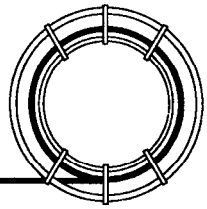
Hints for the Capillary Chromatographer



Using Electron Capture Detectors

Electron capture detectors (ECDs) are common GC detectors used to analyze compounds with electronegative functional groups such as nitroaromatics, halogens, and oxygenates. Many of these compounds are frequently encountered in analyses including pesticides, polychlorinated biphenyls, lead containing compounds, and clinical/forensic samples.

ECDs are very sensitive detectors providing accurate responses in the picogram and femtogram range. They are considered selective detectors because their response is not uniform and is very dependent on the individual component's affinity for electrons. Therefore, a polyhalogenated compound will have a much greater response than a monohalogenated compound.

Detector Operation

The ECD uses a radioactive source placed within the cell to emit beta particles. The carrier gas flows past the beta source and is ionized producing positive ions and a cloud of free electrons within the cell. These free electrons are captured by a positive electrode producing a stable background current which is amplified and used as a reference. When a sample component with an electron affinity enters the detector, it captures some of these electrons and decreases the current. This indicates the presence of the sample component within the detector. The ECD is the only common GC detector that uses a decrease in signal as a method of detection.

The ^{63}Ni pulsed detector is the most commonly used ECD. The ^{63}Ni foil contains a very small amount of radiation (usually less than 15 millicurie) and is sealed by the manufacturer inside the detector cell. Normally the GC manufacturer holds a general radiological license which covers their ECDs and a specific site license is not required by the NRC. To comply with NRC regulations, it is necessary to perform a radioactivity leak test every six months to verify the cell is not leaking radiation above the allowable limit. Arrangements can be made with the manufacturer or through an outside agency to obtain a leak test kit. *

Detector Gases

For proper ECD operation, the detector make-up gas must be ionizable. Helium and hydrogen, the two most common carrier gases used for capillary chromatography, do not readily ionize and, therefore, are not recommended as an ECD make-up gas. Since capillary column carrier gas flow rates are low (typically <10cc/min), an ionizable make-up gas can be used to produce the desired electron cloud. The make-up gas is added at high flow rates to produce a stable signal (Table I). The two most common make-up gases used with ECDs are nitrogen and 5% methane in argon (Ar/CH_4). Nitrogen gives better sensitivity than Ar/CH_4. However, Ar/CH_4 yields a greater dynamic range than nitrogen. Both nitrogen and Ar/CH_4 are not recommended as carrier gases with capillary columns and should only be used as make-up gases.

Operating Hints

Because ECDs are extremely sensitive detectors, it is imperative the entire GC system be absolutely leak-free. Otherwise oxidation of the ^{63}Ni foil will occur and increased noise, baseline drift, and decreased lifetime of the detector will result. The best way to check the system for leaks is with a thermal conductivity leak detector (TCD) (cat.# 21605 or 20130). TCDs are recommended over liquid leak detectors for capillary chromatographic systems because they are very sensitive, easy to use, and there is no risk of contamination. Using a liquid leak detector like Snoop@ can result in contamination of both the column and the detector if a leak is present. Even though the system is under positive pressure, liquid leak detectors can be drawn into the column at the leak point via the Venturi effect.

Moisture and oxygen traps are necessary for both the carrier gas and make-up gas or excessive detector noise will result. An indicating oxygen trap (cat.# 20624 or 20602) should be installed at the bulkhead inlet fitting to remove oxygen from

Table I
Operating Hints from Various Manufacturers

	Radiation Source	Detector Insertion Distance	Make-up Flow Rate
HP 5890	^{63}Ni	7.2cm (back of nut)	50-60ml/min.
Varian 3300/3400, 3600, 3700	^{63}Ni	13.2cm (back of nut) 11.5cm (back of nut)**	20-30ml/min.
Shimadzu 9A,14A,17A	^{63}Ni	9.0cm (tip of ferrule)	30-40ml/min.
PE Autosystem	^{63}Ni	6.5cm (back of nut)	30ml/min.

* Restek has been satisfied with the services of Detector Service Center (919)469-0259 and C.J. Bruyn & Co. (800)252-7896. Each wipe test costs approximately $20 to $25.
**metal column insertion distance

both the carrier gas and makeup gas lines. A molecular sieve trap (cat.# 20686) must be installed prior to the oxygen purifier to remove trace levels of water. Excessive noise and baseline instability will result if a molecular sieve trap is not used on an ECD, particularly if the GC does not come equipped with a small internal carrier/make-up gas line trap.* A hydrocarbon trap is not usually necessary since ECDs do not respond to hydrocarbon contamination. Also, be sure to use carrier gas and make-up gas regulators that are equipped with stainless steel diaphragms to avoid oxygen permeation.

Because ECDs are so sensitive, always precondition columns out of the detector. Install the column into the injector but not into the detector. Verify flow through the column and condition the column at the maximum test temperature for several hours, preferably overnight. Remember, the detector port must be capped to prevent air from oxidizing the ^{63}Ni foil. Before removing or installing a column into the ECD, always cool the detector below 100°C to prevent oxidation of the ^{63}Ni foil. Never *heat the ECD without a column installed or without capping the detector port!*

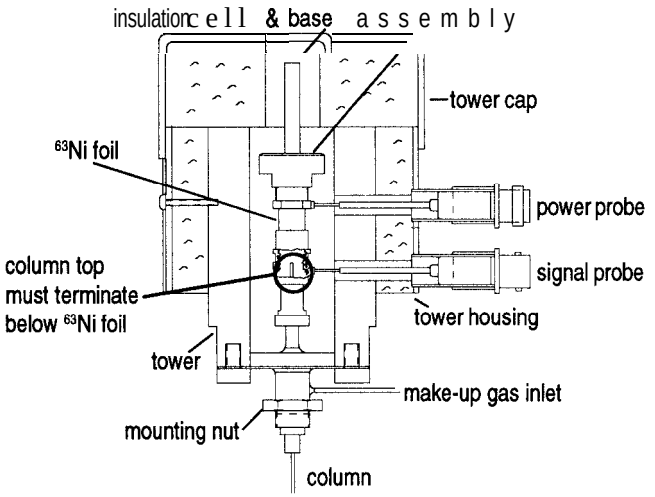
Detector Maintenance

Baseline instability or a high background signal is often an indication of a contaminated ECD cell.** With HP ECDs, a signal greater than 50 (500 Hz) indicates a contaminated system. A signal greater than 10 indicates contamination in Varian ECDs. Often, contaminants deposited on the radioactive foil can be removed by heating. For routine maintenance, thermal cleaning is recommended. To thermally clean an ECD, first cool the detector below 100°C, remove the column and cap off the detector port. Next, establish a make-up gas flow of 50 to 60 ml/min. and set the oven temperature to 250°C. For HP GCs, heat the ECD to 350°C for 3 to 12 hours. If the background signal continues to be high (>60), the detector should be returned to HP for cleaning. Varian recommends heating their ECD to 400°C for 6-12 hours. Monitor the output signal. It should initially increase in magnitude, then decrease. When the signal has reached a stable plateau, the foil has been cleaned as much as possible. Varian also suggests thermally cleaning their ECDs using hydrogen as a purging agent.7

Troubleshooting

Changes in sensitivity are sometimes related to the detector. A reduced response is often the result of an incorrect installation distance. It is critical that the column end terminates within the electron cloud located inside the cell. If the column end is installed too far into the detector and terminates above the cloud, or if the column is not installed far enough and terminates below the electron cloud, reduced response of sample components will be observed (Figure 1). Always install columns to the manufacturer's recommended insertion distance. Common detector insertion distances are shown in Table I.

Figure 1 - Adhere to manufacturer's insertion distances or optimize distance based on response.



Make-up gas flow also has a great impact on sensitivity. If the make-up gas flow is set improperly reduced sensitivity can result. Regularly check make-up gas flow and adjust if necessary. Set make-up gas flows according to the manufacturer's instructions.

Another common problem associated with electron capture detectors is caused by frequent heating and cooling of the detector when making changes to the system. The base screws and/or Vespel®/graphite ferrules can loosen with temperature changes. Always make sure all connections to the ECD are leak-free to prevent oxygen influx.

Once electron capture detectors are set up properly configured, they require little optimization. Remember, the ECD is a concentration dependent detector. Therefore, carrier gas flow rates must be kept constant and leaks eliminated. Since ECDs are very sensitive, they are easily affected by contamination. Molecular sieve and oxygen traps must be placed on all gas lines and changed on a regular basis. Every effort should be taken to prevent foil contamination which can lead to reduced sensitivity.

References:

1. ***Varian 3300/3400 Gas Chromatograph Operator's Manual,*** Vol. 2, Varian Associates, Inc. 1990.
2. ***HP 5890 Series II Reference Manual,*** Edition 2, Hewlett-Packard, October 1989.
3. Gas ***Chromatograph GC-14A Instruction Manual,*** Shimadzu Corporation.
4. Buffington, Rosemary and Wilson, Michael K., ***Detectors for Gas Chromatography -A Practical Primer,*** Hewlett-Packard Co., Avondale, PA, 1991.
5. Hill, Herbert and McMinn, Dennis, ed., Detectors for Capillary Chromatography, John Wiley & Sons, New York, 1992.
6. ***Perkin Elmer Auto System GC Operator's Manual,*** Perkin Elmer Corp. June 1991.

*Often excessive ECD noise or baseline instability can be traced to a contaminated internal trap. Routine replacement is highly recommended.
**Negative peaks in the baseline indicate an 0, leak present in the system. A positive baseline rise is often indicative of column or detector contamination.
†For more information on hydrogen cleaning, refer to the electron capture detector section of the Varian manual.