Designation: E1698 – 95 (Reapproved 2010)

Standard Practice for Testing Electrolytic Conductivity Detectors (ELCD) Used in Gas Chromatography[1]

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

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,

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

Current edition approved Nov. 1, 2010. Published November 2010. Originally approved in 1995. Last previous edition approved in 2005 as E1698 – 95 (2005). DOI: 10.1520/E1698-95R10.

[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.

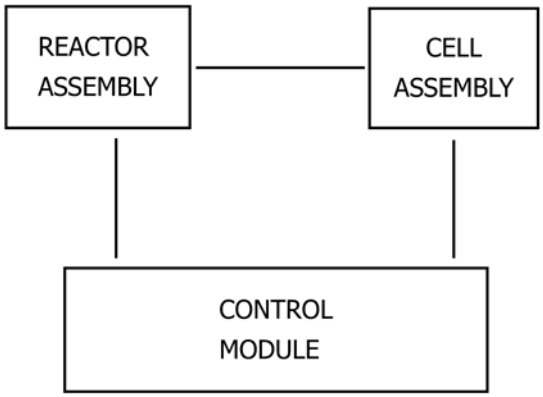

FIG. 1 ELCD—Principal Components

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 products in a suitable solvent, and measuring the change in electrical conductivity using a conductivity detector cell. Other suitable non-catalystic 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

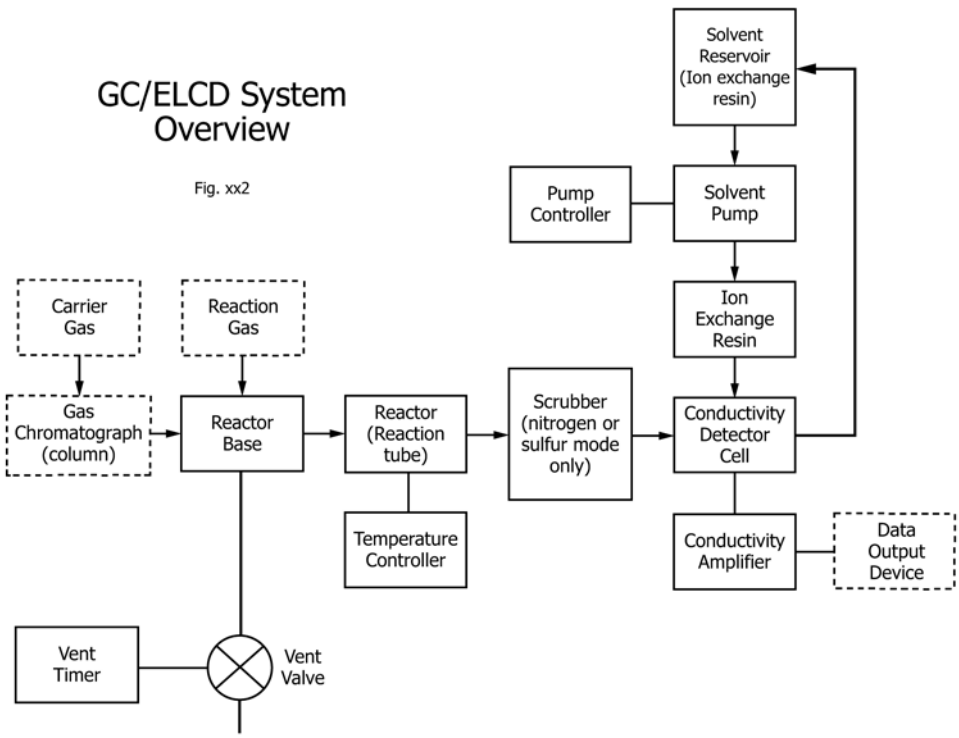

FIG. 2 GC/ELCD System Overview

TABLE 1 Pyrolysis Reaction Products Formed Under Oxidizing or Reducing Conditions

Oxidizing	Element	Reducing
CO_2	C	CH_4
H_2O	H	H_2
NO/N_2	N	NH_3
HX, HOX	X	HX
O_2	O	H_2O
SO_2/SO_3	S	H_2S

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 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 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

TABLE 2 Reaction Products Produced in the ELCD Using a Nickel Reaction Tube

Compound	Main Reaction Products	Comments
Reductive Conditions:		
Halogen compounds	HX	HX can be removed by N-mode scrubber and is selectively detected in X-mode.
Sulfur compounds	H_2 S	H_2 S can be removed by N-mode scrubber and is poorly ionized in the X-mode.
Nitrogen compounds	NH_3	NH_3 is poorly ionized in the X-mode and selectively detected in N-mode.
Alkanes	CH_4 , Lower Alkanes	Products are not ionized in any mode.
Oxygen compounds	H_2 O	H_2 O gives little response in X-mode and N-mode.
Oxidative Conditions:		
Halogen compounds	HX, HOX	HX can be removed by S-mode scrubber.
Sulfur compounds	SO_2	SO_2 is selectively detected in S-mode.
Nitrogen compounds	N_2 and certain nitrogen oxides at elevated temperatures	No or little response.
Alkanes	CO_2 , H_2 O	CO_2 is poorly ionized in S-mode. H_2 O gives little or no response.

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 glass liners and columns) should be avoided since they have been shown to poison the reactor tube.

6.5 *Reactor Temperature*—The target reactor temperature is 800 to 900°C. However, other reactor temperatures may be found to provide better results with certain compound types. Some typical reactor temperatures are given as follows:

6.5.1 800 to 900°C for most halogen-mode applications,

6.5.2 850 to 925°C for most nitrogen-mode applications,

6.5.3 950 to 1000°C for polychlorinated biphenyls (PCBs), and

6.5.4 900 to 950°C for sulfur compounds, such as sulfides.

6.6 *Reaction Gas Flow Rate*—Reaction gas flow rates fall within a range from 50 to 100 mL/min, depending upon detector design and application. Consult the manufacturer for recommendations.

6.7 *Solvent*—Typical solvents for each mode of operation are listed as follows. Other solvents may be substituted in order to enhance selectivity or sensitivity. However, there is usually a sacrifice in selectivity in order to gain sensitivity and vice-versa.

Halogen Mode	Sensitivity	Selectivity
1-Propanol	Normal	Normal
isopropyl Alcohol	Normal	Normal
Methanol	Highest	Lowest
Ethanol	Higher	Lower
1-Butanol	Lowest	Highest
Sulfur Mode		
Methanol	Lower	Higher
Methanol/20 % Water	Normal	Normal
Ethanol	Lowest	Highest
Nitrogen Mode		
10 % *t*-Butyl Alcohol/Water	Higher	Higher
50 % 1-Propanol/50 % Water	Normal	Normal

6.7.1 In solvent systems requiring water, use only deionized water with a resistivity of 18 MΩ or better. It should also be noted the binary solvent systems will change in their proportions due to normal evaporation. It is suggested that those solvents be checked biweekly and the reservoir topped off with fresh solvent.

6.8 *Solvent Flow*—Electrolyte flow rates range from 25 to 750 µL/min, depending upon detector cell design and application. Consult the manufacturer for recommendations.

7. Performance Evaluation

7.1 *Test for Response*—The detector can be determined to be responding by using one of the following test samples:

7.1.1 *Halogen Mode*—The headspace in a bottle of chloroform ($CHCl_3$) or methylene chloride (CH_2 Cl_2).

7.1.2 *Nitrogen Mode*—The headspace in a bottle of nitromethane, acetonitrile, one of the NOx gases, or some other low-boiling nitrogen compound.

7.1.3 *Sulfur Mode*—The headspace in a bottle of carbon disulfide (CS_2) or methyl or ethyl mercaptan.

7.1.4 Turn on the recorder, integrator, or data system to be used and adjust the baseline. Inject into the column 1 to 2 µL of the headspace of the sample as noted above. If the system is working, a large off-scale response should be observed in a few seconds to a few minutes, depending on the column being used.

7.2 *Noise:*

7.2.1 Noise (short term) is the amplitude, expressed in volts, of the baseline envelope which includes all random variations of the detector signal of a frequency on the order of one or more cycles per minute. Some sources of this type of noise include 60 Hz (or higher) high-voltage noise which can be suppressed or eliminated by shielding the detector cell or covering the detector cell, or both.

7.2.1.1 Other noise includes fluctuations of the baseline envelope of a frequency less than one cycle per minute. The amplitude of these fluctuations may actually exceed the short-term noise. Such fluctuations are difficult to characterize and are not typically to be expected. They are usually caused by

other chromatographic components such as the column, system contaminants, and flow variations. These other noise contributions are not derived from the detector itself and are difficult to quantitate in a general manner. It is, however, important for the practicing chromatographer to be aware of the occurrence of this type of noise contribution.

7.2.2 *Method of Measurement:*

7.2.2.1 Make noise measurements over short periods of time only, based on the expected peak width of the sample peaks; the suggested time interval is one minute for typical peaks. This noise corresponds to the observed noise only. The actual noise of the system may be larger or smaller than the observed value depending upon the method of data collection or signal monitoring from the detector, since observed noise is a function of the frequency, speed of response, and the bandwidth of the electronic filtering circuit measuring the detector signal.

7.2.2.2 With the attenuator set at maximum sensitivity (minimum attenuation) adjust the detector output with the "zero" control to read near mid-scale on the recorder. Allow at least 30 min of baseline to be recorded.

7.2.2.3 Draw two parallel lines to form an envelope which encloses the random noise excursions with greater than on-second period. Measure the distance between the parallel lines at right angles to the edge of the chart paper (see Fig. 3). Measure five adjacent one-minute sections and average the values. Express the values as volts of noise, peak-to-peak.

7.3 *Drift:*

7.3.1 Drift is the average slope of the noise envelope expressed in volts per hour as measured over 30 min at constant temperature and flow rates.

7.3.2 Measure the net change in volts of the lower line on the noise envelope over 30 min and multiply by two. Express the value as volts per hour drift.

7.4 *Sensitivity (Response):*

7.4.1 Sensitivity (response) of the electrolytic conductivity detector is the signal output per unit mass of halogen, nitrogen, or sulfur in the test substance injected, in accordance with the following relationship:

$$S = A_i/m \tag{1}$$

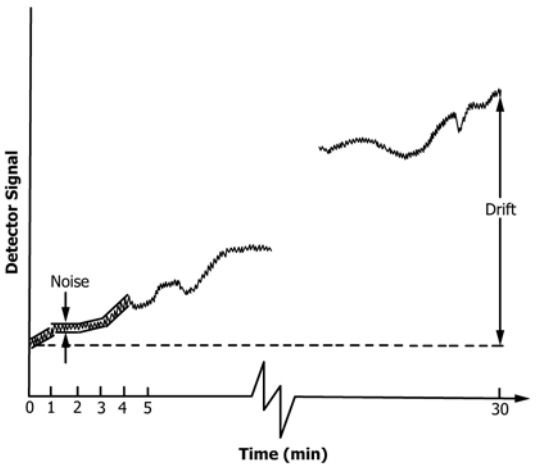

FIG. 3 Linear Range and Minimum Detectability

where:

S = sensitivity (response) in volts-seconds/gram, V·s/g,
A_i = integrated peak area, and
m = mass in grams of halogen, nitrogen, or sulfur injected, g.

7.4.2 *Test Conditions:*

7.4.2.1 Azobenzene is the preferred standard nitrogen-containing test substance. Lindane or chlorobenzene is the preferred standard halogen-containing test substance. Thimet is the preferred standard sulfur-containing test substance. The measurement must be made within the linear range of the detector.

7.4.2.2 The measurement must be made at a signal level at least 200 times greater than the noise level and should be made under the same conditions as the noise measurement.

7.4.2.3 The test substance and the conditions under which the detector sensitivity is measured must be stated.

7.5 *Specificity*—Specificity is defined as the ratio of the response per gram halogen, nitrogen, or sulfur in the test substance to the response per gram carbon in the octadecane. This can be calculated as sensitivity for halogen, nitrogen, or sulfur divided by the sensitivity for carbon, as calculated in 7.4.

7.6 *Minimum Detectability*—Minimum detectability is defined as the mass flow rate of halogen, nitrogen, or sulfur in the carrier gas that gives a detector signal equal to twice the noise level values as follows:

$$D = 2N/S \tag{2}$$

where:

D = minimum detectability, g/s,
N = noise level, V, and
S = sensitivity of the detector, measured at the same conditions and preferably at the same time.

7.6.1 When starting the minimum detectability, state the noise level on which the calculation was based.

7.7 *Linear Range:*

7.7.1 The linear range of an electrolytic conductivity detector is the range of mass flow rates of halogen, nitrogen, or sulfur in the carrier gas, over which the sensitivity of the detector is constant to within 5 % as determined from the linearity plot. This range must start at the calculated minimum detectability.

7.7.2 *Method of Measurement*—Use a set of test sample ranging in concentration from about 1 µg/L to about 1 mg/L to determine the detector sensitivity over a range of mass flow rates. For each test sample, calculate the detector sensitivity according to 7.4.1. Determine the mass flow rate by dividing the mass of X, N, or S injected by the peak base width, as shown below:

$$\textit{mass flow rate} \tag{3}$$

$$= \frac{(\text{Volume injected})(\text{Concentration of sample})(\%\text{X,N,S in sample})}{\text{peak width}} \tag{4}$$

For N in azobenzene:

$$m = \frac{(\text{Volume in µL})(\text{Concentration in g/L})(15.38) \times 10^{-8}}{(\text{peak width in seconds})} \tag{5}$$

7.7.2.1 Plot the sensitivity versus the mass flow rate for halogen, nitrogen, or sulfur from each test sample. This graph is called the linearity plot; a typical example is shown in Fig. 4.

7.7.3 The linear range may be expressed as the ratio of the upper limit of linearity (obtained from the linearity plot) to the minimum detectability (both measured for the same test substance) as follows:

$$LR = mmax/D \text{ (dimensionless)} \quad (6)$$

where:

LR = linear range of the detector,
mmax = upper limit of the linearity obtained from the linearity plot, g/s, and
D = minimum detectability, g/s.

7.7.3.1 If the linear range is expressed by this ratio, the minimum detectability must also be stated.

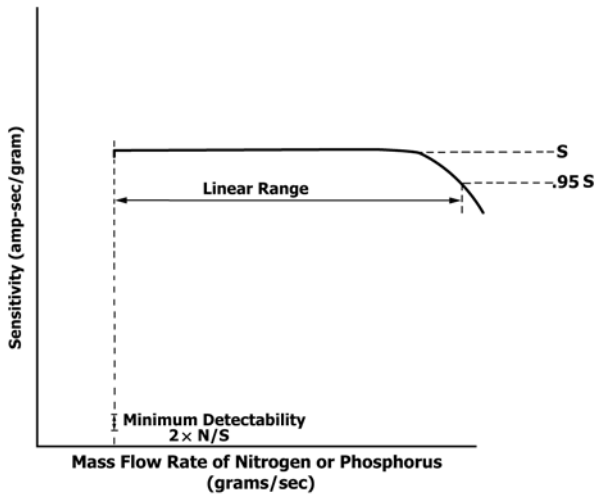

FIG. 4 Noise and Drift

7.7.4 The linear range may also be expressed by giving the minimum detectability and the upper limit of linearity (for example, from 1 × 10 exp-12 g/s to 1 × 10 exp-5 g/s).

7.7.5 As another alternative, the linear range may be expressed by giving the linearity plot itself, with the minimum detectability indicated on the plot.

8. Standard Values

8.1 Detector characteristics measured at optimum conditions recommended by the manufacturer may be expected to fall within the typical range of values listed in Table 1. These values should be expressed as indicated in Table 3.

9. Data Handling

9.1 All manufacturers supply an integral electrometer to allow the small electrical voltages (μV) changes to be coupled to recorders/integrators/computers. The preferred system will incorporate one of the newer integrators or computers that converts an electrical signal into clearly defined peak area counts in units such as uVolt-seconds. These data can then be readily used to calculate the linear range.

9.1.1 Another method uses peak height measurements. This method yields data that are very dependent on column performance and therefore not recommended.

9.1.2 Regardless of which method is used to calculate linear range, peak height is the only acceptable method for determining minimum detectability.

9.2 *Calibration*—It is essential to calibrate the measuring system to ensure that the nominal specifications are acceptable and particularly to verify the range over which the output of the device, whether peak area or peak height, is linear with respect to input signal. Failure to perform this calibration may introduce substantial errors into the results. Methods for calibration will vary for different manufacturer's devices but many include accurate constant voltage supplies or pulse-generating equipment. The instruction manual should be studied and thoroughly understood before attempting to use electronic integration for peak area or peak height measurements.

TABLE 3 Detector Characteristics

Characteristic	Units	Halogen	Nitrogen	Sulfur
Sensitivity	Ampere-seconds/gram (*X*,*N*,*S*)	TBD[A]	TBD[A]	TBD[A]
Specificity	Gram (*X*,*N*,*S*)/gram C	> 1×10 exp6	> 1×10 exp6	> 1×10 exp5
Minimum detectability	grams (*X*,*N*,*S*)/second	1-5×10 exp-13	0.4-4×10 exp-12	5-10×10 exp-13
Linear range	... ...	> 1×10 exp6	> 1×10 exp4[B]	> 1×10 exp4[B]
Noise	Volts or µV	< 1 % F.S.[C]	< 1 % F.S.	< 1 % F.S.
Drift	Volts/hour	TBD[A]	TBD[A]	TBD[A]

[A] TBD = to be determined or specified.
[B] Some “new” ELCDs can extend the linear range for these modes by software interpolation using polynomial regression.
[C] Full scale of recorder output at highest sensitivity setting on control module.