

# DETECTORS

## Dry Electrolytic Conductivity Detector - DELCD

### Overview

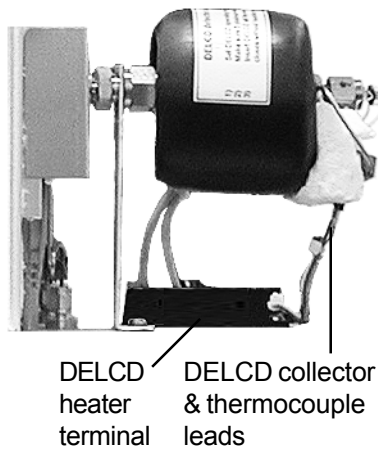
The Dry Electrolytic Conductivity detector, or DELCD, is selective to chlorinated and brominated molecules. It differs from the traditional wet ELCD in that it does not use a solvent electrolyte, and the reaction products are detected in the gaseous phase. The SRI DELCD is available alone or in combination 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.



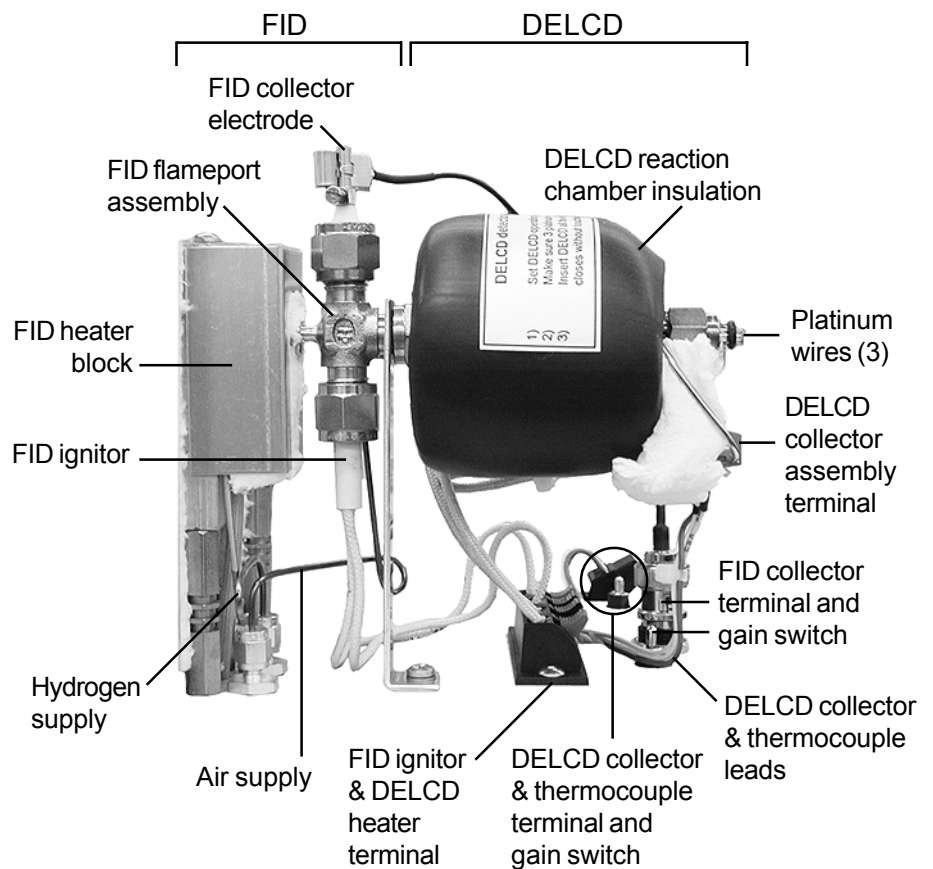
DELCD on an 8610C GC

### DELCD - À la carte

Close-up of the same DELCD detector



### FID / DELCD Combo Detector



# DETECTORS

## Dry Electrolytic Conductivity Detector - DELCD

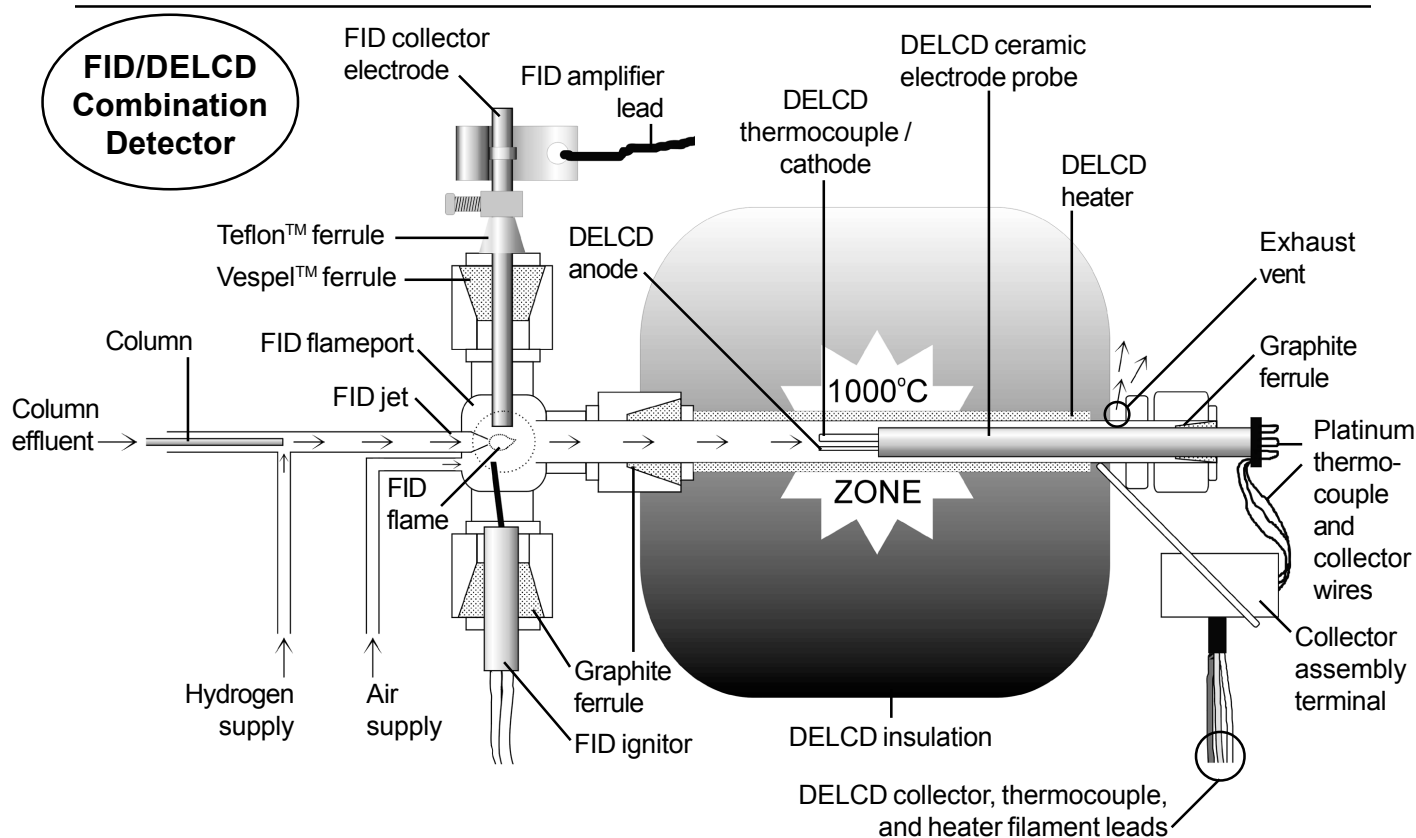
### Theory of Operation

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.

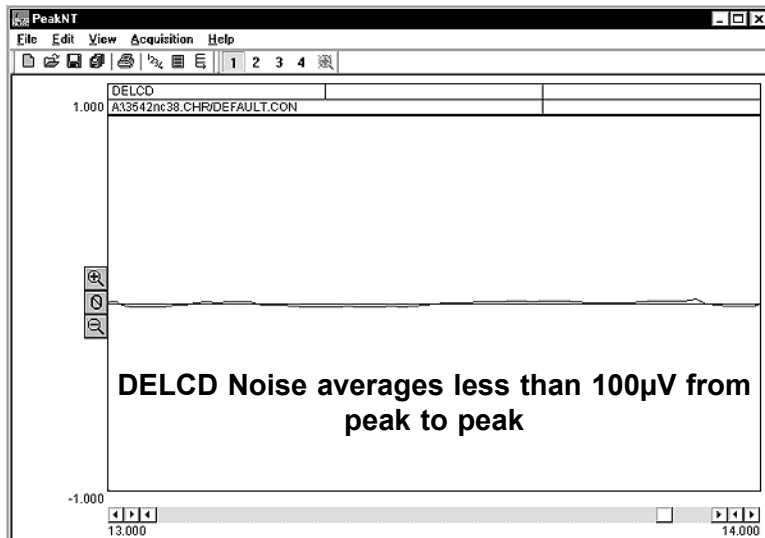
A DELCD only detector receives the sample laden carrier gas directly from the column or from a non-destructive detector outlet, like the PID. It is mounted on the heater block on the column oven wall so that the column effluent is maintained at a temperature consistent with the analysis. This type of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



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## 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

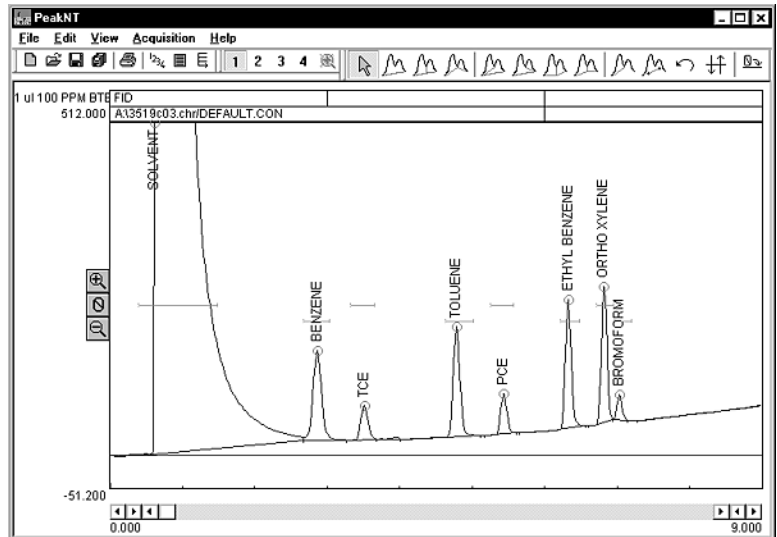
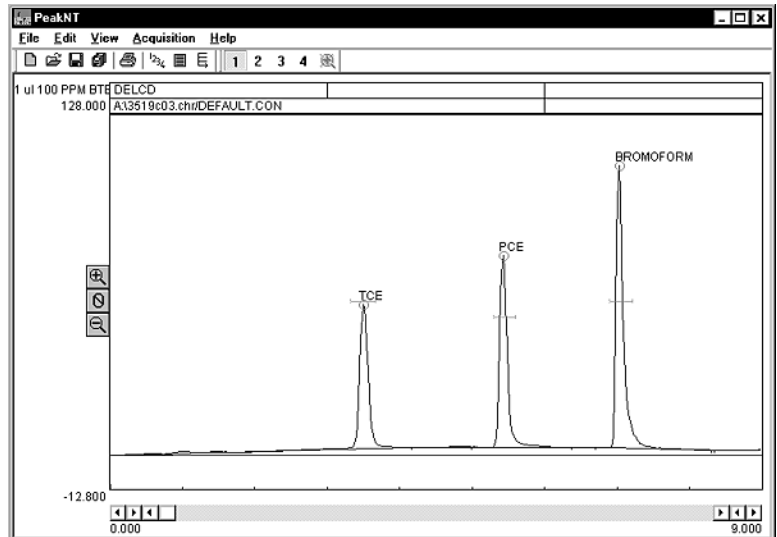
DELCD Results:

Component	Retention	Area
TCE	3.483	463.5080
PCE	5.416	532.2900
Bromoform	7.016	759.6650
<b>Total</b>		<b>1755.4630</b>

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
<b>Total</b>		<b>149793.3505</b>



# DETECTORS

## Dry Electrolytic Conductivity Detector - DELCD

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### *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 1ppm—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  $\text{ClO}_2$  and  $\text{BrO}_2$ , which are detected by the DELCD. Water must also be eliminated; at the high temperatures inside the DELCD, hydrogen disassociates from the  $\text{H}_2\text{O}$  molecule and becomes available as a reactant to form  $\text{HCl}$  and  $\text{HBr}$ , 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 1  $\mu\text{L}$  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

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### *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

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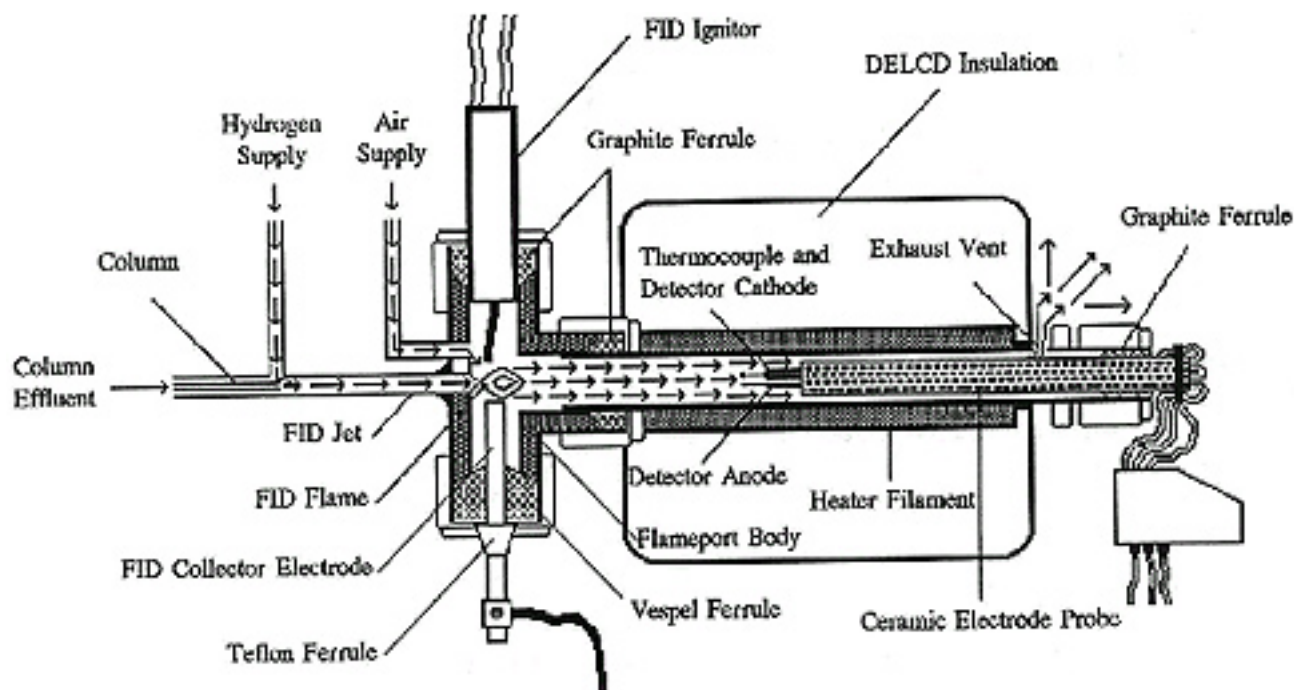
### *Troubleshooting and Maintenance*

#### **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.

## DETECTORS FID/DELCD



As diagrammed above, the sample enters the FID flame from the column where hydrocarbons are ionized and combusted. Electrons liberated in the ionization are collected by the FID collector electrode. About half the gas effluent (carrier gas + hydrogen + air + combustion products) flows out through the FID collector electrode which has an internal diameter of .040 (1 mm.). The restriction caused by the small collector i.d. splits the flow of exhaust gases so that the other half of the gases pass through the DELCD. The DELCD consists of a small ceramic tube which is heated to 1000°C. In the center of the heated tube is a platinum thermocouple which measures the temperature and a DELCD collector electrode which measures the conductivity of the gases flowing through the DELCD. Since the response is very dependent on the temperature, the control circuit must maintain the temperature within a fraction of a degree at 1000°C.  $\text{ClO}_2\text{-BrO}_2$  exhibits extremely high conductivity at 1000°C. So the DELCD actually responds to the  $\text{ClO}_2\text{-BrO}_2$  concentration of the gases in the FID exhaust. Because other molecules are not detected, the DELCD is almost completely selective for chlorine and bromine. Fluorine and iodine are not well detected.

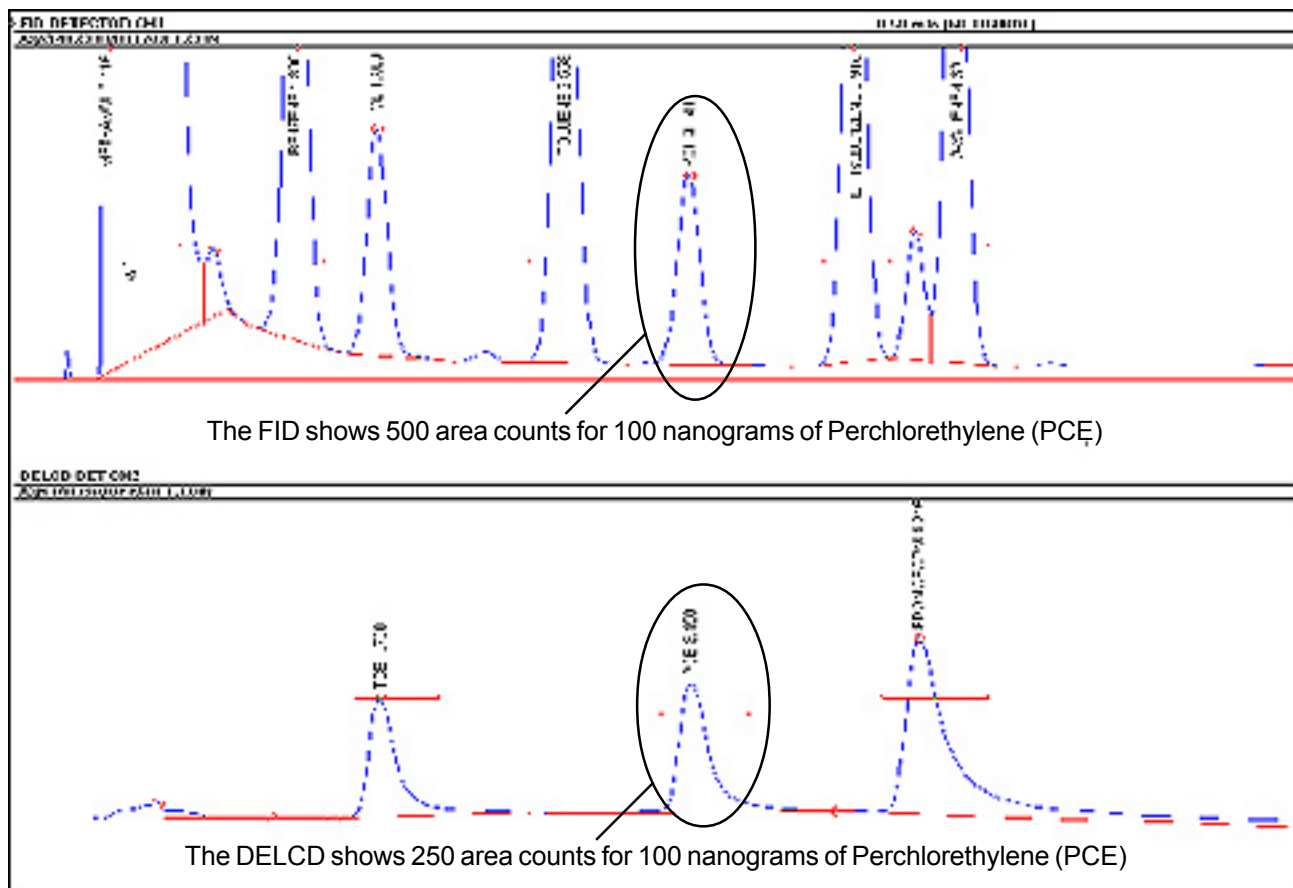
# DETECTORS

## FID/DELCD

### *Operating the FID/DELCD in the Combo mode*

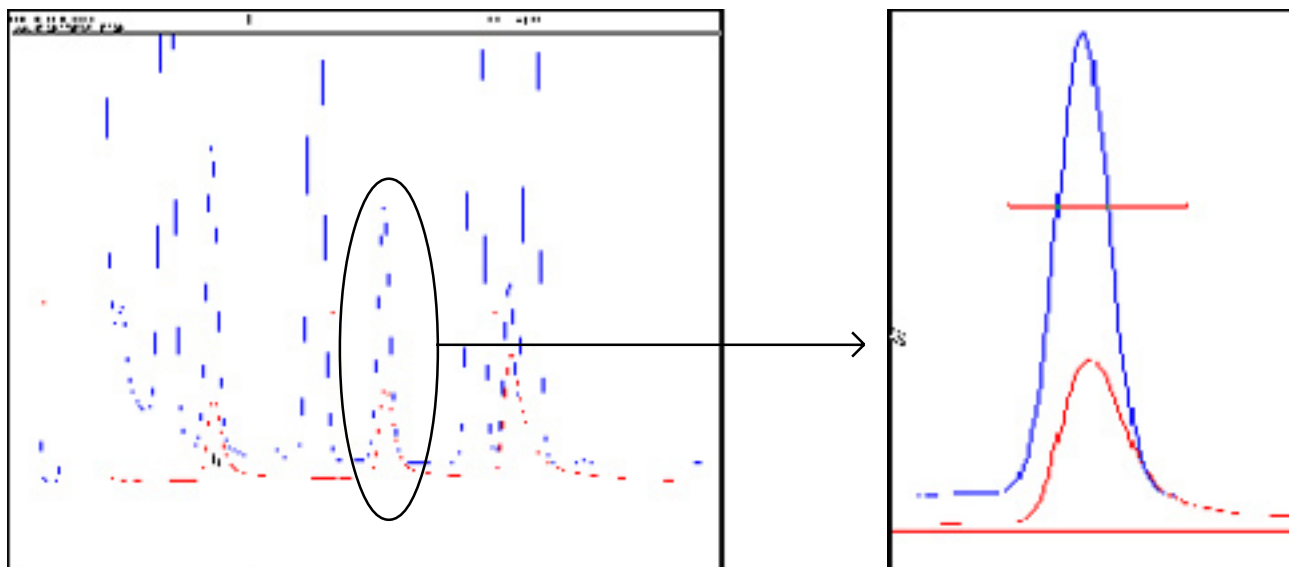
In the combo mode, the DELCD is operated after the FID. The FID signal is usually connected to Channel 1 on the PeakSimple data system. The DELCD signal may be on Channel 2 or 3. Each detector amplifier is labeled at the factory with the data channel to which it has been connected. Detector signals may be connected to any available data channel by simply attaching the white and black signal wires to the screw terminals on the A/D board inside the GC.

- 1) Set the FID hydrogen and air flows for normal FID operation. This is typically 25 ml/min hydrogen (corresponds to 25 psi) and 250 ml/min air (typically 6 psi). The exact pressure required for each flow is labeled on the GC's right hand side.
- 2) Set the DELCD temperature setpoint to 260 using the front panel adjustments. This number actually represents 1000°C. The DELCD will heat up to about 254 and stabilize. The quartz collector electrode will appear a bright red color due to the 1000C temperature.
- 3) In the FID/DELCD combo mode, the FID is normally operated on high gain or on hi-filtered gain if the peaks are more than 10 second wide at the base. The hi-filtered gain position is identical to the high gain except that extra noise filtering results in a quieter baseline. The DELCD amplifier is normally operated on low gain. In this configuration the FID and DELCD produce approximately the same response to chlorinated peaks such as TCE ( same peak area counts ). The FID will generate approximately 4 area counts per nanogram injected on column while the DELCD will generate 2-4 area counts per nanogram of chlorinated hydrocarbon. ( see example chromatogram below ).





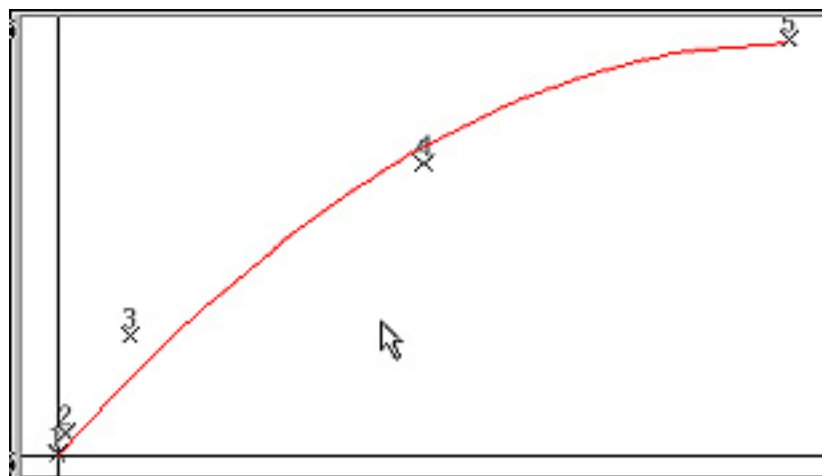
## Operating the FID/DELCD in the Combo mode



DELCD peak overlaid on FID peak for PCE, then expanded for clarity. The smaller peak is the DELCD response.

- 1) As shown in the chromatogram above, the DELCD peak for PCE occurs at the same time as the FID peak for PCE. Notice that the DELCD peak exhibits a little bit of tailing compared to the FID response.
- 2) In the FID/DELCD combo mode, the minimum detectable amount is approximately 1 nanogram. Assuming a 1 microliter injection, this translates into approximately 1 ppm. The exact detection limit will depend on the analyte molecule ( how much chlorine/bromine in the compound ) and the chromatographic conditions. A sharp peak is always more detectable than a short fat peak.
- 3) The detection limit will be worse when using the built-in air compressor for FID/DELCD flame combustion instead of clean dry tank air. While the built-in air compressor is useful and convenient, low levels of halogenated compounds in the ambient air ( even levels below 1 ppm ) cause the DELCD to lose sensitivity, and fluctuations in the level of organics in the ambient air may cause additional baseline noise.
- 4) In the FID/DELCD mode the DELCD response 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 as long as the operator calibrates with sufficient data points to accurately model the detector response curve. Where a 5 point calibration would normally be required, the DELCD may demand a 6 point calibration.

The DELCD calibration curve shown at right illustrates the quadratic response from 1–1000 nanograms of TCE injected



## DETECTORS

### FID/DELCD

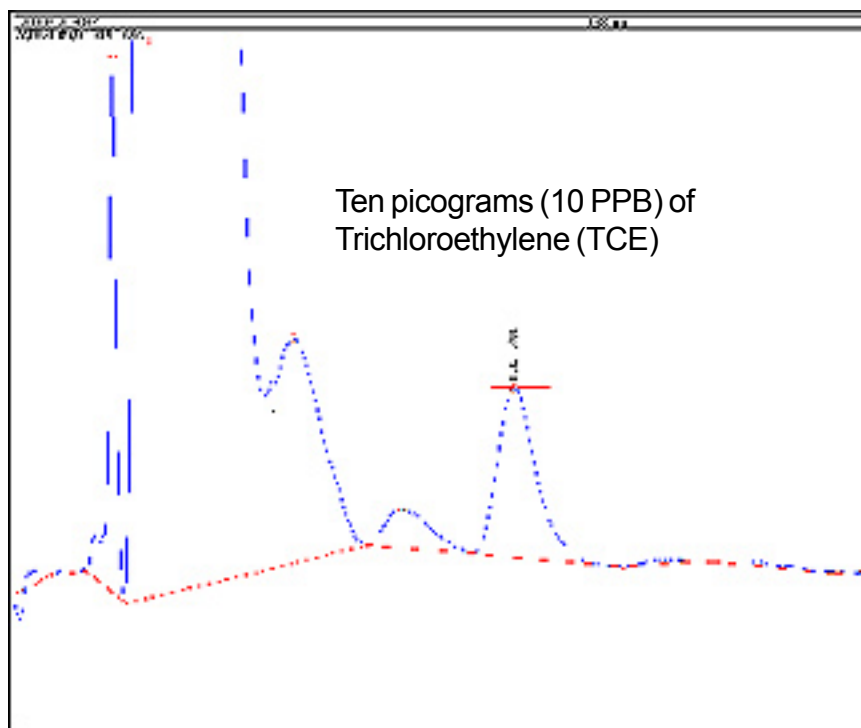
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#### ***Operating the FID/DELCD in the high sensitivity DELCD only mode***

- 1) The DELCD can be operated in a high sensitivity mode by eliminating the hydrogen from the reactions which lead up to the detection of the  $\text{ClO}_2\text{-BrO}_2$ . Because the chlorine/bromine atoms prefer to react with hydrogen to form non-detectable  $\text{HCl-HBr}$ , than with oxygen to form detectable  $\text{ClO}_2\text{-BrO}_2$  by a factor of 100-1000 to 1, eliminating the hydrogen improves the DELCD sensitivity by at least 100 times. Water must also be eliminated as at the high temperatures inside the DELCD, hydrogen becomes dissociated from the  $\text{H}_2\text{O}$  molecule and available as a reactant. In practice, this means turning off the hydrogen and using clean dry tank air (not the built-in air compressor).
- 2) Remove the hydrogen supply from the GC by disconnecting the hydrogen supply at the GC's inlet bulkhead on the left hand side of the instrument. Reduce the air flow to the DELCD to 50 ml/min by turning the air pressure setpoint down to 1-2 psi. An additional air flow restrictor consisting of 12" of .067 tubing (1/16", 1.58mm) with an internal diameter of .010 (0.25mm) can easily be added to the air supply immediately below the detector to enable the flow to be controlled more precisely at higher pressures. With the extra restrictor installed a pressure setpoint of 10 psi will deliver an air flow of approximately 50 ml/min.
- 3) If using a capillary column, push the column through the FID jet until it just enters the ceramic tubing of the DELCD. This will improve the peak shape somewhat because the column effluent will be discharged into the flowing airstream and will be immediately swept into the DELCD detector volume. When switching back to FID/DELCD combo mode remember to pull the column back into the FID jet.
- 4) Remove the FID collector electrode and replace it with a 1/4" cap fitting. The FID collector electrode allows some gas to escape from the FID combustion area, and this is not desirable when operating in the high sensitivity mode.

The DELCD chromatogram shown at right illustrates the response to 10 picograms (1ul of 10 PPB) of TCE in the high sensitivity mode.

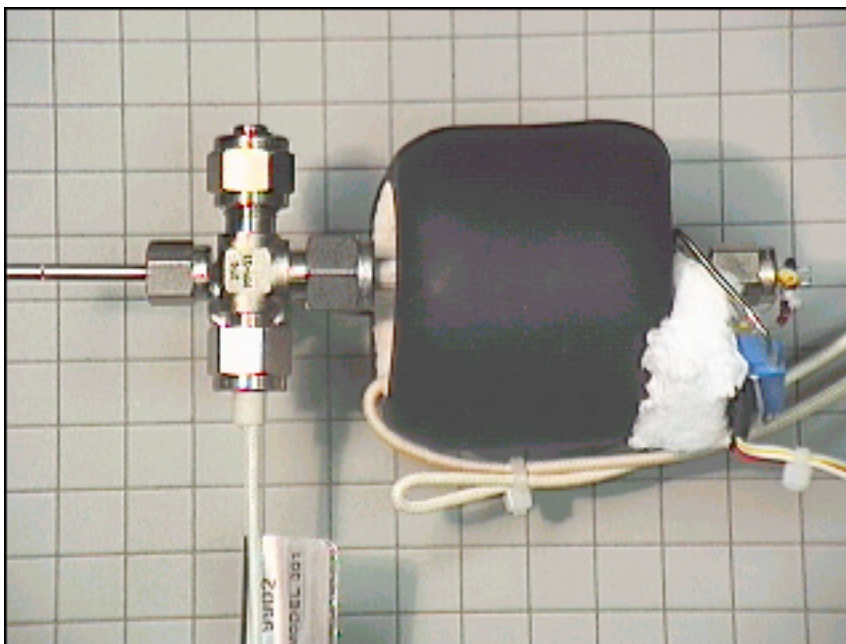
Note that in high sensitivity mode, there is some response to the methanol solvent.



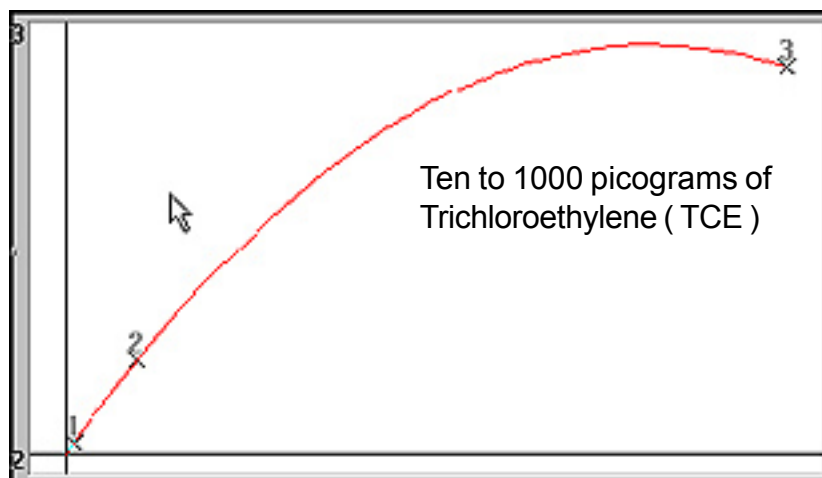
## *Operating the FID/DELCD in the high sensitivity DELCD only mode*

The FID/DELCD detector is shown at right configured for the high sensitivity mode.

The collector electrode is removed and a 1/4" cap installed instead.



- 1) Just as the DELCD response curve is quadratic in the FID/DELCD combo mode, the response is also quadratic in the high sensitivity mode, but sensitivity is increased by 100-1000 times. In the high sensitivity mode the DELCD is most useful in the range of 1-1000 picograms which assuming a 1 microliter injection translates into 1-1000 PPB.
- 2) In the high sensitivity mode, the DELCD can perform much like an Electron Capture Detector (ECD) except that the DELCD is more selective for halogens and blind to oxygen.
- 3) Although the DELCD will not be damaged by large quantities of chlorine/bromine, there is a short term loss of sensitivity for an hour or so following the injection of 1  $\mu$ l of Methylene Chloride for example.
- 4) When possible quantitate by the internal standard method, using a chlorinated/brominated compound for the internal standard peak. Using an internal standard will correct for changes in the DELCD detector's response.



DELCD linearity in high sensitivity mode is shown at right from 10 to 1000 picograms (10-1000PPB).

At levels above 10 nanograms, the detector is saturated.