



Designation: E1698 – 95 (Reapproved 2005)

Standard Practice for Testing Electrolytic Conductivity Detectors (ELCD) Used in Gas Chromatography¹

This standard is issued under the fixed designation E1698; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers testing the performance of an electrolytic conductivity detector (ELCD) used as the detection component of a gas chromatographic system.

1.2 This practice is directly applicable to electrolytic conductivity detectors that perform a chemical reaction on a given sample over a nickel catalyst surface under oxidizing or reducing conditions and employ a scrubber, if needed, to remove interferences, deionized solvent to dissolve the reaction products, and a conductivity cell to measure the electrolytic conductivity of ionized reaction products.

1.3 This practice covers the performance of the detector itself, independently of the chromatographic column, in terms that the analyst can use to predict overall system performance when the detector is coupled to the column and other chromatographic system components.

1.4 For general gas chromatographic procedures, Practice E260 should be followed except where specific changes are recommended herein for the use of an electrolytic conductivity detector. For definitions of gas chromatography and its various terms see Practice E355.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*²

E260 Practice for Packed Column Gas Chromatography

¹ This practice is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and is the direct responsibility of Subcommittee E13.19 on Chromatography.

Current edition approved Sept. 1, 2005. Published September 2005. Originally approved in 1995. Last previous edition approved in 2000 as E1698 – 95 (2000). DOI: 10.1520/E1698-95R05.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

E355 Practice for Gas Chromatography Terms and Relationships

3. Significance and Use

3.1 Although it is possible to observe and measure each of the several characteristics of the ELCD under different and unique conditions, in particular its different modes of selectivity, it is the intent of this practice that a complete set of detector specifications should be obtained at the same operating conditions, including geometry, gas and solvent flow rates, and temperatures. It should be noted that to specify a detector's capability completely, its performance should be measured at several sets of conditions within the useful range of the detector. The terms and tests described in this practice are sufficiently general so that they may be used at whatever conditions may be chosen for other reasons.

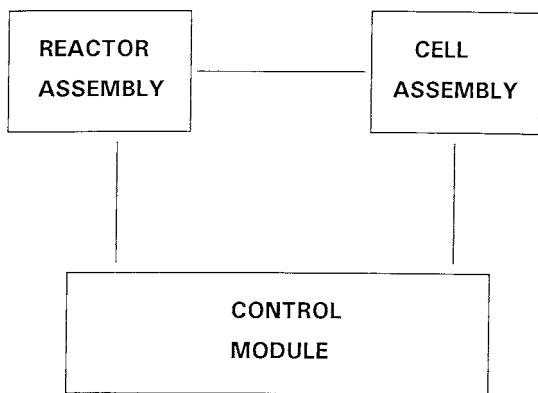
3.2 Linearity and speed of response of the recorder used should be such that it does not distort or otherwise interfere with the performance of the detector. Effective recorder response should be sufficiently fast so that it can be neglected in sensitivity of measurements. If additional amplifiers are used between the detector and the final readout device, their characteristics should also first be established.

4. Principles of Electrolytic Conductivity Detectors

4.1 The principle components of the ELCD are represented in Fig. 1 and include: a control module, a reactor assembly, and, a cell assembly.

4.1.1 The control module typically will house the detector electronics that monitor or control, or both, the solvent flow, reaction temperatures, and the conductivity detector cell. It can be functionally independent of the gas chromatography or, in some varieties, designed into the functional framework of the gas chromatograph. However, the reactor and cell assemblies are designed for specific models of gas chromatographs so it is important the proper components be assembled on the appropriate chromatographic equipment.

4.2 Fig. 2 is a block diagram representation of the GC/ELCD system. The electrolytic conductivity detector detects compounds by pyrolyzing those compounds in a heated nickel catalyst (housed in the reactor), removing interfering reaction products with a scrubber (if needed), dissolving the reaction



ELCD - PRINCIPAL COMPONENTS

FIG. 1 ELCD—Principal Components

products in a suitable solvent, and measuring the change in electrical conductivity using a conductivity detector cell. Other suitable non-catalytic reaction tubes can be used for more selective response characteristics. Using the conditions set forth in this practice, halogen (Cl, Br, I, F) compounds, nitrogen compounds, and sulfur compounds can be measured selectively, even in the presence of each other.

4.3 The electrolytic conductivity detector pyrolyzes compounds as they elute from the chromatographic column through a hot nickel reaction tube. Halogen and nitrogen compounds are detected under reducing conditions while sulfur compounds are detected under oxidizing conditions. The effluent from the gas chromatographic column is combined with either hydrogen (reducing conditions) or air (oxidizing conditions) before entering the heated (800 to 1000°C) nickel reaction tube. The compound is converted to small inorganic reaction products depending upon the reaction conditions as shown in Table 1.

4.4 Table 2 shows the chemistry and modes of selective response for the detector. Depending upon the mode of operation, various interfering reaction products are removed by employing a selective gas scrubber before the product gases reach the detector cell. In the nitrogen-specific mode, halogen and sulfur products are removed by reaction with a caustic scrubber. In the sulfur-specific mode, halogen products are removed by a silver thread (or wire) scrubber. No scrubber is required for halogen mode operation.

4.5 The reaction products pass to the conductivity cell where they are combined with the solvent. The following solvents are typically used for normal operation in each indicated mode. Other solvents may be used to provide changes in selectivity and sensitivity (see 6.7):

Model	Solvent
Halogen	1-Propanol
Sulfur	100 % Methanol
Nitrogen	10 % t-Butyl Alcohol/90 % Water

4.6 The increase in electrical conductivity of the solvent as a result of the introduction of the reaction products is measured

by the sensing electrodes in the conductivity cell. The solvent passes through the cell after being deionized through an ion exchange resin bed located between the conductivity cell and solvent reservoir. In most instruments the solvent is recycled by taking the solvent from the cell back into the solvent reservoir.

5. Detector Construction

5.1 There is some variation in the method of construction of this detector. In general, the geometry and construction of the conductivity cell is the single distinguishing component between detector designs. It is not considered pertinent to review all aspects of the different detector designs available but rather to consider one generalized design as an example and recognize that variants may exist.

5.2 *Detector Base*—The base extends into the gas chromatography oven and permits an inert low dead volume interface of the column to the reactor. The carrier gas, the reaction gas, and the make-up gas (if needed) are introduced at the detector base. The base is heated and controlled by the gas chromatograph or allowed to track the gas chromatograph oven temperature.

5.3 *Reaction Tube*—The nickel pyrolysis tube interfaces to the detector base and is heated by a heating element called the reactor which surrounds the tube. The normal operating temperature is 800 to 1000°C for most applications.

5.4 *Scrubber*—A coiled tube, used in either the nitrogen or sulfur mode, containing a specific scrubbing material is placed between the exit of the pyrolysis tube and the entrance of the conductivity cell in order to remove certain reaction products which may interfere in the specific mode of operation. Replacement of the scrubber is mandated by response to any halogen compound.

5.5 *Conductivity Cell*—The conductivity cell consists of a plastic block containing two metal electrodes that measure the electrolytic conductivity of the solvent. It is connected to the reactor exit by means of an inert (usually TFE-fluorocarbon) transfer tube. It provides the conductivity signal for the specific compound. Gaseous products from the reaction tube enter into the front of the cell and contact the solvent which is introduced through the side of the cell. Together, these entities pass through the electrode area and then out through the back of the cell.

5.6 *Solvent*—The solvent is selected to provide the desired sensitivity and selectivity for each mode of operation. The solvent must be deionized, having a low conductivity, neutral pH, and must be able to dissolve the appropriate reaction products. The increase in conductivity of the solvent due to the presence of the reaction products results in a peak response corresponding to the original analyte. The solvent level in the reservoir should be maintained weekly and the solvent completely replaced every three months using high-purity solvents for best results.

5.7 *Solvent Delivery System*—The system consists of a pump and an ion exchange resin system which works to both deionize and neutralize the pH of the solvent. A by-pass system is used to allow the pump to run at a normal speed while still delivering the low solvent flow rates (30 to 100 µL/min) required by the detector. For operation in the nitrogen mode

GC/ELCD System Overview

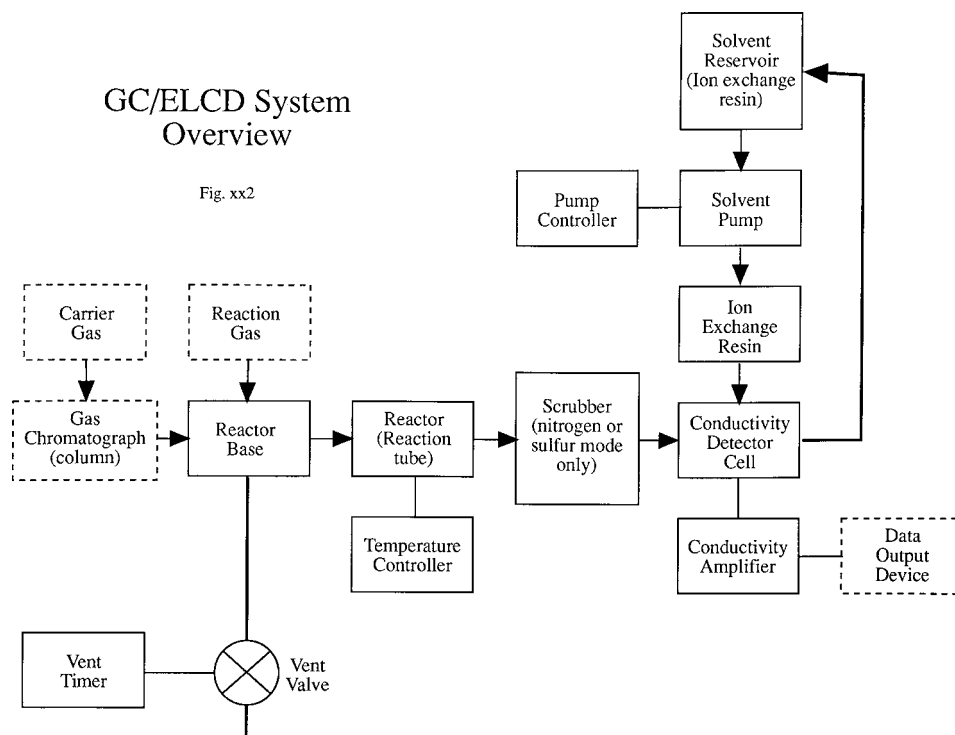


FIG. 2 GC/ELCD System Overview

TABLE 1 Pyrolysis Reaction Products Formed Under Oxidizing or Reducing Conditions

Oxidizing	Element	Reducing
CO ₂	C	CH ₄
H ₂ O	H	H ₂
NO/N ₂	N	NH ₃
HX, HOX	X	HX
O ₂	O	H ₂ O
SO ₂ /SO ₃	S	H ₂ S

the base. It is important that the gas flow from the vent (if used) be measured daily to ensure reproducible results and retention times.

6. Equipment Preparation

6.1 The detector will be evaluated as part of a gas chromatograph using injections of gases or liquid samples which have a range of component concentrations.

6.2 *Gases*—All gases passing through the reactor should be ultra-high purity (99.999 %) grade. Helium or hydrogen can be used as the GC column carrier gas. Nitrogen is extremely detrimental to the performance of the detector in all modes, and therefore cannot be used as a carrier of makeup gas nor can it be tolerated as a low level contaminant. No attempt will be made here to guide the selection of optimum conditions, except to state that experience has shown that gases of the highest available purity result in far fewer detector problems and difficulties. Poor quality, hydrogen has been found to be the cause of noise, low response, wandering baseline, and peak tailing when operating in the halogen or nitrogen modes. Similarly, the highest grade of air works best for the sulfur mode.

6.3 *Hardware*—High-purity gases require ultra-clean regulators, valves, and tubing. Use of clean regulators, employing stainless steel valves, diaphragms, and tubing have been found to result in far fewer detector problems and difficulties.

6.4 *Columns*—All columns, whether packed or capillary, should be fully conditioned according to supplier’s specifications prior to connecting to the detector. Certain liquid phases that are not compatible with the mode of operation should be avoided. Use of silanes (such as those used in deactivation of

special solvent delivery systems may be required to ensure the pH of the water-based solvent remains neutral. Refer to specific instructions provided by the manufacturer of the respective detector you are employing on your gas chromatograph. It is important to note that each mode will require specific resins which will require periodic replacement and attention given to expiration dates for their useful life-time. Resins should be mixed thoroughly before adding or replacing as the anion/cation mixture used by most manufacturers will separate unless a prepacked resin cartridge is used.

5.8 *Module*—All operational functions, except for detector base temperature, are controlled from the module. On some systems, vent time can be controlled from the gas chromatograph as an external event.

5.9 *Vent Valve*—When opened, the vent valve provides a way of preventing unwanted column effluents from entering the reaction tube. These effluents may include substances such as the sample injection solvent and column bleed which can cause fouling or poisoning of the nickel reaction tube’s catalytic surface. The valve is otherwise kept closed to allow the compounds of interest to pass into the reaction tube so that they may be detected. The valve interfaces with the detector base by means of a vent tube connected at the column exit in