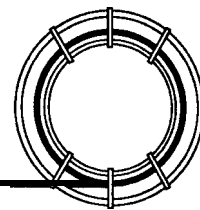


Hints for the Capillary Chromatographer



Using Electrolytic Conductivity Detectors

The electrolytic conductivity detector (ELCD) was developed in the early 1960's for the detection of organics in aqueous solutions. The ELCD is a highly selective, destructive detector for organic molecules containing fluorine, chlorine, bromine, nitrogen, and sulfur. It can be operated in three different modes: halogen, nitrogen, or sulfur. The ELCD is extensively used in the environmental field for the analysis of halogenated organics compounds such as those monitored in EPA Methods 502.1, 502.2, 601, 602, 8010, and 8021. It can also be used for various other environmental applications, where compounds containing nitrogen, sulfur, or chlorine are of interest, such as organochlorine pesticides, PCBs, organophosphorus pesticides, and nitro-samines. It is also commonly used for pharmaceutical samples.

Detector Design and Operation

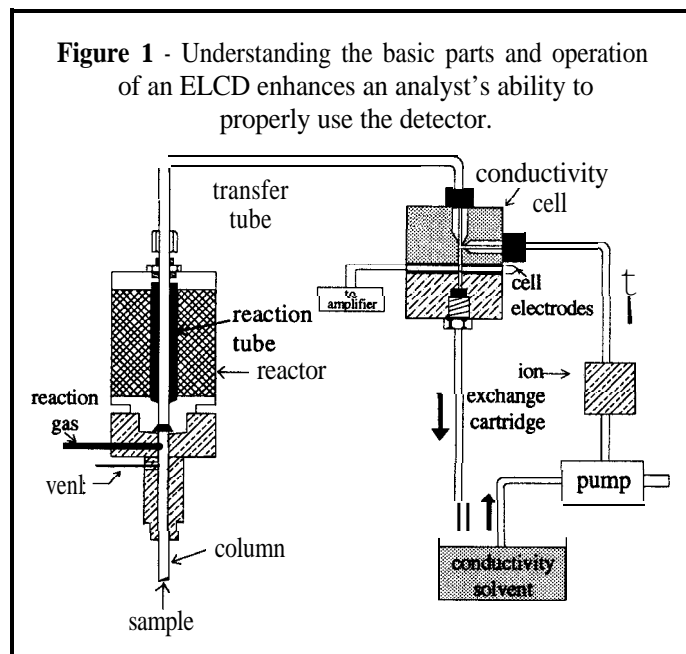
The ELCD operates as an electrical conductivity measuring device. However, it is the chemical aspect of the ELCD that provides the basis for its selectivity. The ELCD system consists of four main areas: reactor, conductivity cell, solvent, and electronic detection system.

Reactor tube

The reactor is the bridge between the capillary column and the conductivity cell. It consists of the detector base, reaction tube, and heating element. Organic compounds eluting from the capillary column, enter the detector base, combine with reaction gas, and proceed through a high temperature reaction tube usually made of nickel or fused silica. In the reaction tube, most of the compounds are pyrolyzed and, with the presence of an active gas such as hydrogen or oxygen, chemical reactions will occur. In the sulfur mode, the sample components are oxidized using O₂ reaction gas to form SO₂. In the halogen and nitrogen modes, the sample components are reduced using hydrogen as a reaction gas to form HCl, HBr, HF, or NH₃. The reaction tube acts as a catalyst to help speed up the reaction.

Conductivity cell

The reacted sample is then swept through a Teflon transfer line into the conductivity cell. In the conductivity cell, species formed in the reaction tube are dissolved and ionized in a deionized conductivity solvent flowing through the conductivity cell. Different solvents are used depending on the reaction mode. The change in the conductivity, caused by the reacted sample, is measured in the conductivity cell. Any species which is ionized during dissolution gives increased conductivity to the cell.



Solvent/ Resin Beds

In order to obtain a good response from the conductivity cell, the solvent flow and pH must be optimized. The sensitivity of the detector is inversely proportional to flow rate. Therefore, higher flow rates can be used where sensitivity is of little concern. The pH of the solvent is controlled by passing it through an ion exchange resin located in the solvent reservoir bottle. The proper resin mixture will provide the correct pH for the solvent. The halogen and sulfur modes are acidic and require an acidic solvent, whereas the nitrogen mode is basic and requires a basic solvent.

Detection Modes

Halogen compounds

The most common use of the ELCD is for the detection of volatile halocarbons in water. The ELCD reduces halogenated compounds in a nickel reaction tube (850-1000°C) to haloacids by mixing them with hydrogen reaction gas. Non-halogenated hydrocarbons are reduced to methane which is non-ionic. The haloacids are dissolved in n-propanol and the change in solvent conductivity is measured at the cell.

Sulfur compounds

In the sulfur mode, air is used as a reaction gas. Sulfur compounds are oxidized in a nickel reaction tube (800°C) producing SO₂ and/or SO₃. Hydrocarbons in the sample are

oxidized to form CO or CO₂. Pure methanol or a methanol/water mixture is the preferred solvent for this mode because it allows ionization of the sulfur compounds but minimizes the formation of CO₂. To eliminate the interference of haloacids from halogenated compounds in the sample, a scrubber is positioned after the reactor, but prior to the conductivity cell. The scrubber is made of stainless steel or copper tubing with several strands of silver wire positioned inside the tubing. The silver complexes with the haloacids and removes them from the sample stream.

Nitrogen compounds

The nitrogen mode reduces nitrogen containing compounds using hydrogen reaction gas in a nickel reaction tube (800°C) to form NH₃. The NH₃ will not completely ionize unless it is dissolved in an aqueous solution. Therefore, water containing a small amount of an organic solvent is recommended for greater sensitivity and better performance. A scrubber containing quartz thread is used for the nitrogen mode to remove other components from the sample.

Operating Hints

ELCD performance depends on the reactor, conductivity cell, and the solvent system. Because the reaction tube is the major part of the reactor, the tube should be replaced routinely. Hydrocarbons and column bleed can coat the inside of the reaction tube and decrease its catalytic activity. A drop in sensitivity, especially of brominated compounds, is a good indication the reaction tube needs to be replaced. Other factors, like baseline instability and ghost peaks, are also an indication the reaction tube may be fouled and requires replacement. A solvent vent, controlled by a solenoid valve, is located between the GC column and the reaction tube. This valve allows venting of the solvent to prevent premature fouling of the reaction tube. It may be necessary to condition a new reaction tube after replacement. Conditioning the tube with the reaction gas (H₂) flowing for 24 hours is recommended. Cooling the reactor before removing the capillary column from the detector is critical. If room air is allowed into the detector while the reactor is still hot, the nickel reaction tube will oxidize. An oxidized nickel reaction tube can result in sensitivity loss and tailing peaks.

The internal volume of the electrolytic conductivity cell is also important in determining ELCD performance. Older ELCDs have large cell volumes that were developed for use with packed columns operated at high flow rates. If these older detectors are used with capillary columns at low flow rates, excessive peak tailing will occur. Newer ELCDs have much smaller conductivity cells which significantly reduce peak tailing, even when operated at lower flow rates.

The Teflon transfer line, located between the reactor and the conductivity cell, requires cleaning and replacement depending on its usage. Clean the transfer line by rinsing with methanol or, for a more thorough cleaning, rinse with a 10% solution of HCl, followed by a methanol rinse. Dry the tubing before reinstalling it. With the time and effort required to clean the transfer line, it may be more cost effective to simply replace it.

Table I - Troubleshooting Hints for ELCDs

Symptom	Remedy
Noisy baseline	Clean transfer line from reactor to cell. Replace reaction tube. Use pure carrier gas and filters. Replace quartz insert.
Peak tailing	Clean conductivity cell/backflush. Increase reactor temperature. Replace reaction tube. Clean transfer line. Replace or cut 10cm off the detector end of the column.
Low response	Replace reaction tube. Clean or replace transfer line. Use correct solvent and replace if necessary. Optimize detector parameters.
High background	Incompatible column phase (F,N) Contaminated gases. Incorrect column installation. Condition column. Condition reaction tube.

Always use high purity solvents (HF¹LC grade for halogen mode) in the ELCD. The pH and background conductivity of the solvent are maintained by circulation through an ion-exchange resin. It is recommended to change the resin every six months. Problems often associated with the solvent reservoir may be sudden low or negative response, or baseline instability. It is important to maintain the proper solvent pH in the nitrogen mode to avoid the presence of negative peaks. The solvent may be slightly acidic due to trace amounts of CO₂. This can cause neutralization of low levels of NH₃, resulting in negative peaks. One way to avoid this problem is to totally exclude CO₂ from the solvent system by using nonpermeable tubing.

Table I lists some of the common problems experienced with ELCDs and troubleshooting hints.

Electrolytic conductivity detectors are excellent for environmental and pharmaceutical analyses due to their highly selective nature. Because of the selectivity of the ELCD, sample cleanup procedures do not have to be as stringent as with other detectors where interference can be a problem. However, because the ELCD is a more complex detector, frequent maintenance and optimization of detector flow rates is required. Attention to the basic operating hints, as outlined above, will result in a highly sensitive, reliable detection system.

References:

- Hill, Herbert and Dennis McMinn, ed., *Detectors for Capillary Chromatography*, John Wiley & Sons, New York, 1992.
- Buffington, Rosemary and Michael K. Wilson, *Detectors for Gas Chromatography - A Practical Primer*, Hewlett-Packard Co., Avondale, PA, 1991.