response to hydrocarbons. In contrast, the CFID appears to yield more uniform response to all organic compounds ir-

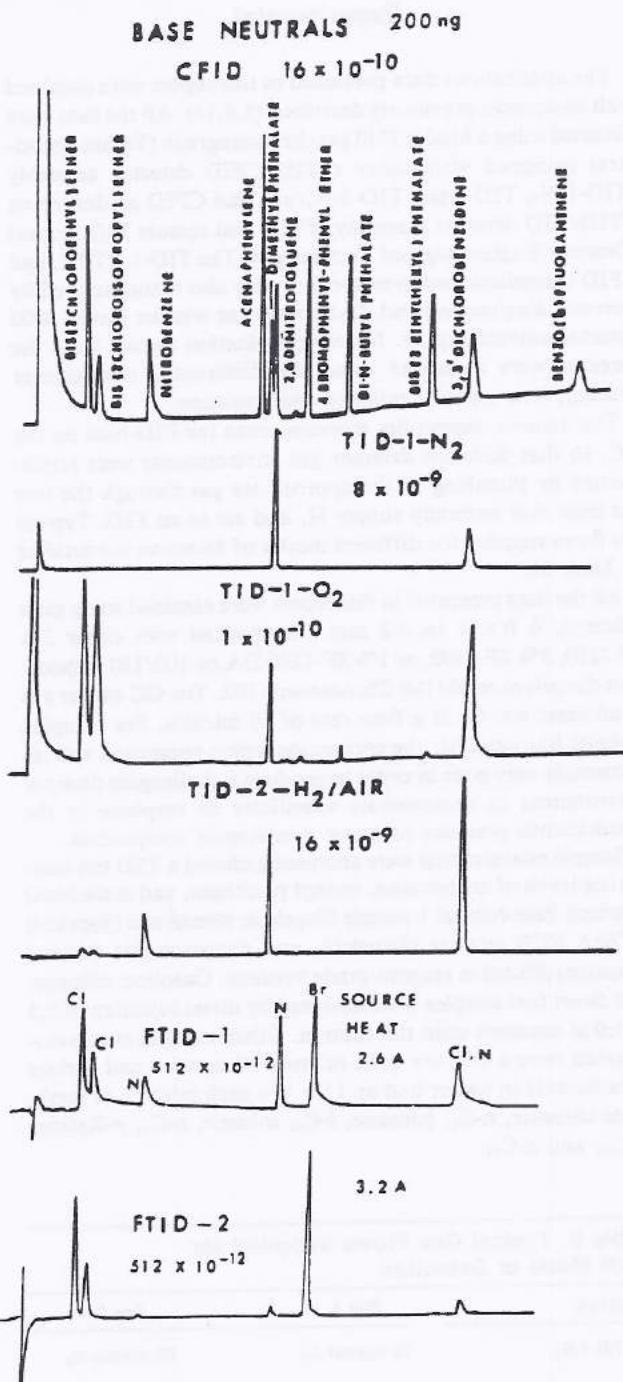


Figure 7. Chromatograms showing six different modes of detector response to a sample of base neutral compounds. In increasing order of retention time, the components of the sample are bis(2-chloroethyl)ether; bis(2-chloroisopropyl)ether; nitrobenzene; acenaphthylene; dimethylphthalate; 2,6-dinitrotoluene; 4-bromophenyl-phenyl ether; di-*n*-butylphthalate; bis(2-ethylhexyl)phthalate; 3,3'-dichlorobenzidine; and benzo(*b*)fluoranthene. Column: SP-2250; 100°C, held for 4 min, then 100° to 270°C at 16°/min.

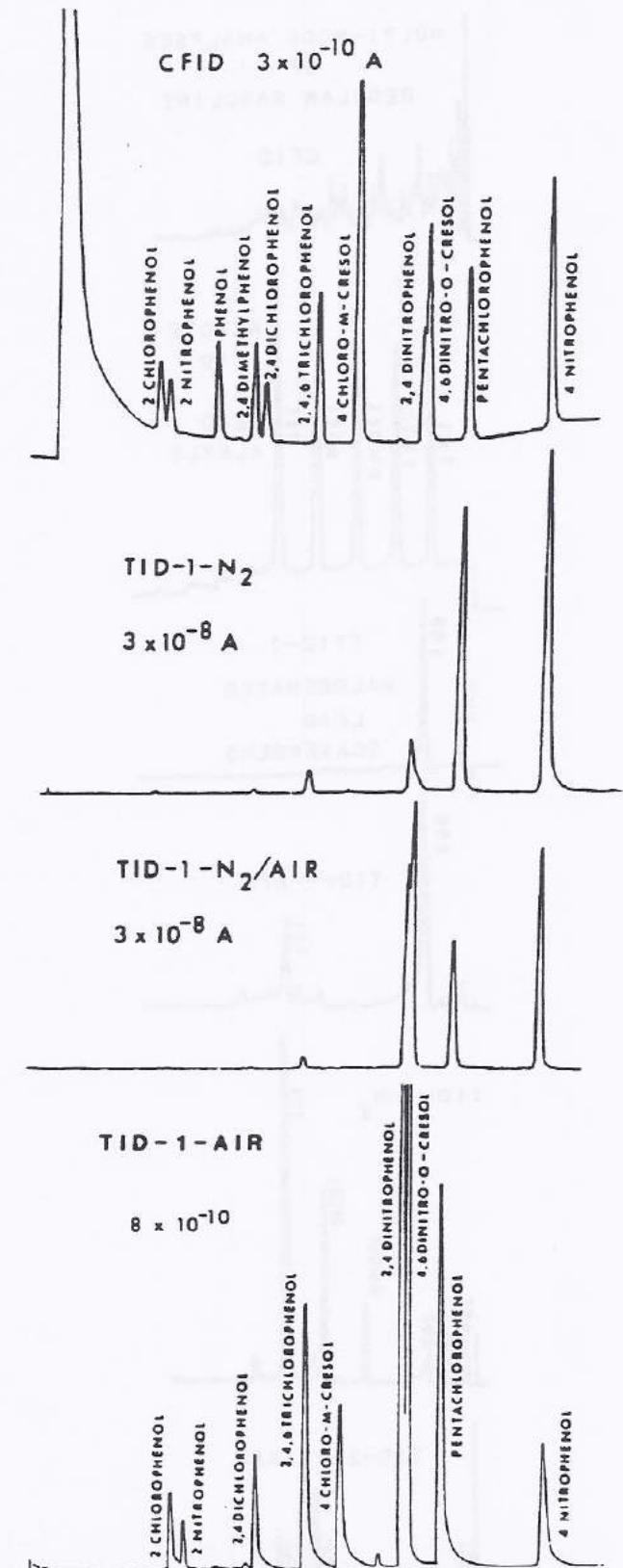


Figure 8. Chromatograms showing different modes of detector response to phenol sample containing 2-chlorophenol; 2-nitrophenol; phenol; 2,4-dimethylphenol; 2,4-dichlorophenol; 2,4,6-trichlorophenol; 4-chloro-*m*-cresol; 2,4-dinitrophenol; 4,6-dinitro-*o*-cresol; pentachlorophenol; and 4-nitrophenol in order of increasing retention time. Column: SP-1240, 100° to 210°C at 8%/min.

respective of whether they are hydrocarbon or heteroatom compounds. This is the result of the additional ionization process that occurs at the surface of the catalytic CFID source.

As anticipated, the TID-1- $N_2$  mode in Figure 8 provides high specificity and sensitivity to certain nitro- and polychlorinated-phenols. The responses to pentachlorophenol and 4-nitrophenol are more than 100 times larger than the CFID responses to these compounds. Comparing the responses of 4-nitrophenol and 2-nitrophenol again illustrates a significantly greater TID-1- $N_2$  response for the isomer with the nitro group located at the 4-position in the molecule.

In the third chromatogram in Figure 8, the low work function thermionic source (TID-1) was operated in a detector gas environment comprised of approximately equal flows of  $N_2$  and air. This illustrates that the composition of the gas environment is an additional parameter which can be used to suppress the response to certain compounds while enhancing the response to others.

The bottom chromatogram in Figure 8 shows the analysis of the phenol sample for the case where both detector gases 1 and 2 are air. Responses are now obtained for all the chlorinated and nitro-phenols, with the dinitro-compounds continuing to give the dominant responses. The responses to 2-nitrophenol and 4-nitrophenol are now comparable, in contrast to the TID-1- $N_2$  response in which there was significant preference for the nitro group in the 4-location vs. the 2-location.

Figure 9 demonstrates the high specificity for lead alkyls in

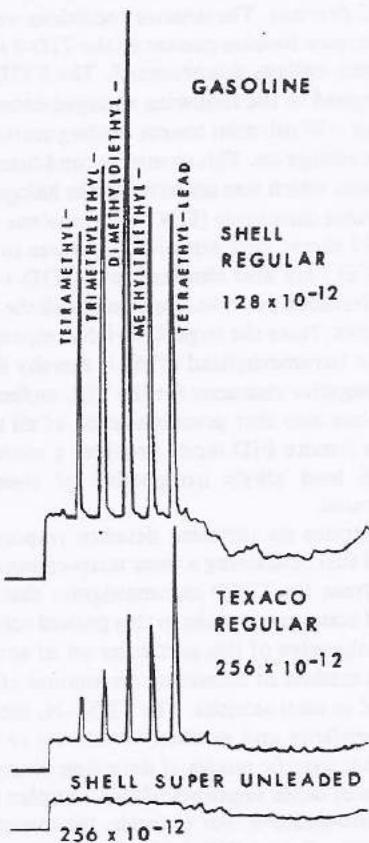


Figure 9. Chromatograms illustrating the specific detection of lead alkyls in gasoline using the remote FID. Data correspond to samples randomly obtained from local gasoline stations. Column: SP-2100, 50° to 230°C at 15%/min.

gasoline provided by the remote FID mode of detection. Previously, GC/atomic absorption spectroscopy (AAS) instrumentation has been described for the specific detection of lead alkyls in gasoline or other samples (15). By comparison with AAS, the remote FID provides excellent sensitivity and specificity, and is considerably simpler and less expensive to operate. The data shown in Figure 9 were obtained by direct injections of 0.8- $\mu$ l amounts of the gasolines onto a temperature-programmed, packed column.

The remote FID mode of detection has some configuration similarities to a hydrogen atmosphere flame ionization detector (HAFID), which has also been reported to provide specific detection of lead alkyls in gasoline (16). Both the remote FID and HAFID use a collector electrode well removed from the flame jet structure. However, the signals in the remote FID are largest with an oxygen-rich flame, whereas the HAFID requires a hydrogen-rich atmosphere doped with silane.

Gasoline is a readily available, complex mixture of organic compounds which is especially well suited to demonstrating the different responses obtained in the family of thermionic detection modes. Figure 10 shows multiple modes of analysis of a sample of regular gasoline. The chromatographic separation was performed on a packed column to purposely create the demanding situation in which many overlapping compounds are present in the detector volume at the same time. This situation is shown to be the case by the CFID response. When the same gasoline sample is chromatographed using the remote FID mode, selective responses are obtained only for the five lead alkyls. The remote FID data in Figure 10 were obtained with an FTID detector assembly and a TID-2 source mounted on a Model 3700 GC (Varian). The detector conditions were  $H_2 = 30$ , air = 200 ml/min; zero heating current to the TID-2 source; and flame ion-suppress voltage disconnected. The FTID-2 data in Figure 10 correspond to the following changed detector conditions;  $H_2 = 30$ , air = 80 ml/min; source heating current = 3.2 A; and ion-suppress voltage on. This change in conditions produced an FTID-2 response which was selective for the halogenated lead scavengers, ethylene dichloride (EDC) and ethylene dibromide (EDB). Figure 10 shows that selective responses to EDB and tetraethyllead (TEL) are also obtained in the TID-1-air mode, while the TID-1-N<sub>2</sub> mode provides responses to all the lead alkyls and lead scavengers. Note the large TID-1-N<sub>2</sub> response to TEL in comparison to tetramethyllead (TML), thereby illustrating a greater electronegative character for the TEL molecular structure vs. TML. Note also that precombustion of all samples in the flame of the remote FID mode provides a more uniform response for all lead alkyls irrespective of their original molecular structures.

Figure 11 illustrates six different detector responses in the analysis of diesel fuel containing a trace nitro-compound additive. It is clear from the CFID chromatogram that there are many unresolved component peaks in this packed column analysis. A primary objective of this particular set of analyses was to define the best method of measuring the amount of the nitro-compound added to such samples. The TID-1-N<sub>2</sub> mode clearly gives the best specificity and excellent sensitivity to the nitro-additive. The other specific modes of detection illustrate selective enhancement of other segments of this complex sample in addition to the nitro-additive. For example, the cluster of peaks at late retention times in the TID-2-H<sub>2</sub>/air chromatogram undoubtedly corresponds to other N-compounds in the sample. The two FTID-1 chromatograms illustrate that the H<sub>2</sub>-air mixture ratio is a further means of significantly altering the FTID re-

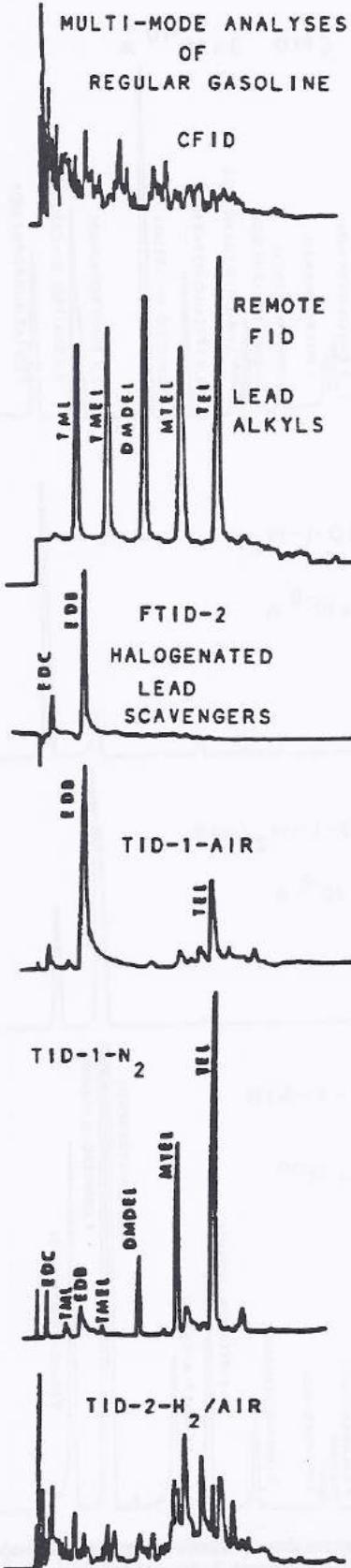


Figure 10. Chromatograms showing multiple modes of detector response to a sample of regular leaded gasoline. Column and program same as in Figure 9.

sponse. The mixture of 20 ml/min H<sub>2</sub>, 100 ml/min air represents an oxygen-rich flame, while the mixture of 35 ml/min H<sub>2</sub>, 70 ml/min air is a hydrogen-rich flame. Generally, stoichiometric or oxygen-rich flames are the most useful for the FTID.

Figure 12 shows multiple mode analyses of a commercial brand of cologne. These sets of chromatograms illustrate the advantageous use of the specific detection modes to enhance responses for trace fragrance components in colognes. The TID-1-N<sub>2</sub> mode is especially useful because it is non-destructive. Therefore, TID-1-N<sub>2</sub> emits exhaust gases that are characterized

by distinctly different fragrances that change with time as the various segments of the chromatogram elute. For the cologne shown, as well as for other brands that have been examined, the set of chromatograms obtained from the different modes of thermionic detection provide a characteristic fingerprint that distinguishes one brand from another.

All the modes of detection described in this article measure negative ionization currents. The magnitudes of these currents are very dependent on the electronegative character of the chemical species adjacent to the heated thermionic source.

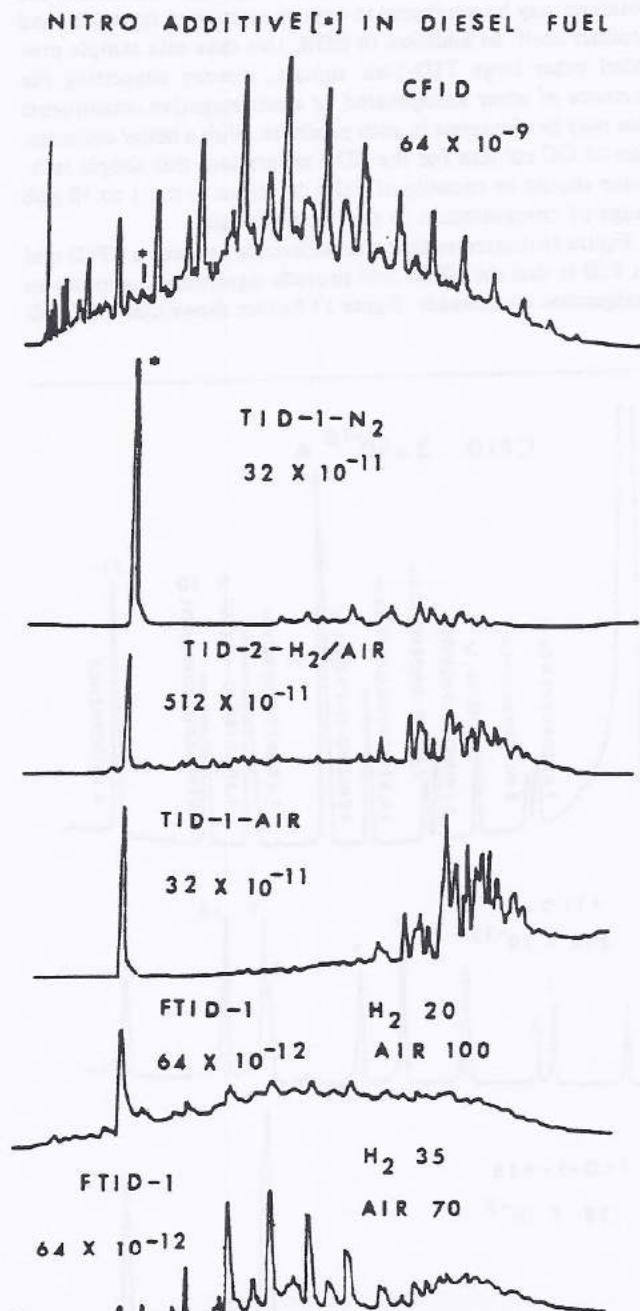


Figure 11. Chromatograms showing different detector responses to a sample of diesel fuel containing a trace nitro-compound additive identified by the asterisk. Column: SP-2100, 90° to 270°C at 10°/min.

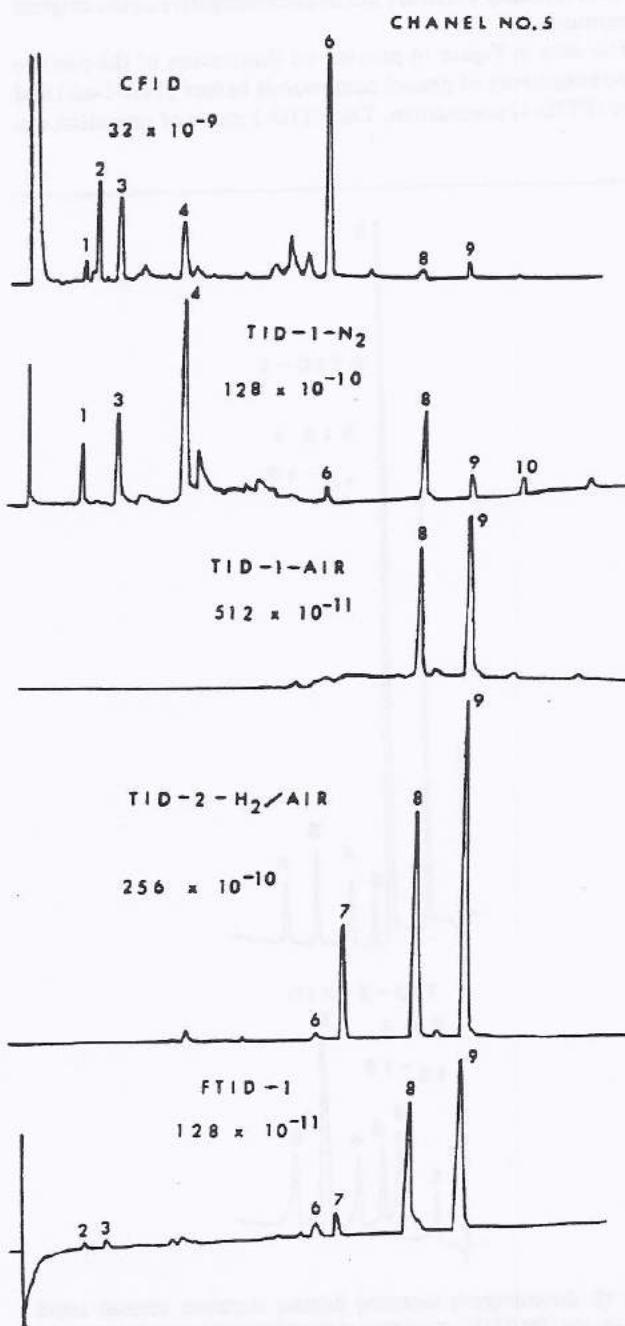


Figure 12. Chromatograms showing multiple modes of detector response to a brand of cologne randomly obtained. Column: SP-2100, 100° to 270°C at 16°/min.

Figure 13 illustrates how the response to a group of polychlorinated biphenyl (PCB) compounds changes with precombustion of the compounds. The data obtained with a TID-2 source in an air environment exhibit large differences in response between the different PCB compounds, similar to the known characteristics of an ECD. The FTID-2 data show that the precombustion of the PCBs yield negative ionization currents, which are larger in magnitude as well as more uniform per Cl atom. In this case of PCBs, precombustion improves the detectability by producing chemical species more electronegative than the original compounds. For other compound types, precombustion sometimes causes the opposite effect of producing combustion products which are not as electronegative as the original compound.

The data in Figure 14 provide an illustration of the relative electronegativity of phenol compounds before (TID-1-air) and after (FTID-1) combustion. The FTID-1 mode of operation can

be easily converted to the TID-1-air mode by simply turning off the H<sub>2</sub> fuel to the FTID flame. Figure 14 shows that the FTID-1 mode produces a much more uniform response for all the chloro- and nitrophenols of this sample, but the absolute magnitudes of FTID response for the dinitrophenols, pentachlorophenol, and 4-nitrophenol are substantially lower than the TID-1-air response to these compounds.

Figure 15 illustrates the use of the TID-1-air mode to detect EDB in food products. A simple headspace technique was used for the data. One of the advantages of the TID-1-air mode is that it is insensitive to the large air component in the injection headspace vapors. Hence, all chromatographic peaks that are obtained may be attributed to vapors emanating from the food product itself. In addition to EDB, this cake mix sample provided other large TID-1-air signals, thereby suggesting the presence of other halogenated or electronegative constituents that may be of interest in such products. With a better optimization of GC column for the EDB separation, this simple technique should be capable of EDB detection in the 1 to 10 ppb range of concentration in the food product.

Figure 16 illustrates that one difference between a CFID and an FID is that the CFID will provide significant responses to halogenated compounds. Figure 17 further shows that the CFID

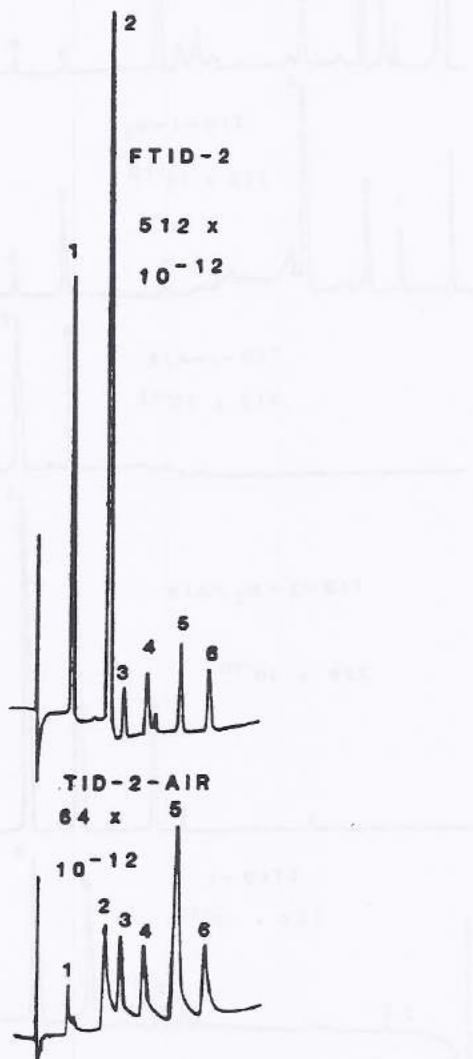


Figure 13. Chromatograms illustrating detector responses obtained before (TID-2-air) and after (FTID-2) combustion of polychlorinated biphenyl compounds. PCB peak identifications: 1 = 1000 ng 2-chloro-, 2 = 1000 ng 3,3'-dichloro-, 3 = 100 ng 2,4,5-trichloro-, 4 = 100 ng 2,2',4,4'-tetrachloro-, 5 = 100 ng 2,3',4,5',6-pentachloro-, 6 = 100 ng 2,2',3,3',6,6'-hexachlorobiphenyl. Column: SP-2250, 200° to 270°C at 10%/min.

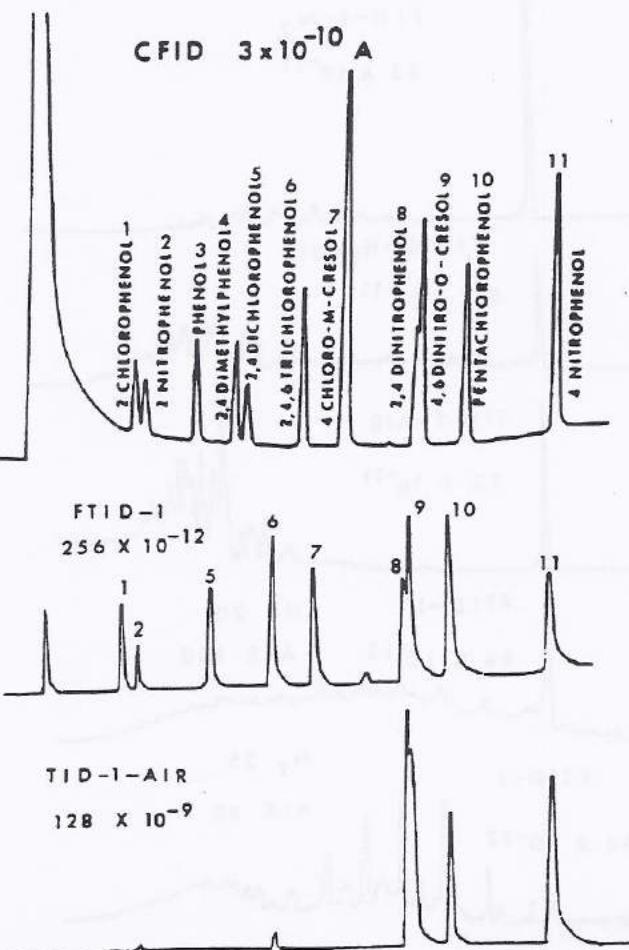


Figure 14. Chromatograms illustrating detector responses obtained before (TID-1-air) and after (FTID-1) combustion of phenol compounds. Sample, column, and program were the same as in Figure 8.

response to halogenated compounds can be selectively enhanced by increasing the source heating current, while the CFID responses to hydrocarbons remain unchanged. Consequently, by judiciously adjusting the source heating current, the CFID response to halogenated and some other heteroatom compounds can be tuned to yield about the same response factor as obtained for hydrocarbons.

## Summary

The preceding data have demonstrated that thermionic ionization techniques and equipment have applications in gas chromatography that go well beyond the usual NP detection, such as that of TID-2-H<sub>2</sub>/air. To achieve the best possible signal-to-noise ratio and specificity for each mode of detection, the specific chemical composition of the thermionic emission source needs to be matched with the temperature and gas phase environment in which the source is operated.

From their extensive use in NP detection, thermionic ionization detectors are known to often exhibit decreasing sensitivity with increasing operating time as a result of depletion of the thermionic source activity. Consequently, the thermionic source usually needs to be replaced at periodic intervals. Of the different modes of detection described in this report, the NP mode is the most demanding with regard to the operating life of the thermionic source. Generally, in modes of detection (e.g., TID-1-N<sub>2</sub>) where the operating temperature is lower and the gas environment is less reactive, the thermionic sources maintain their responses over longer periods of time. For all modes of detection, a practical guideline for achieving the longest possible source lifetime is to operate the thermionic source just hot enough to achieve the response required.

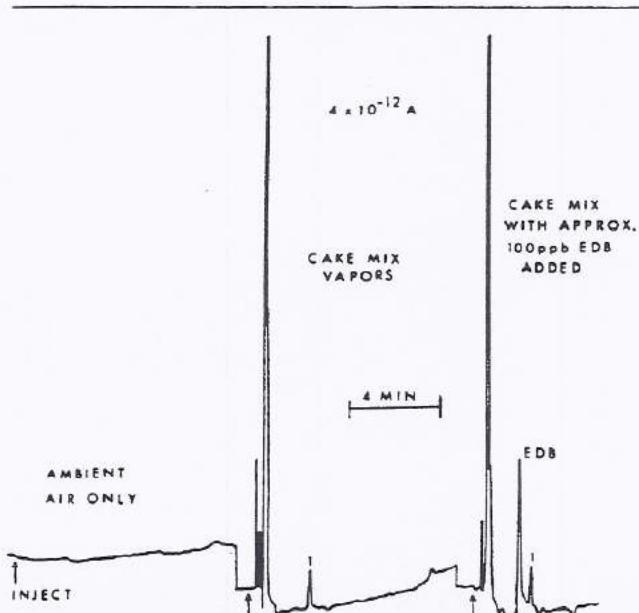


Figure 15. Example of TID-1-air application to determine EDB in cake mix. Sample: headspace vapors from 0.7 gm Duncan Hines Deluxe Yellow Cake Mix in a sealed 2-ml vial. Sampling procedure: heat sealed sample vial to 120°C; extract 200  $\mu$ l headspace vapor with gas-tight syringe; inject into GC and start column oven temperature program. Column: SP-2100, 40° to 110°C at 10°/min.

The developments of thermionic techniques in GC have also spawned applications of the technology in liquid chromatography detection (17), thin layer chromatography (18), and mass spectrometry ion sources (19). Since there remain to be studied many different combinations of thermionic source compositions, thermionic source temperatures, and gas environment compositions, it is probable that the technology will continue to evolve in coming years.

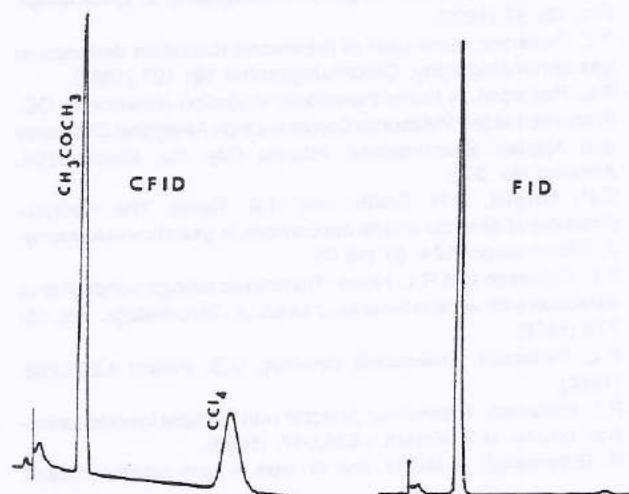


Figure 16. Comparison of CFID and FID responses to a water sample containing acetone and carbon tetrachloride. Column: Chromosorb 102, isothermal 120°C.

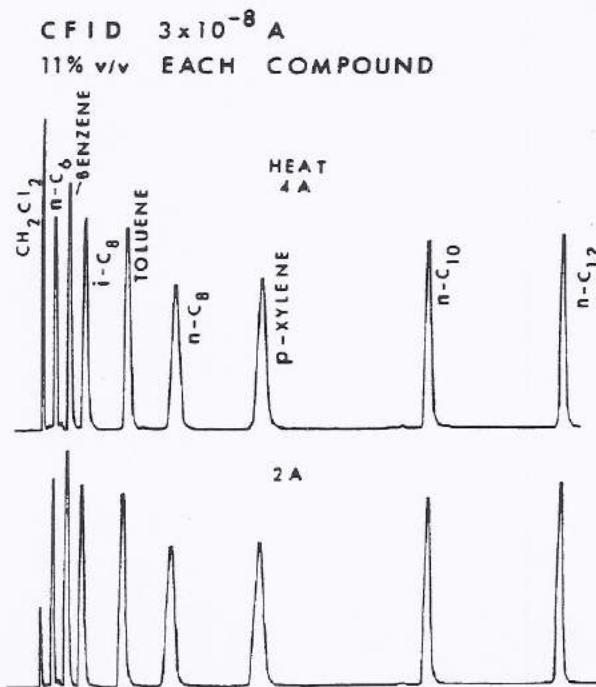


Figure 17. Comparison of CFID responses to sample of methylene chloride and various hydrocarbons at two different magnitudes of heating current to the catalytic source. Column: SP-2100, 40° to 180°C at 10°/min.

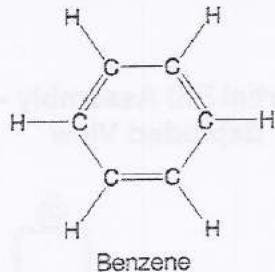
## References

1. B. Kolb and J. Bischoff. A new design of a thermionic nitrogen and phosphorus detector for GC. *J. Chromatogr. Sci.* 12: 625 (1974).
2. P.L. Patterson. Selective responses of a flameless thermionic detector. *J. Chromatogr.* 167: 381 (1978).
3. B. Kolb, M. Auer, and P. Pospisil. Reaction mechanism in an ionization detector with tunable selectivity for carbon, nitrogen and phosphorus. *J. Chromatogr. Sci.* 15: 53 (1977).
4. P.L. Patterson, R.A. Gatten, and C. Ontiveras. An improved thermionic ionization detector for gas chromatography. *J. Chromatogr. Sci.* 20: 97 (1982).
5. P.L. Patterson. New uses of thermionic ionization detectors in gas chromatography. *Chromatographia* 16: 107 (1982).
6. P.L. Patterson. A flame thermionic ionization detector for GC. Presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 1984, Abstract No. 372.
7. C.H. Burgett, D.H. Smith, and H.B. Bente. The nitrogen-phosphorus detector and its applications in gas chromatography. *J. Chromatogr.* 134: 57 (1977).
8. P.L. Patterson and R.L. Howe. Thermionic nitrogen-phosphorus detection with an alkali-ceramic bead. *J. Chromatogr. Sci.* 16: 275 (1978).
9. P.L. Patterson. Thermionic detector. U.S. Patent 4,203,726. (1980).
10. P.L. Patterson. Thermionic detector with multiple layered ionization source. U.S. Patent 4,524,047. (1985).
11. R. Greenhalgh, J. Müller, and W. Aue. A pure rubidium/quartz source for alkali flame ionization detectors. *J. Chromatogr. Sci.* 16: 8 (1978).
12. T. Fujii and H. Arimoto. Thermionic ionization detector with lanthanum hexaboride/silicon dioxide thermionic emitter material for gas chromatography. *Anal. Chem.* 57: 490 (1985).
13. C.M. White, A. Robbat, Jr., and R.M. Hoes. Evaluation of a thermionic ionization detector for nitrated polycyclic aromatic hydrocarbons. *Anal. Chem.* 56: 232 (1984).
14. P.L. Patterson. New modes of response for thermionic detectors in GC. Presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 1983, Abstract No. 423.
15. Y.K. Chau, P.T.S. Wong, G.A. Bengert, and J.L. Dunn. Determination of dialkyllead, trialkyllead, tetraalkyllead and lead (II) compounds in sediment and biological samples. *Anal. Chem.* 56: 271 (1984).
16. M.D. DuPuis and H.H. Hill, Jr. Analysis of gasoline for antiknock agents with a hydrogen atmosphere flame ionization detector. *Anal. Chem.* 51: 292 (1979).
17. V.I. McGuffin and M. Novotny. Thermionic detection in microcolumn liquid chromatography. *Anal. Chem.* 55: 2296 (1983).
18. P.L. Patterson. A specific detector for nitrogen and halogen compounds in TLC on coated quartz rods. *Lipids* 20: 503 (1985).
19. D. Bombick, J.D. Pinkston, and J. Allison. Potassium ion chemical ionization and other uses of an alkali thermionic emitter in mass spectrometry. *Anal. Chem.* 56: 396 (1984).

Manuscript received October 2, 1985;  
revision received November 18, 1985.

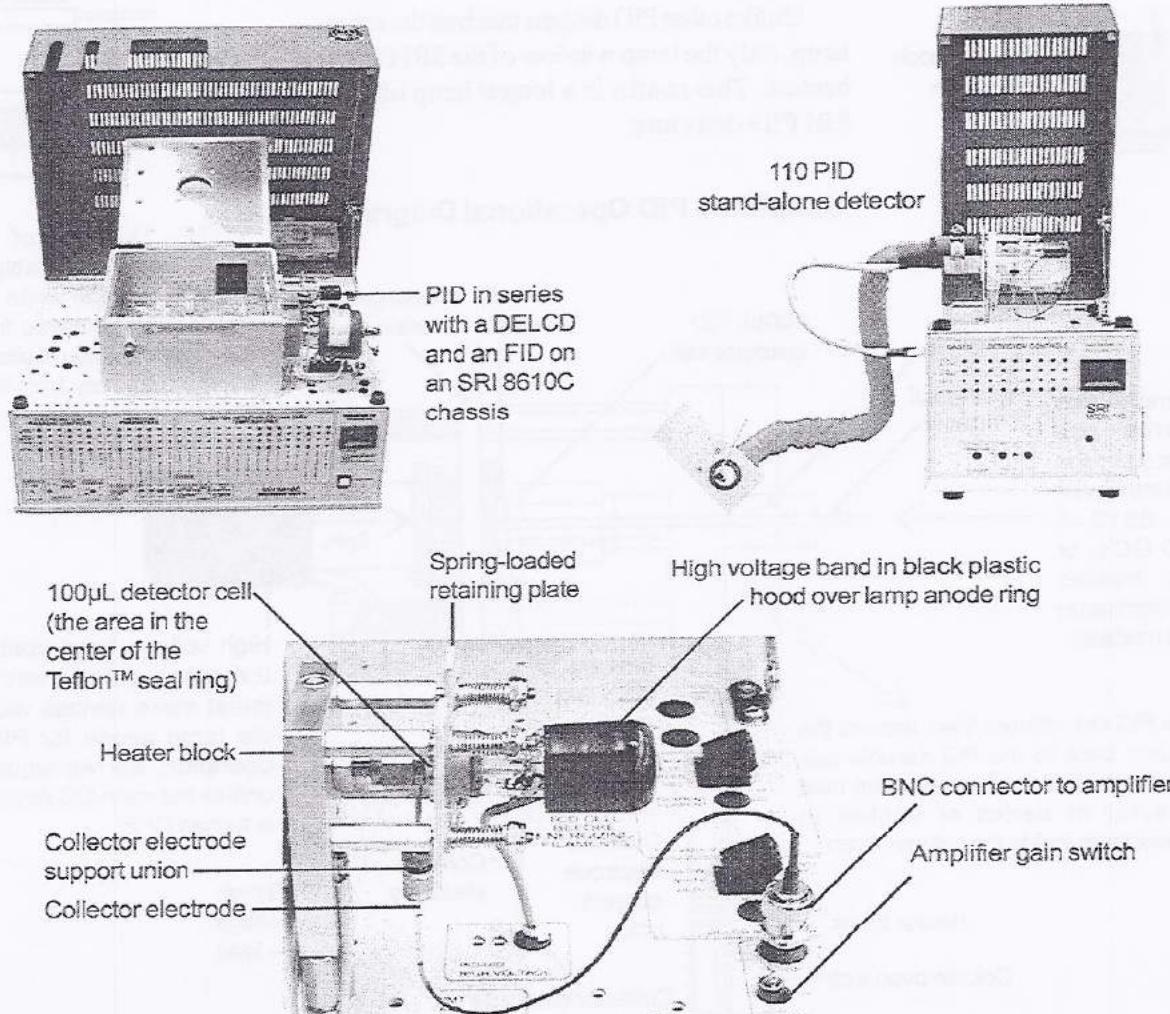
## DETECTORS

### Photo Ionization Detector - PID



#### Overview

The Photo Ionization Detector (PID) responds to all molecules whose ionization potential is below 10.6 eV, including aromatics and molecules with carbon double bonds. The PID is nondestructive, so the sample can be routed through the PID and on to other detectors. It is often used in series with the FID and / or DELCD. PID detection limits for aromatics are in the ppb range; purge and trap concentration of the sample can lower detection limits to the ppt range. Because of its selective sensitivity, use of the PID is mandated in several EPA methods. The PID detector consists of a 10.6 electron volt (eV) UV lamp mounted on a thermostatted, low-volume (100 $\mu$ L), flow-through cell. The temperature is adjustable from ambient to 250°C. Three detector gain levels (LOW, MEDIUM and HIGH) are provided for a wide range of sample concentrations. The PID lamp is held in place by a spring-loaded plate, so that the lamp may be quickly removed for cleaning and replaced without any special tools. The PID can run on air carrier for gasless operation, or for stream monitoring applications where the entire stream of sample is directed through the detector (no column is used).

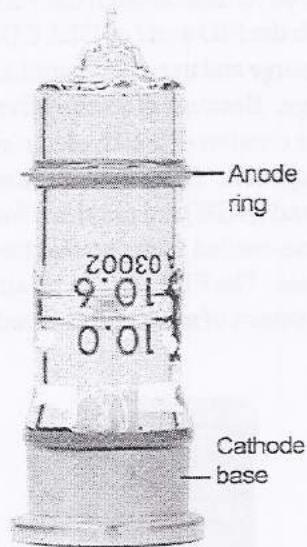


## DETECTORS

### Photo Ionization Detector - PID

#### Theory of Operation

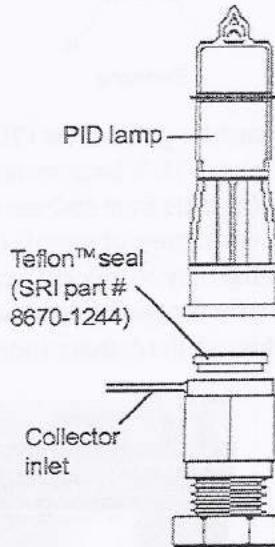
##### 10.6eV PID Lamp (SRI Part # 8670-1242)



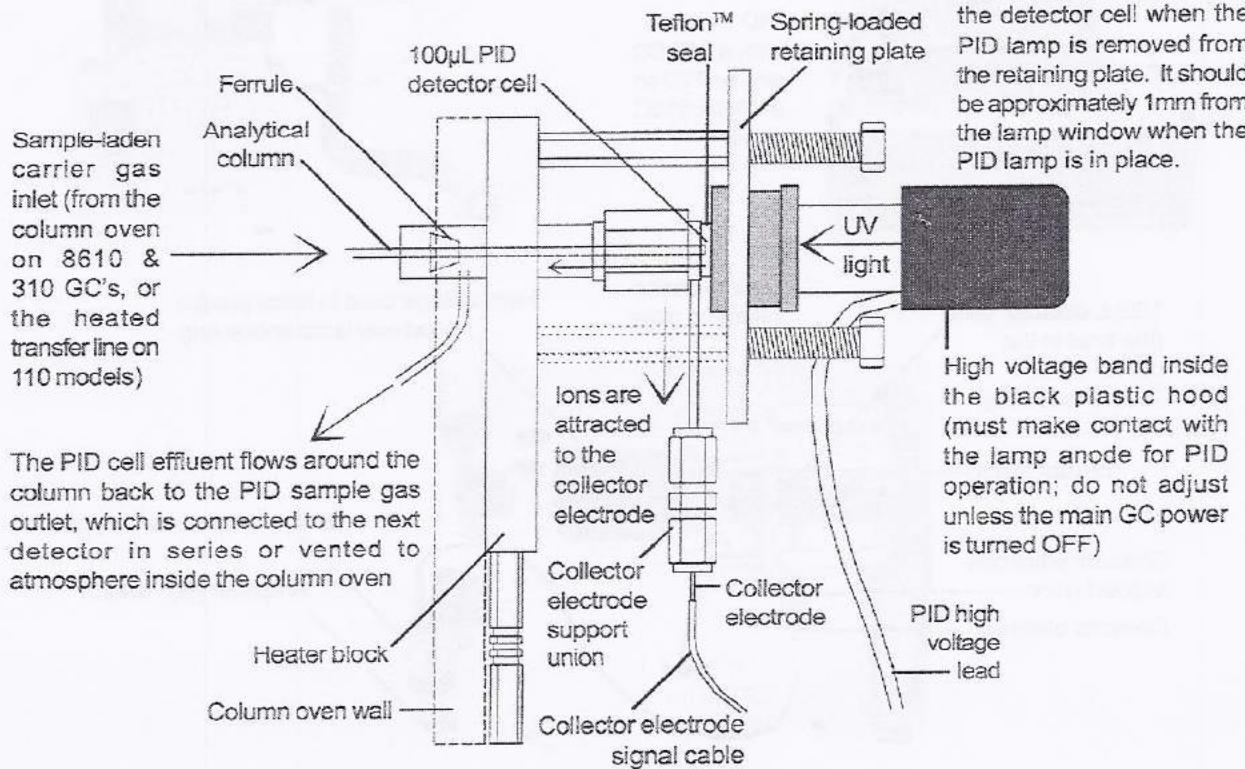
The SRI PID design uses a 10.6eV lamp with a high voltage power supply. Sample laden carrier gas flows from the analytical column into the PID sample inlet, where it is streamed through a 100 $\mu$ L flow-through cell. When sample molecules flow into the cell, they are bombarded by the UV light beam. Molecules with an ionization potential lower than 10.6eV release an ion when struck by the ultraviolet photons. These ions are attracted to a collector electrode, then sent to the amplifier to produce an analog signal, which is acquired by the PeakSimple data system.

Unlike other PID designs that heat the entire lamp, only the lamp window of the SRI PID is heated. This results in a longer lamp life for SRI PID detectors.

#### Partial PID Assembly - Exploded View

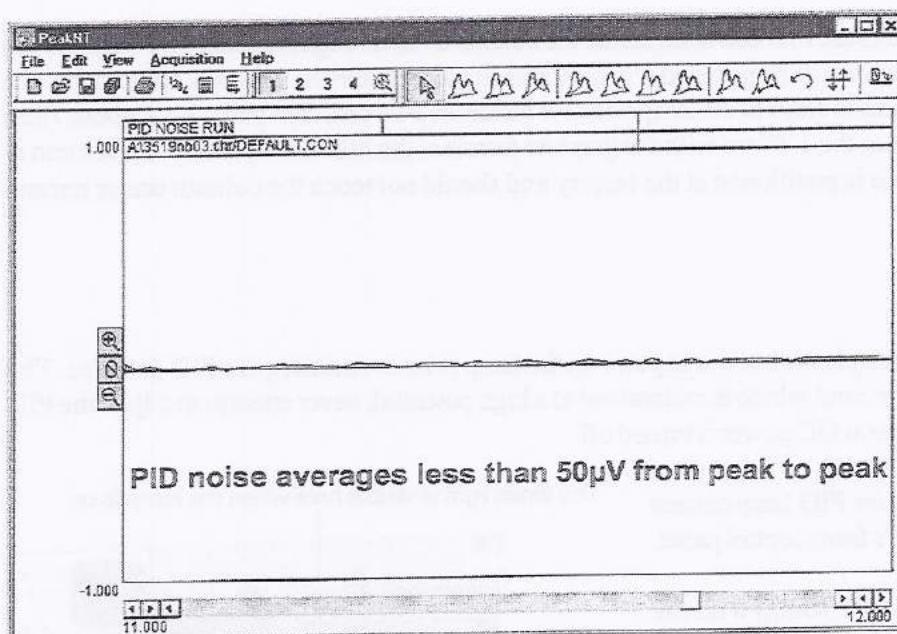


#### Simplified PID Operational Diagram



**DETECTORS**  
**Photo Ionization Detector - PID**

*Expected Performance*



**PID Noise Run**

Column: 15m MXT-VOL  
 Carrier: Helium @ 10mL/min  
 PID gain: LOW  
 PID temp: 150°C  
 PID current: 70

**PID BTEX Analysis (in series with FID and DELCD)**

Sample: 1µL 100ppm

BTEX plus

Column: 15m MXT-VOL

Carrier: Helium @ 10  
mLs/min

PID gain: LOW

PID temp: 150°C

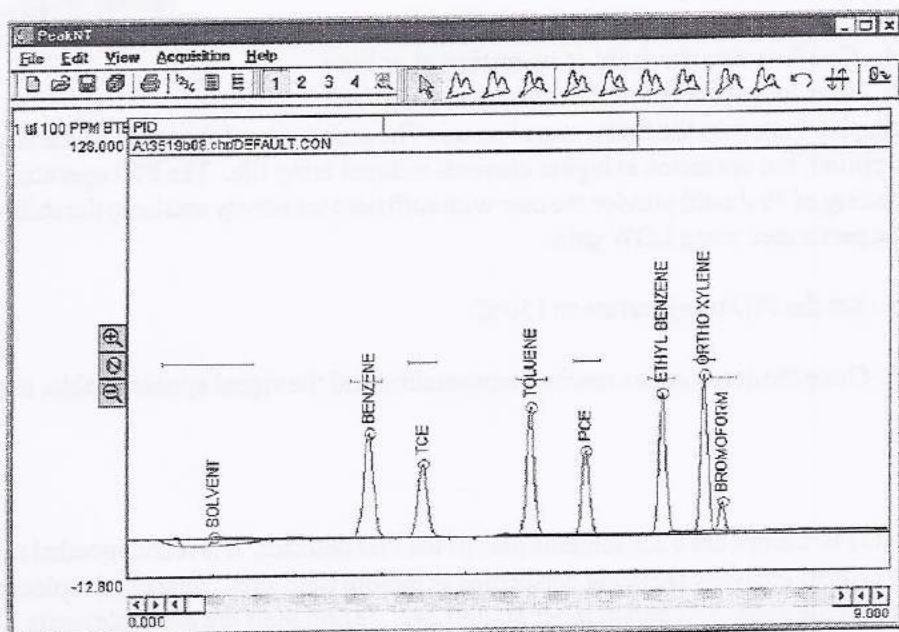
PID current: 70

Temperature program:

Initial	Hold	Ramp	Final
40°C	2.00	15.00	240°C
240°C	10.00	0.00	240°C

Results:

Component	Retention	Area
Benzene	2.418	313.0540
TCE	3.065	231.5120
Toluene	4.600	309.2120
POE	5.433	216.6230
Ethyl Benzene	6.700	286.0900
Ortho Xylene	7.383	298.9190
Bromoform	7.650	55.9460
Total		1711.3560



## DETECTORS

### Photo Ionization Detector - PID

#### *General Operating Procedure*

The capillary column enters the PID cell from inside the column oven through the bulkhead fitting in the insulated oven wall. The column may be installed with the lamp in place. Insert the capillary column into the PID detector inlet until the column stops at the lamp window inside the PID cell, then pull it back about 1 mm from the lamp window. Tighten the 1/8" nut with the graphite ferrule at the PID inlet to secure the column in place. The collector electrode is positioned at the factory and should not touch the column under normal circumstances.

1. Always ensure that the black plastic hood is in place on the lamp prior to operating the PID detector. The hood contains the high voltage band which is maintained at a high potential; never attempt to adjust the PID high voltage band unless the main GC power is turned off.

2. Turn ON the GC. Turn ON the PID lamp current with the flip switch on the GC's front control panel.

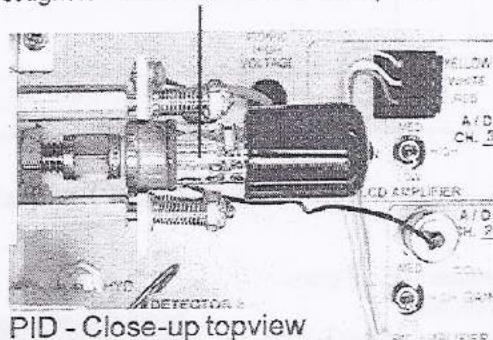
3. Set the PID current to 70 (= 0.70ma) with the trimpot setpoint on the top edge of the GC's front control panel. Use the flat blade screwdriver provided with your GC to adjust the trimpot. The lamp should emit a violet-colored light visible down the center of the tube

4. Confirm that the lamp is operating at or near 0.70ma by pressing the PID detector ACTUAL display button on the front control panel. The sensitivity of the lamp increases proportionally to the current applied, but operation at higher currents reduces lamp life. The PID operating current range is 70-125. A setting of 70 should provide the user with sufficient sensitivity and lamp durability. Most PID applications can be performed using LOW gain.

5. Set the PID temperature to 150°C.

6. Once the detector has reached temperature and the signal appears stable, sample may be introduced.

The violet light is visible here when the lamp is on



NOTE: Lamps are a consumable part of the PID detector. It is recommended to have a spare lamp available if critical analyses are being performed at remote field sites. Spare and replacement 10.6eV PID lamps are available under SRI part number 8670-1242. Teflon seals are available under SRI part number 8670-1244.

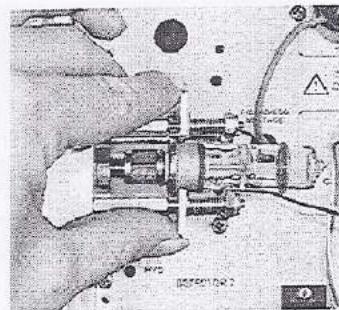
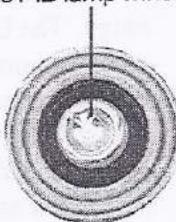
**DETECTORS**  
**Photo Ionization Detector - PID**

**Troubleshooting and Maintenance**  
**Cleaning the PID Lamp**

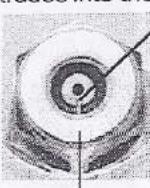
Over time, during normal operation, a film of contaminants will condense on the PID lamp window. Typically, this film is a result of stationary phase column bleed. To minimize contaminant condensation and thus lamp window cleaning, avoid heating the column any higher than absolutely necessary. Contaminant condensation can block the photons, reducing lamp emissions and sensitivity. Therefore, the PID lamp window must be cleaned when an appreciable change in sensitivity has been observed by the operator. Because the response change resulting from cleaning the lamp window usually requires detector recalibration, frequent cleaning is not recommended.

1. Turn the PID current OFF with the switch on the GC's front control panel. Turn the GC OFF and let the PID detector assembly cool enough to touch it without getting burned.
2. Disconnect the high-voltage band from the lamp anode by removing the black plastic hood.
3. Grasp the spring-loaded retainer plate with the fingers of one hand and push or pull it toward the PID lamp; it doesn't take much force to move the plate enough for lamp removal. Slide the PID lamp up and out of the PID detector assembly.
4. Clean the lamp window using a mild abrasive cleanser like Bon Ami or Comet. Wet your finger, and make a paste with a small amount of cleanser. Scrub the lamp window clean in a circular motion with your finger.
5. Rinse the lamp window clean with water. Dry the lamp with a paper towel.
6. Inspect the Teflon™ seal for cuts or nicks. A damaged seal will not affect the PID response, but it may provide a leak site that will reduce the amount of sample delivered to any subsequent detector.
7. With the lamp removed, the collector electrode is visible where it protrudes into the cell. Check the collector electrode for any visible residues, films, discolorations, etc. If present, they may impede the flow of ions from the sample molecules to the collector electrode. To clean the collector electrode, gently use a small file to remove any residues from its tip. Blow the residue off the collector electrode and surrounding areas.
8. Open the spring-loaded retainer plate and replace the PID lamp snug against the seal. The lamp window has a slightly larger diameter than the seal; try to center it against the seal. Replace the high voltage band / black plastic lamp hood.
9. Recalibrate the PID detector before returning it to service.

The PID lamp window

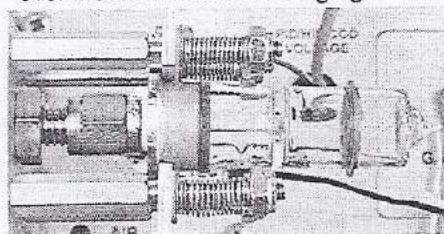


The collector electrode  
protrudes into the cell



Teflon™ seal

Make sure the lamp window is centered over the Teflon seal and snug against it

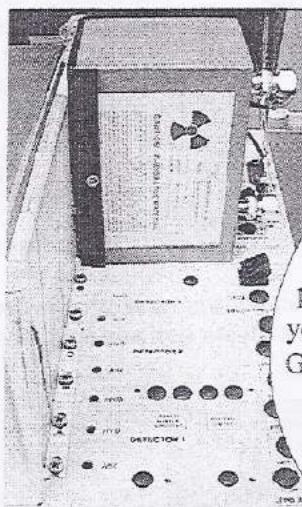
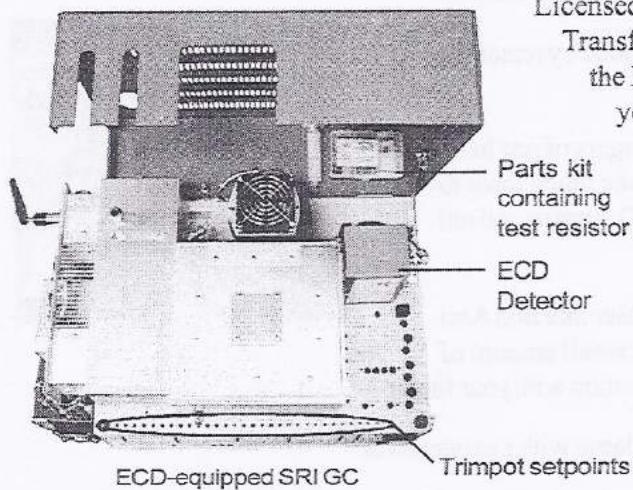


## OVERVIEW

The Electron Capture Detector (ECD) is selective to electronegative compounds, especially chlorinated, fluorinated, or brominated molecules. It is sensitive to some of these compounds in the parts per trillion (ppt) range. The ECD detector requires nitrogen or argon / 5% methane (P5) to operate. The ECD detector is mounted immediately adjacent to the right rear column oven wall on your SRI GC chassis. Two BNC cables connect the anode and cathode, respectively, to the ECD amplifier. The ECD detector consists of a stainless steel cylinder containing 5 millicuries of radioactive Nickel 63 in an oven enclosure that is thermostatically controllable from ambient temperature to 375°C. Since the detector contains only 5 millicuries of Nickel-63, the ECD is covered by a "General License" requiring a periodic wipe test and the filing of a form with your state's Department of Health. The documentation necessary to authorize your possession of a radioactive source is included in the ECD manual from Valco, the manufacturers. This documentation transfers possession of the ECD directly to you from Valco; SRI provides the ECD installation service and the GC. There are four important documents to look for: 1) Certification of Sealed Source, 2) Conditions for Acceptance of a Generally

Licensed Device, 3) Test Specifications, and 4) Record of Source Transfer. Valco may print your address on the multiple copies of the Record of Source Transfer, which are to be completed by you and filed with the appropriate state and local authorities.

The other documents remain with the ECD detector, and are necessary to prove authorized possession of the ECD.



Close-up view of the ECD detector  
on an SRI GC

<b>W.H.</b>	<b>W.H. Instruments Co., Inc.</b>	1
<b>CERTIFICATION OF SEALED CONTAINERS</b>		
<p>This document certifies that the following sealed containers have been checked and found to contain the materials described below. These containers will be held until further notice or until otherwise directed by the customer.</p> <p>Customer: <u>John T. Smith</u>      Date received: <u>09/07/02</u>      Address: <u>123 Main Street</u>      Date issued certificate: <u>09/07/02</u>      City: <u>Bethel, NY</u>      File number: <u>123-45678</u>      State: <u>NY</u>           Zip code: <u>12801</u>      Remarks:      DATE: <u>12/07/02</u>      APPROVAL: <u>R. J. Johnson</u>      APPROVED: <u>John T. Smith</u>      APPROVAL DATE: <u>12/07/02</u>  <small>Notarized documents may be used for personal property tax purposes in NYS C.R.S. 01.0005</small> </p>		

THE DEPARTMENT OF HEALTH  
MANUAL OF SANITATION CONTROL

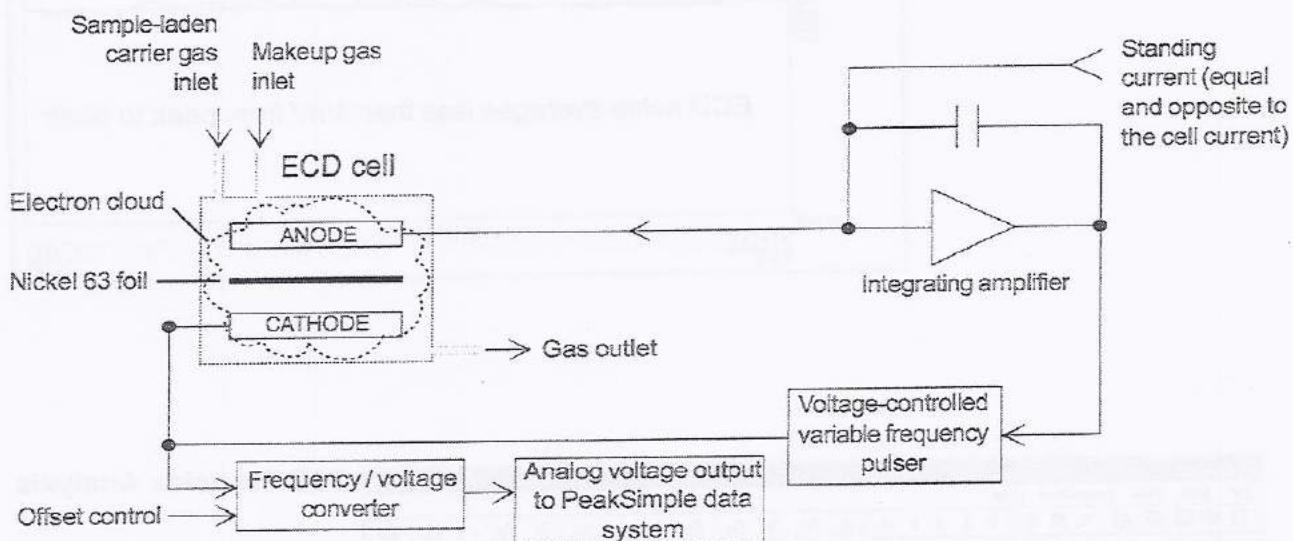
## DETECTORS

### Electron Capture Detector - ECD

#### Theory of Operation

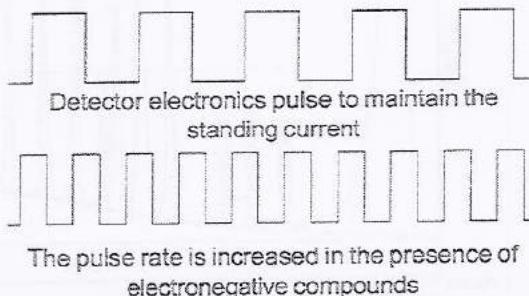
The radioactive Nickel 63 sealed inside the ECD detector emits electrons (beta particles) which collide with and ionize the make-up gas molecules (either nitrogen or P5). This reaction forms a stable cloud of free electrons in the ECD detector cell. The ECD electronics work to maintain a constant current equal to the standing current through the electron cloud by applying a periodic pulse to the anode and cathode. The standing current value is selected by the operator; the standing current value sets the pulse rate through the ECD cell. A standing current value of 300 means that the detector electronics will maintain a constant current of 0.3 nanoamperes through the ECD cell by periodically pulsing. If the current drops below the set standing current value, the number of pulses per second increases to maintain the standing current.

#### ECD Detector Operational Diagram



When electronegative compounds enter the ECD cell from the column, they immediately combine with some of the free electrons, temporarily reducing the number remaining in the electron cloud. When the electron population is decreased, the pulse rate is increased to maintain a constant current equal to the standing current. The pulse rate is converted to an analog output, which is acquired by the PeakSimple data system. Unlike other detectors which measure an increase in signal response, the ECD detector electronics measure the pulse rate needed to maintain the standing current.

#### Example Pulse Trains

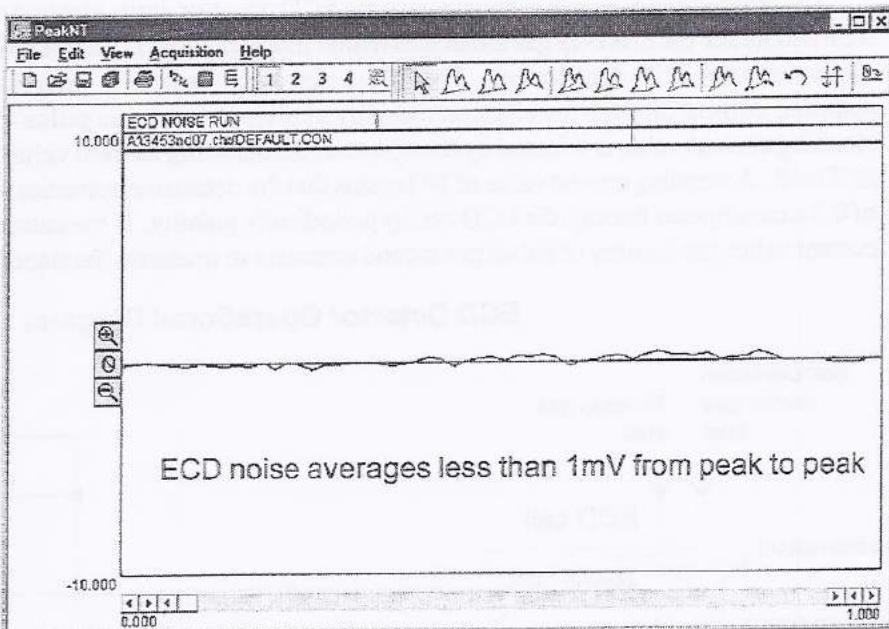


**DETECTORS**  
**Electron Capture Detector - ECD**

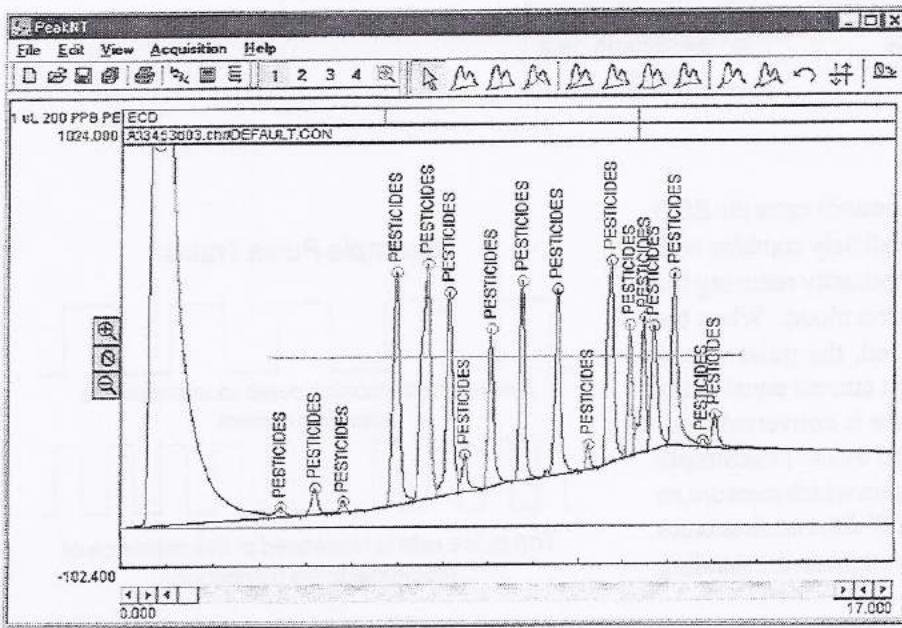
*Expected Performance*

**ECD Noise Run**

Column: 15m MXT-5 capillary  
Carrier: Helium @ 10mL/min  
Makeup: Nitrogen @ 60mL/min  
ECD Temp: 250°C  
ECD standing current: 300  
Offset before zeroing the data system signal: 280mV



**ECD Pesticide Analysis**



Sample: 1 $\mu$ L 200ppb chlorinated pesticides  
Column: 15m MXT-5 capillary  
Carrier: Helium @ 10mL/min  
Makeup: Nitrogen @ 60mL/min  
ECD temp: 250°C  
ECD standing current: 300

Results:  
Component Retention Area  
Pesticides 2.850 45792.4350

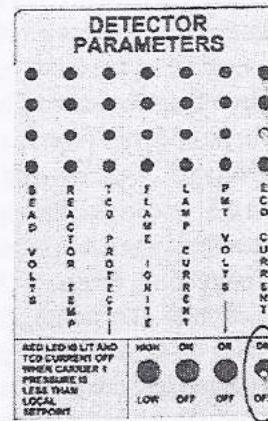
## DETECTORS

### Electron Capture Detector - ECD

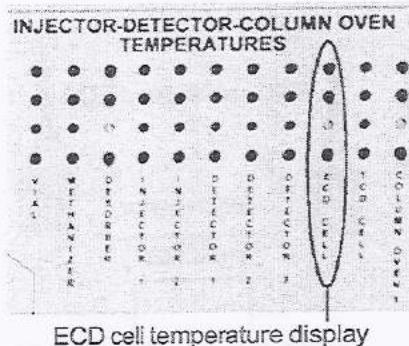
#### General Operating Procedure

The following suggestions are specific to your SRI ECD-equipped GC. Consult the Valco ECD detector manual for carrier gas purity requirements, carrier gas system configuration, and other general ECD detector information. Keep in mind that the electronics shematics in the Valco manual do not apply to your ECD-equipped SRI GC.

1. Cap off the carrier inlet to the ECD cell (in the column oven).
2. Connect the makeup gas and let it flow through and purge the ECD cell. Makeup flow is 40-100mL; typically 60mL.
3. Heat the ECD detector to 150°C to verify that the baseline noise and offset are normal. 150°C is hot enough to evaporate off water but low enough to avoid oxidation of the nickel foil which can occur at high temperatures in the presence of oxygen. Once you have verified the ECD's operation at this temperature, you may heat it to higher temperatures.
4. Turn on the ECD standing current (the ECD current ON / OFF switch is located on the front control panel of the GC, under "DETECTOR PARAMETERS"). As a rule of thumb, an ECD detector requires enough nitrogen makeup flow (40-100mL/min) to significantly dilute the carrier in order to help keep detector noise down; the ECD can tolerate a 6:1 ratio of nitrogen to helium.



ECD standing current  
ON/OFF switch



With the carrier and makeup gas connected and flowing, check the offset from zero. The millivolt reading should be between 100 and 500mV. If the signal offset is less than 100mV, the standing current needs to be increased. If the signal offset is higher than 500mV, the standing current needs to be decreased. Once the signal is relatively quiet and stable, set the temperature to whatever is appropriate for your analysis by adjusting the trimpot setpoint with the flat blade screwdriver provided.

5. When the ECD detector cell reaches temperature, let the system stand until you get a stable milliVolt reading. Once the system exhibits a stable baseline, reconnect the column. Observe the signal in the presence of the carrier flow. If it is significantly higher, it indicates contamination introduced on the carrier flow. If the milliVolt reading is still relatively stable in the presence of carrier flow, then sample may be injected. Avoid samples with high concentrations of electronegative compounds; they may effect ECD operation for some time thereafter, as they could take too long to dissipate.

6. You may need to adjust the ECD standing current using its trimpot setpoint. The trimpot setpoints are located on the top edge of the front control panel, directly above the display push-buttons for each controlled zone. Remember, increasing the standing current increases the ECD's sensitivity and raises the baseline offset.

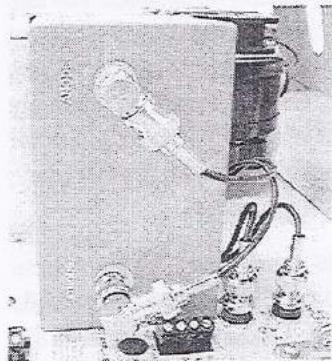
DETECTORS  
Electron Capture Detector - ECD

### ECD Troubleshooting

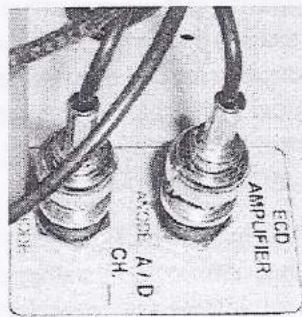
If you are experiencing baseline offset and noise problems with your ECD detector, try the following two diagnostic tests:

1. Verify that the ECD amplifier electronics are working properly by removing the detector from the circuit and inserting a 1000MΩ test resistor in its place. The parts kit in the tackle box included with your GC under the red lid contains a 1000MΩ resistor for this test. Turn the ECD current off. The anode and cathode connections are BNC connectors located on the GC chassis near the base of the ECD detector housing. Disconnect these two BNC connectors from the detector electronics, and install the 1000MΩ test resistor as a jumper between the center conductor in the anode BNC jack and the center conductor in the cathode BNC jack. Zero the data system signal. Turn the ECD current back on, and check the signal offset (observe the mV reading in the upper right area of the PeakSimple chromatogram window). With the test resistor in the detector's place, the signal offset should be 120-150mV with the standing current at 300. If the signal offset is pegged up or down (5000mV or 1500mV, respectively), there is a problem with your ECD detector electronics. Try turning off the GC power for at least 30 seconds, with the test resistor still in place, then turning it back on to see if the signal offset still indicates a problem. If the signal offset is at zero with the test resistor in place, check to make sure that you are looking at the correct detector channel. If you are observing a signal offset of zero in the ECD detector channel, call technical support.

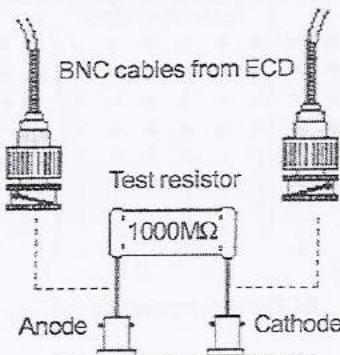
The ECD anode and cathode  
are connected to the ECD  
amplifier via BNC cables



Anode and cathode  
BNC connectors



ECD electronics test

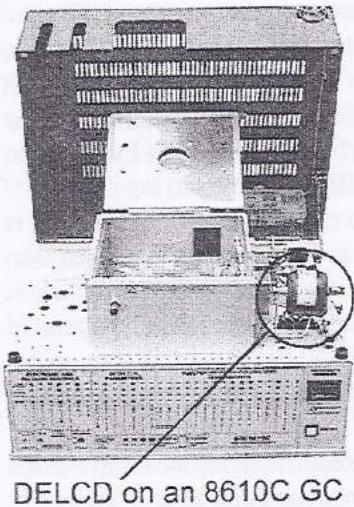


2. Operate the ECD on make-up gas only by disconnecting the column from the ECD. With the standing current still set at 300, observe the signal offset and noise. If it drops, then the problem is being introduced into the GC and ECD by the carrier gas through the column.

Tip: In most situations, the ECD will be used to detect sample components that are reactive with metal. Use glass, fused silica, or fused silica lined metal capillary columns to help avoid reactive sites and ghost peaks.

## DETECTORS

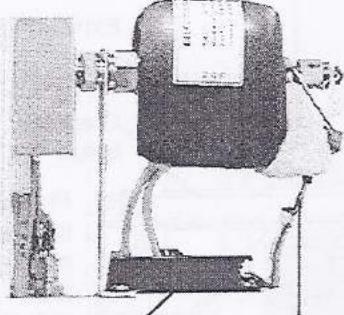
### Dry Electrolytic Conductivity Detector - DELCD



DELCD on an 8610C GC

#### DELCD - À la carte

Close-up of the same  
DELCD detector

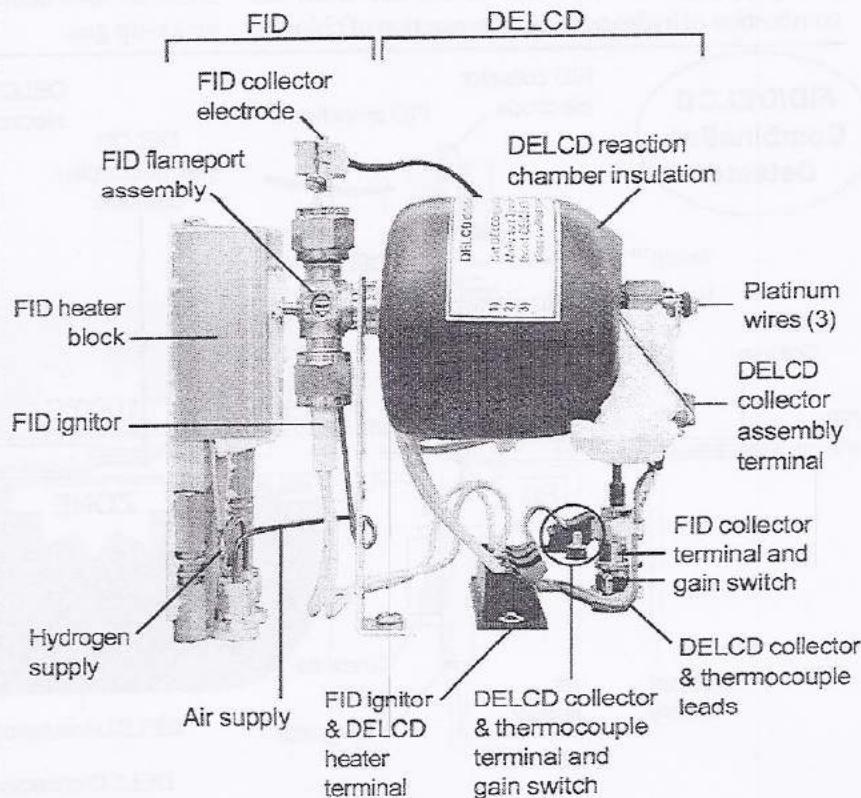


DELCD  
heater  
terminal  
DELCD collector  
& thermocouple  
leads

#### Overview

The Dry Electrolytic Conductivity detector, or DELCD, is selective to chlorinated and brominated molecules. It differs from the traditional wet ELCD in that it does not use a solvent electrolyte, and the reaction products are detected in the gaseous phase. The SRI DELCD is available alone or in combination with the FID detector. On its own, the detection limits of the DELCD are in the low ppb range. In combination with the FID, its detection limits are in the low ppm range. The FID/DELCD combination enables the operator to reliably identify hydrocarbon peaks detected by the FID as halogenated or not. Because the DELCD operates at 1000°C, it can tolerate the water-saturated FID effluent, measuring the chlorine and bromine content simultaneously with the FID measurement of the hydrocarbon content. All hydrocarbons are converted by the FID flame to CO<sub>2</sub> and H<sub>2</sub>O prior to reaching the DELCD, thus preventing contamination of the DELCD by large hydrocarbon peaks.

#### FID / DELCD Combo Detector



## DETECTORS

### Dry Electrolytic Conductivity Detector - DELCD

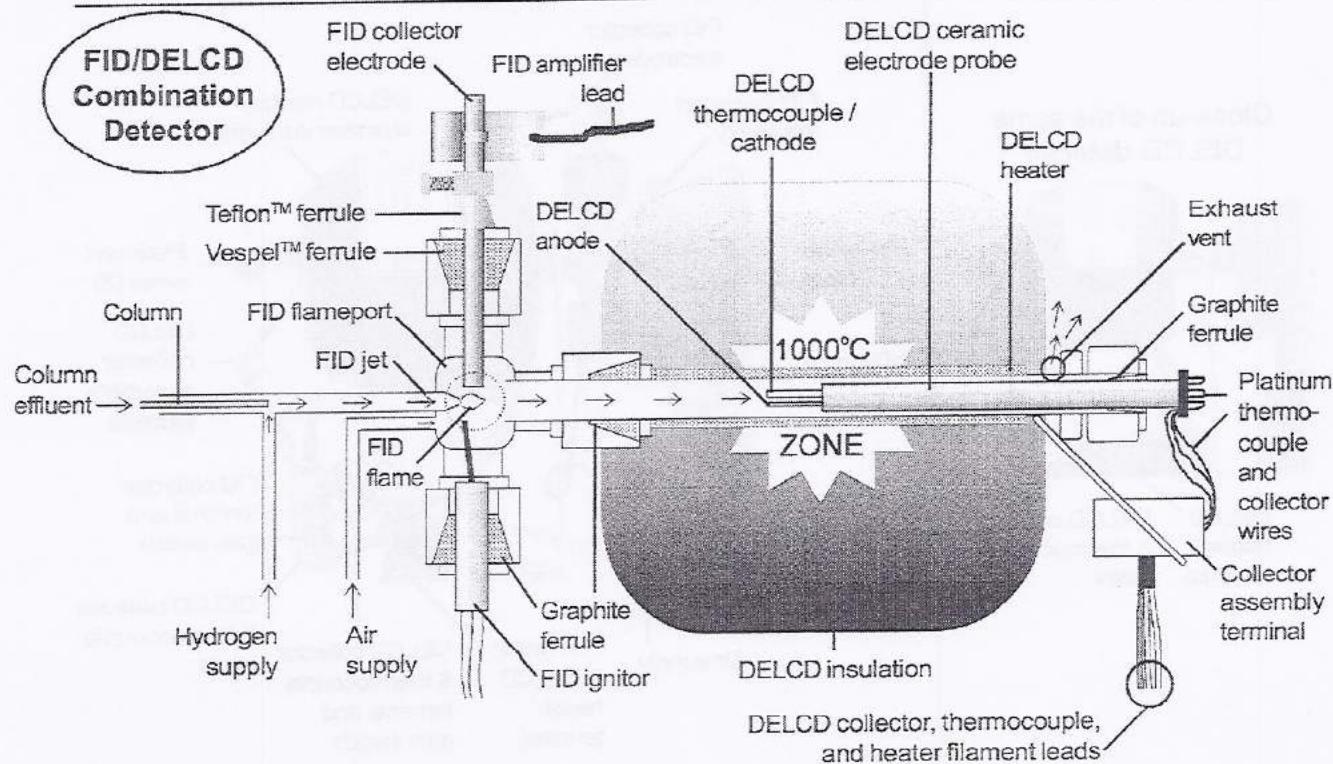
#### Theory of Operation

The DELCD consists of a small ceramic tube—the DELCD reactor—heated to 1000°C. Inside the reactor, a platinum thermocouple measures the detector temperature, and a nichrome collector electrode measures the conductivity of the gases flowing through the DELCD. The detector response is dependent upon its temperature. Therefore, the control circuit must maintain the temperature, within a fraction of a degree, at 1000°C.

When combined with the FID detector, the DELCD is mounted on the FID exhaust. Column effluent enters the FID flame where hydrocarbons are ionized and combusted. Electrons freed in the ionization process are collected by the FID collector electrode, which has an internal diameter of 1mm (0.040"). Due to its small I.D., the collector electrode acts as a restrictor, splitting the FID exhaust gases so that it takes about half of the flow, and the remainder is directed to the DELCD. The FID exhaust gases consist of un-combusted hydrogen and oxygen, nitrogen, and water and carbon dioxide from the combustion of hydrocarbons. The reaction of chlorine

or bromine and hydrogen forms HCl and HBr, and the reaction of chlorine or bromine and oxygen forms ClO<sub>2</sub> and BrO<sub>2</sub>. The DELCD detects the oxidized species of chlorine and bromine, such as ClO<sub>2</sub> and BrO<sub>2</sub>. It does not detect the acids HCl or HBr like the conventional wet ELCD. In the hydrogen rich effluent from the FID flame, the chlorine and bromine preferentially react with hydrogen (or the hydrogen in water) to make HCl-HBr. Given equal availability of hydrogen and oxygen molecules, a chlorine atom is 100 times more likely to react with the hydrogen than the oxygen. Therefore, the FID/DELCD combination is 100 times less sensitive than the DELCD operated with the FID off. The SRI FID/DELCD is operable as a combination detector, as an FID only, or as a DELCD only.

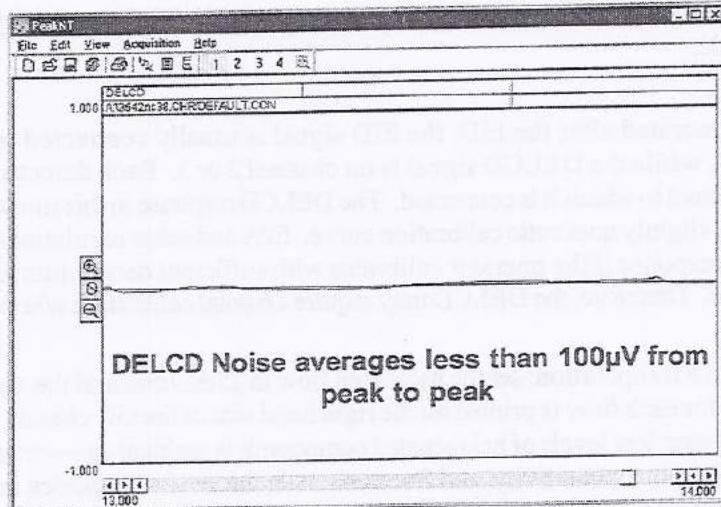
A DELCD only detector receives the sample laden carrier gas directly from the column or from a non-destructive detector outlet, like the PID. It is mounted on the heater block on the column oven wall so that the column effluent is maintained at a temperature consistent with the analysis. This type of high sensitivity DELCD uses helium or nitrogen carrier gas and air make-up gas.



# DETECTORS

## Dry Electrolytic Conductivity Detector - DELCD

### Expected Performance



#### DELCD Noise Run

Column: 15m MXT-VOL  
 Carrier: helium @ 10mL/min  
 DELCD gain: LOW  
 DELCD heater block temp: 150°C  
 DELCD reactor setpoint: 260

Temperature program:

Initial	Hold	Ramp	Final
80°C	20.00	0.00	80°C

#### FID / DELCD Combo Test Run

Sample: 1µL 100ppm BTEX Plus

Column: 15m MXT-VOL

Carrier: helium @ 10mL/min

Temperature program:

Initial	Hold	Ramp	Final
40°C	2.00	15.00	240°C

DELCD gain: LOW

DELCD heater block temp: 150°C

DELCD reactor setpoint: 260

DELCD Results:

Component	Retention	Area
TCE	3.483	463.5080
PCE	5.416	532.2900
Bromoform	7.016	759.6650
Total		1755.4630

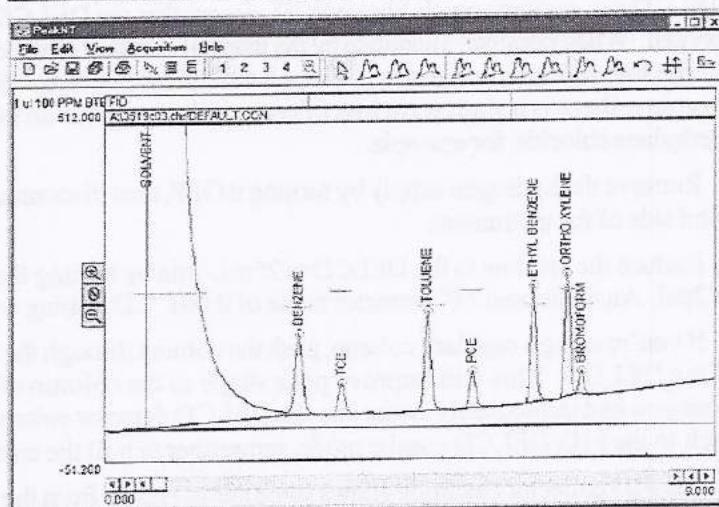
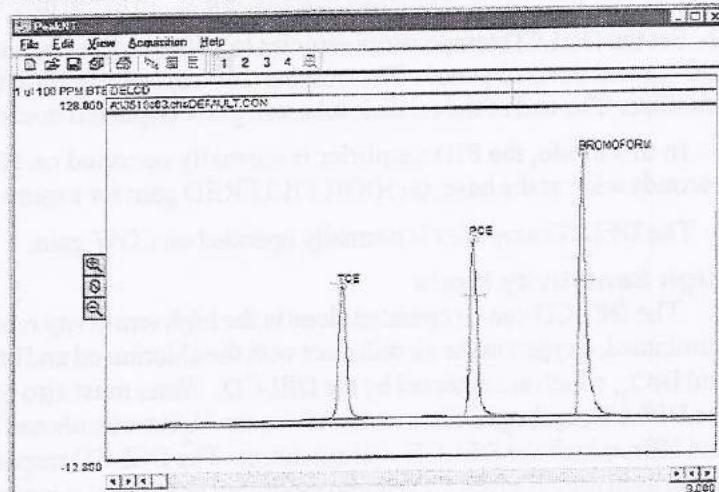
FID gain: HIGH

FID temp: 150°C

FID ignitor: -400

FID Results:

Component	Retention	Area
Solvent	0.600	144406.8420
Benzene	2.850	1074.0740
TCE	3.500	378.3505
Toluene	4.766	1109.8590
PCE	5.416	364.5700
Ethyl Benzene	6.316	1103.6370
Ortho Xylene	6.800	1135.6855
Bromoform	7.016	220.3325
Total		149793.3505



## DETECTORS

### Dry Electrolytic Conductivity Detector - DELCD

#### ***General Operating Procedure***

The FID/DELCD combination detector can be operated in the Combo Mode, the High Sensitivity Mode (DELCD only), or the FID only mode.

##### **Combo Mode**

In the Combo Mode, the DELCD is operated after the FID; the FID signal is usually connected to Channel 1 on the PeakSimple data system, while the DELCD signal is on channel 2 or 3. Each detector amplifier is factory labeled with the data channel to which it is connected. The DELCD response in this mode is useable from 1 to 1000 nanograms with a slightly quadratic calibration curve. EPA and other regulations allow the use of detectors with non-linear response if the operator calibrates with sufficient data points to accurately model the detector response curve. Therefore, the DELCD may require a 6 point calibration where 5 point calibration is normally required.

1. Set the hydrogen and air flows for normal FID operation: set the hydrogen flow to 25mL/min and the air flow to 250mL/min. The pressure required for each flow is printed on the right hand side of the GC chassis. (NOTE: If you're using a built-in air compressor, low levels of halogenated compounds in ambient air—even levels below 1 ppm—can cause the DELCD to lose sensitivity, and fluctuations in the level of organics in ambient air may cause additional baseline noise. To avoid this, use clean, dry tank air.)
2. Set the DELCD temperature setpoint to 260 by adjusting the appropriate trimpot on the top edge of the GC's front control panel. The number 260 represents 1000°C; the DELCD will heat to about 254 and stabilize. The end of the ceramic tube will glow bright red due to the high temperature.
3. In this mode, the FID amplifier is normally operated on HIGH gain or, if the peaks are more than 20 seconds wide at the base, on HIGH FILTERED gain for a more quiet baseline.
4. The DELCD amplifier is normally operated on LOW gain.

##### **High Sensitivity Mode**

The DELCD can be operated alone in the high sensitivity mode by eliminating hydrogen. With hydrogen eliminated, oxygen in the air will react with the chlorinated and brominated molecules at 1000°C to form ClO<sub>2</sub> and BrO<sub>2</sub>, which are detected by the DELCD. Water must also be eliminated; at the high temperatures inside the DELCD, hydrogen disassociates from the H<sub>2</sub>O molecule and becomes available as a reactant to form HCl and HBr, which the DELCD will not detect. The DELCD response curve is quadratic in the high sensitivity mode as in the FID/DELCD combo mode, but sensitivity is increased by 100 to 1000 times. In this mode, the DELCD can perform much like an ECD, except that the DELCD is more selective for halogens and blind to oxygen. When possible, quantitate by the internal standard method, using a chlorinated/brominated compound for the internal standard peak. Although the DELCD will not be damaged by large quantities of chlorine/bromine, there is a short term loss of sensitivity for about an hour following the injection of 1µL of pure methylene chloride, for example.

1. Remove the hydrogen supply by turning it OFF, then disconnecting it at the GC's inlet bulkhead on the left hand side of the instrument.
2. Reduce the air flow to the DELCD to 25mL/min by turning the the air pressure trimpot setpoint down to 1 or 2psi. An additional 24" restrictor made of 0.001" I.D. tubing would be useful for fine pressure adjustment.
3. If you're using a capillary column, push the column through the FID jet until it just enters the ceramic tubing of the DELCD. This will improve peak shape as the column effluent will be discharged into the flowing airstream and immediately swept into the DELCD detector volume by the air make-up gas. (When switching back to the FID/DELCD combo mode, remember to pull the column back into the FID jet.)
4. The FID collector electrode allows some gas to escape from the FID combustion area, which is undesirable for the high sensitivity mode. Remove the FID collector electrode and replace it with a 1/4" cap fitting.

## DETECTORS

### Dry Electrolytic Conductivity Detector - DELCD

#### *General Operating Procedure continued*

##### **FID/DELCD - FID Only**

1. Remove the DELCD heater wires from the push terminals. Remove the three DELCD collector and thermocouple wires (yellow, white and red) from the screw terminals.
2. Disconnect the DELCD detector assembly from the FID exhaust by using a wrench to loosen the 1/4" Swagelok fitting securing the two detector parts together.
3. Use a cap nut to seal the DELCD connection on the FID flameport.
4. Set the FID amplifier gain switch to HIGH for most hydrocarbon applications. If peaks of interest go off the scale (greater than 5000mV), set the gain to MEDIUM. When peaks of interest are 20 seconds wide or more at the base and extra noise immunity is desired, set the gain switch to HIGH (filtered). This setting broadens the peaks slightly.
5. Set the FID hydrogen flow to 25mL/min, and the FID air supply flow to 250mL/min. The approximate pressures required are printed in the gas flow chart on the right-hand side of the GC.
6. Ignite the FID by holding up the ignitor switch for a couple of seconds until you hear a small POP. The ignitor switch is located on the front panel of your SRI GC under the "DETECTOR PARAMETERS" heading (it is labelled vertically: "FLAME IGNITE").
7. Verify that the FID flame is lit by holding the shiny side of a chromed wrench directly in front of the collector outlet. If condensation becomes visible on the wrench surface, the flame is lit.

##### **DELCD Only**

1. Set the helium carrier gas flow to 10mL/min and the air make-up flow to 25mL/min. Clean, dry tank air helps to obtain the best achievable DELCD sensitivity and signal stability.
2. Set the DELCD reactor temperature setpoint to 260 (= 1000°C) by adjusting the trimpot on the top edge of the GC's front control panel. The DELCD will heat to about 254 and stabilize. The ceramic tube will glow bright red from the heat.
3. By adjusting the appropriate trimpot, set the thermostatted DELCD heater block temperature to 25°C higher than the "Final" temperature you have entered in the temperature program.
4. The DELCD amplifier is normally operated on LOW or MEDIUM gain.

## **DETECTORS**

### **Dry Electrolytic Conductivity Detector - DELCD**

---

#### ***Troubleshooting and Maintenance***

##### **Installing the Spare DELCD Cell**

Each SRI DELCD detector is shipped with a spare DELCD cell. Because the DELCD heater operates close to 1000°C, it will burn out and fail eventually. Follow the instructions below to remove the old cell and install the new one.

1. With the GC power OFF, remove the DELCD heater wires (2) from the push terminals and the DELCD thermocouple and collector wires (3) from the screw terminals.
2. Remove the DELCD cell by using a wrench to loosen the 1/4" fitting that secures it on the FID exhaust port or on the heater block. You may have to hold the insulation aside to freely access the fitting; it is soft and may be compressed by hand.
3. Position the new cell on the fitting with the label facing up, as the DELCDs are shown on the **Overview** page. Be sure to push the DELCD cell all the way into the FID.
4. Secure the new DELCD cell into place by tightening with a wrench the fitting that holds it onto the FID exhaust or the heater block.
5. Carefully lower the red lid to make sure that it does not touch the DELCD cell; the cell will crack if the lid hits it. There should be at least 0.5" of clearance between the red lid and the edge of the DELCD cell.
6. Sensitivity may improve for the first 24 hours of operating time with the new cell installed.