Designation: E 697 – 96

Standard Practice for Use of Electron-Capture Detectors in Gas Chromatography[1]

This standard is issued under the fixed designation E 697; 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 is intended to serve as a guide for the use of an electron-capture detector (ECD) as the detection component of a gas chromatographic system.

1.2 This practice is intended to describe the operation and performance of the ECD as a guide for its use in a complete chromatographic system.

1.3 For general gas chromatographic procedures, Practice E 260 or Practice E 1510 should be followed except where specific changes are recommended in this practice for use of an ECD. For a definition of gas chromatography and its various terms, see Practice E 355. These standards also describe the performance of the detector in terms which the analyst can use to predict overall system performance when the detector is coupled to the column and other chromatographic components.

1.4 *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.* For specific safety information, see Section 3.

2. Referenced Documents

2.1 *ASTM Standards:*

E 260 Practice for Packed Column Gas Chromatography[2]

E 355 Practice for Gas Chromatography Terms and Relationships[2]

E 1510 Practice for Installing Fused Silica Open Tubular Capillary Columns in Gas Chromatographs[2]

2.2 *CGA Standards:*

CGA P-1 Safe Handling of Compressed Gases in Containers[3]

CGA G-5.4 Standard for Hydrogen Piping Systems at Consumer Locations[3]

CGA P-9 The Inert Gases: Argon, Nitrogen and Helium[3]

CGA V-7 Standard Method of Determining Cylinder Valve Outlet Connections for Industrial Gas Mixtures[3]

CGA P-12 Safe Handling of Cryogenic Liquids[3]

HB-3 Handbook of Compressed Gases[3]

2.3 *Federal Standard:*

Title 10, Code of Federal Regulations, Part 20[4]

3. Hazards

3.1 *Gas Handling Safety*—The safe handling of compressed gases and cryogenic liquids for use in chromatography is the responsibility of every laboratory. The Compressed Gas Association (CGA), a member group of specialty and bulk gas suppliers, publishes the following guidelines to assist the laboratory chemist to establish a safe work environment. Applicable CGA publications include: CGA P-1, CGA G-5.4, CGA P-9, CGA V-7, CGA P-12, and HB-3.

3.2 The electron capture detector contains a radioactive isotope that emits β-particles into the gas flowing through the detector. The gas effluent of the detector must be vented to a fume hood to prevent possible radioactive contamination in the laboratory. Venting must conform to Title 10, Code of Federal Regulations, Part 20 and Appendix B.

4. Principles of Electron Capture Detection

4.1 The ECD is an ionizating detector comprising a source of thermal electrons inside a reaction/detection chamber filled with an appropriate reagent gas. In packed column GC the carrier gas generally fullfills the requirements of the reagent gas. In capillary column GC the make-up gas acts as the reagent gas and also sweeps the detector volume in order to pass column eluate efficiently through the detector. While the carrier/reagent gas flows through the chamber the device detects those compounds entering the chamber that are capable of reacting with the thermal electrons to form negative ions. These electron capturing reactions cause a decrease in the concentration of free electrons in the chamber. The detector response is therefore a measure of the concentration and the change in concentration of electrons **(1-17)**.[5]

4.2 A radioactive source inside the detector provides a source of β-rays, which in turn ionize the carrier gas to produce a source of electrons **(18)**. A constant or intermittent negative potential, usually less than 100 V, is applied across the reaction chamber to collect these electrons at the anode. This flow of“

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

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[2] *Annual Book of ASTM Standards*, Vol 14.02.

[3] Available from Compressed Gas Association, Inc., 1725 Jefferson Davis Highway, Arlington, VA 22202-4100.

[4] Available from Superintendent of Documents, Government Printing Office, Washington, DC 20402.

[5] The boldface numbers in parentheses refer to a list of references at the end of this practice.

secondary" electrons produces a background or "standing" current and is measured by a suitable electrometer-amplifier and recording system.

4.3 As sample components pass through the detector, they combine with electrons. This causes a decrease in the standing current or an increase in frequency of potential pulses depending on the mode of ECD operation (see 5.3). The magnitude of current reduction or frequency increase is a measure of the concentration and electron capture rate of the compound. The ECD is unique among ionizing detectors because it is this loss in electron concentration that is measured rather than an increase in signal.

4.4 The two major classifications of electron-capture reactions in the ECD are the dissociative and nondissociative mechanisms.

4.4.1 In the dissociative-capture mechanism, the sample molecule AB reacts with the electron and dissociates into a free radical and a negative ion: $AB + e \rightarrow A + B^-$. This dissociative electron-capture reaction is favored at high detector temperatures. Thus, an increase in noncoulometric ECD response with increasing detector temperature is evidence of the dissociative electron-capture reaction for a compound. Naturally, detectability is increased at higher detector temperatures for those compounds which undergo dissociative mechanisms.

4.4.2 In the nondissociative reaction, the sample molecule AB reacts with the electron and forms a molecular negative ion: $AB + e \rightarrow AB^-$. The cross section for electron absorption decreases with an increase in detector temperature in the case of the nondissociative mechanism. Consequently, the nondissociative reaction is favored at lower detector temperatures and the noncoulometric ECD response will decrease if the detector temperature is increased.

4.4.3 Beside the two main types of electron capture reactions, resonance electron absorption processes are also possible in the ECD (for example, $AB + e = AB^-$). These resonance reactions are characterized when an electron absorbing compound exhibits a large increase in absorption cross section over a narrow range of electron energies. This is an extremely temperature sensitive reaction due to the reverse reaction which is a thermal electron deactivation reaction. For solutes in this category a maximum detector temperature is reached at which higher temperatures diminish the response to the analyte **(55)**.

4.5 The ECD is very selective for those compounds that have a high electron-capture rate and the principal use of the detector is for the measurement of trace quantities of these materials, 10^{-9}g or less. Often, compounds can be derivatized by suitable reagents to provide detection of very low levels by ECD **(19, 20)**. For applications requiring less sensitivity, other detectors are recommended.

4.6 A compound with a high electron-capture rate often contains an electrophoric group, that is, a highly polar moiety that provides an electron-deficient center in the molecule. This group promotes the ability of the molecule to attach free electrons and also may stabilize the resultant negative molecule-ion. Examples of a few electrophores are the halogens, sulfur, phosphorus, and nitro- and α-dicarbonyl groups **(21-25)**.

4.7 A compound could also have a high electron-capture rate without containing an obvious electrophore in its structure, or its electron-capture rate could be much greater than that due to the known electrophore that might be present. In these cases certain structural features, which by themselves are only weakly electrophoric, are combined so as to give the molecule its electrophoric character. A few examples of these are the quinones, cyclooctatetracene, 3,17-diketosteroids, *o*-phthalates and conjugated diketones **(26-32)**.

4.8 Enhanced response toward certain compounds has been reported after the addition of either oxygen or nitrous oxide to the carrier gas. Oxygen doping can increase the response toward CO_2, certain halogenated hydrocarbons, and polycyclic aromatic compounds **(33)**. Small amounts of nitrous oxide can increase the response toward methane, carbon dioxide, and hydrogen.

4.9 While it is true that the ECD is an extremely sensitive detector capable of picogram and even femtogram levels of detection, its response characteristics vary tremendously from one chemical class to another. Furthermore, the response characteristic for a specific solute of interest can also be enhanced or diminished depending on the detector's operating temperature **(56)** (see 4.4 and 5.5). The detector's response characteristic to a solute is also dependent on the choice of reagent gas and since the ECD is a concentration dependent detector, it is also dependent on the total gas flow rate through the detector (see 5.5). These two parameters affect both the absolute sensitivity and the linear range an ECD has to a given solute. It is prudent of the operator of the ECD to understand the influence that each of the aforementioned parameters has on the detection of a solute of interest and, to optimize the parameters prior to final testing.

5. Detector Construction

5.1 *Geometry of the Detector Cell*:

5.1.1 Three basic types of β-ray ionization-detector geometries can be considered applicable as electron-capture detector cells: the parallel-plate design, the concentric-tube or coaxial-tube design, and recessed electrode or asymmetric type **(34-37)**. The latter could be considered a variation of the concentric-tube design. Both the plane-plate geometry and concentric geometry are used almost exclusively for pulsed operation. Although the asymmetric configuration is primarily employed in the d-c operation of electron-capture detectors, a unique version of the asymmetric design (referred to as a displaced-coaxial-cylinder geometry) has been developed for pulse-modulated operation. The optimum mode of operation is usually different for each detector geometry and this must be considered, where necessary, in choosing certain operating parameters.

5.1.2 In general, more efficient operation is achieved if the detector is polarized such that the gas flow is counter to the flow of electrons toward the anode. In this regard, the radioactive source should be placed at the cathode or as near to it as possible.

5.1.3 Other geometric factors that affect cell response and operation are cell volume and electrode spacing, which may or may not be altered concurrently depending upon the construction of the detector. Of course, both these variables can be

significant at the extremes, and optimum values will also depend upon other parameters of operation. In the pulsed operational mode, the electrons within the cell must be able to reach the anode or collector electrode during the 0.1 to 1.0-μs voltage pulse. Generally, electrode distances of 0.5 to 1.0 cm are acceptable and can be used optimally by the proper choice of operating conditions. Cell volume should be small enough to maintain effective electron capture without encountering other types of electron reactions and also small enough so as not to lose any resolution that may have been achieved by high-resolution chromatographic systems. Typical ECD cell volumes range from approximately 2 to 0.3 cm^3. A detector cell with a relatively low internal volume is particularly important when the ECD is used with open tubular columns. In addition to the preceding electrical and chromatographic requirements, the electrode dimensions of the detector are also determined by the range of the particular β-rays.

5.2 *Radioactive Source*:

5.2.1 Many β-ray-emitting isotopes can be used as the primary ionization source. The two most suitable are ^3H (tritium) **(38, 39)**. and ^{63}Ni **(40)**.

5.2.1.1 *Tritium*—This isotope is usually coated on 302 stainless steel or Hastelloy C, which is a nickel-base alloy. The tritium attached to the former foil material is in the form of Ti_3H_2; however, there is uncertainty concerning the exact means of tritium attachment to the scandium (Sc) substrate of the Hastelloy C foil. The proposed methods of attachment include Sc^3H_3 and $^3H_2$ as the occluded gas. The nominal source activity for tritium is 250 mCi in titanium sources and 1000 mCi in scandium sources. Department of Energy regulations permit a maximum operating temperature of 225°C for the Ti^3H_2 source and 325°C for the Sc^3H_3 source. Naturally, detector temperatures that are less than the maximum values will lengthen the lifetimes of the tritiated sources by reducing the tritium emanation rates. The newer scandium sources are more effective at minimizing the contamination problems associated with electron-capture detectors because of their capability for operation at 325°C. Furthermore, the tritiated-scandium source displays a factor-of-three detectability increase for dissociative electron-capturing species, that is, halogenated molecules. Another advantage of scandium tritide sources is their availability at much higher specific activities than nickel-63 sources; therefore, Sc^3H_3 sources are smaller and permit the construction of detector cells with smaller internal volumes. The maximum energy of the β-rays emitted by tritium is 0.018 MeV.

5.2.1.2 *Nickel-63* (^{63}Ni)—This radioactive isotope is usually either electroplated directly on a gold foil in the detector cell or is plated directly onto the interior of the cell block. Since the maximum energy of the β-rays from the ^{63}Ni is 0.067 MeV and ^{63}Ni is a more effective radiation source than tritium, the normal ^{63}Ni activity is typically 10 to 15 mCi. An advantage of ^{63}Ni is its ability to be heated to 350°C and the concomitant decrease in detector contamination during chromatographic operation. Another advantage of the high detector temperatures available with ^{63}Ni is an enhanced sensitivity for compounds that undergo dissociative electron capture.

5.2.2 Although the energies and the practical source strengths for these two radioactive isotopes are different, no significant differences in the results of operation need be encountered. However, optimum interelectrode distance in the detector cell is generally greater for ^{63}Ni than for tritium, that is, less than 2.5 mm for tritium and 10 mm for ^{63}Ni. Thus, tritium sources have the potential of greater sensitivity for those compounds which undergo undissociative electron attachment because of tritium's higher specific activity and its ability to be used in a smaller volume detector. Because low levels of radioactive ^3H or ^{63}Ni are released to the laboratory environment, it is a wise safety precaution to vent electron-capture detectors by means of hood exhaust systems.

5.3 *Operational Modes*:

5.3.1 Three operational modes are presently available with commercial electron-capture detectors: constant-dc-voltage method **(41)**, constant-frequency method, and the constant-current method **(42-47)**. Within each mode of operation, there lies the ability to optimize performance by selective adjustments of various ECD operational parameters. This may include, among other things, not only the choice of reagent gas to be used in the ECD (see 5.4) but also setting the detector's pulse time constant on the electrometer to correspond to the gas used.

5.3.1.1 *DC-Voltage Method*—A negative d-c voltage is applied to the cathode resulting in an increasing detector current with increasing voltage until saturation is reached. The ECD response for the d-c mode is only linear over a narrow voltage range of approximately 10 to 15 V. Therefore, optimum operation is obtained when the detector current is about 80 % of the saturation level. At higher voltages, the response becomes nonlinear and this nonlinearity becomes extreme on the saturation plateau. At d-c voltages below the optimum range, the response-to-concentration slope is high at low concentrations and decreases with increasing concentration. This effect will over-emphasize small chromatographic peaks and tends to distort peak widths and heights. The d-c voltage required for optimum operation can vary a great deal depending upon such factors as the type of radioactive source, effective source strength, interelectrode distance, detector volume, detector cleanliness, detector temperature, flow rate through the detector, liquid phase bleed from the column, carrier gas, and its purity when it reaches the detector. Since most of these parameters are difficult to change for a given application, experimental variation of the voltage to achieve maximum performance is recommended. Actual operational voltages from +10 to +150 V may be required to obtain optimum performance in the d-c mode. However, regardless of the actual ECD operating voltage, the detector in the d-c mode will still be limited to a narrow linear response range of 10 to 15 V. Since the optimum voltage can change during continuous operation, it is wise to check the current-versus-voltage response frequently. This problem of variable response is sufficient reason for the frequent use of calibration standards during analyses. Because of the availability of electron-capture detectors that operate in the pulse sampling method and the analysis problems inherent in the d-c mode, the dc-voltage method offers few advantages compared to its notoriety for yielding anomalous results. Space charges, contact potentials, and

unpredictable changes in electron energy are three significant factors which contribute to response problems in the d-c detector.

5.3.1.2 *Constant-Frequency Method*—The applied voltage is pulsed at a constant frequency to the cathode in the form of a square wave. Thus, the pulse frequency is held constant and the output variable presented on the recorder is the detector current. The voltage pulses are of short duration, 1 μs or less, and should occur at infrequent intervals, for example, 1 to 10 kHz. In general, the shorter the pulse and the longer the interval that can be used to maintain reasonable current flow, the better the performance of the detector. The sensitivity increases directly with the time interval between collection pulses and the response is normally linear with solute concentration up to absorption of 50 % of the thermal electrons present in the detector. For this reason, optimization of the pulse cycle is recommended to achieve maximum response and to compensate for the many other parameters that could affect detector performance. The applied voltage (or pulse height) can also be varied, but as long as a minimum amount is used to promote current flow, it is not as critical a factor as the pulse cycle. The amplitude of the pulse is usually 50 to 60 V.

5.3.1.3 *Variable-Frequency or Constant-Current Method*—The constant-current ECD has the advantage of an extended linear range, 10^4. In this mode, the detector current is kept constant by an electrical feedback loop which controls the pulse frequency. When an electron-absorbing substance enters the detector and removes electrons, the pulse frequency increases to collect more electrons and thereby keeps the detector current at its constant level. Thus, the change of pulse frequency is proportional to the sample concentration, and a frequency-to-voltage (f/V) converter is used to send the information to a recording device. In actual operation, the difference between the output current from the detector cell and a reference current causes an integrating amplifier to change its output voltage, which in turn is applied to the input of voltage-to-frequency (V/f) converter. The V/f's output frequency therefore changes and is used to control the frequency of the collection pulses. The setpoint of the reference current affects both the detection limit and the linear range, so a compromise is required on the chosen value of the reference current to suit the particular analysis. As in the case of the constant-frequency method, the amplitude of the collection pulses is usually 50 to 60 V.

5.3.1.4 *Gas-Phase Coulometric Method*—This unique technique is based on a 1:1 equivalency at 100 %, or some known constant, ionization between the solute molecules and the number of electrons absorbed by these molecules in the detector. Thus, the number of electrons consumed can be used to calculate the molar quantity by means of Faraday's law. With coulometric ECD, the peak area in ampere-seconds, or coulombs, is related to the mass in grams by the following equation:

$$g = \frac{QM}{F} \tag{1}$$

where: g is the grams of analyte, Q is the number of coulombs, M is the molecular weight of the substance, and $F = 9.65 \times 10^{4}$C/mol. This particular ECD method is applicable only to compounds with ionization efficiencies greater than 90 % and to those compounds whose reaction products do not capture electrons to a significant degree. Unlike the other types of electron-capture detectors which function as concentration-sensitive transducers, the coulometric ECD acts as a mass-sensitive device provided the 1:1 ratio is maintained. Hence, the coulometric detector is to a considerable extent unaffected by changes in temperature, pressure, or flow rate of the carrier gas. Although the coulometric detector appears to be an ideal analytical transducer, its use is presently limited to specific compounds that meet the coulometric criteria.

5.3.2 There are certain advantages and disadvantages for all the basic ECD methods of operation. In general, the d-c mode requires simpler electronics and can be initially adjusted for optimum response and concomitant sensitivity. However, at times the d-c mode is subject to anomalous responses which are related to a number of inherent characteristics, for example, space charges, contact potentials, interference from non-capturing compounds, etc. Furthermore, source contamination and subsequent decreases in the linear range and overall sensitivity can often create difficulties during d-c operation. As previously discussed, the use of ^{63}Ni or tritiated scandium at high temperatures can alleviate the problem of source contamination and significantly reduce the intervals between required cleanings. The higher detector temperatures also permit enhancement of sensitivity with many compounds which undergo dissociative electron attachment. The techniques of ECD operation that involve pulse sampling methods are preferred to the d-c mode in respect to reproducibility and to the diminution of anomalous responses. In many actual laboratory analyses, the ECD has been limited because of its relatively small range of linearity (refer to Section 8 for a description of linear range).

5.3.2.1 For example, the linear range of the normal d-c and constant-frequency ECDs is from 50 to 100. This limited linear range often means that a sample must be injected many times to bring a peak into the linear range before accurate chromatographic quantitation is feasible. Prior to the development of the constant-current mode of ECD operation, Fenimore **(33)** and co-workers described an analog circuit that could be employed to increase ECD linearity. The constant-current ECD systems have been found to have comparatively large linear ranges of 1000 to approximately 10 000. Besides reducing the number of reruns required for quantitation, the extended linear range of the constant-current detector permits the use of automated gas chromatographic systems in ECD analysis. In addition to the expanded linear response range, the pulsed mode is also more sensitive than the d-c operation. Conceptually, the d-c mode is equivalent to a pulse-modulated ECD operating at such a high pulse frequency that the adjacent pulses begin to overlap. Since the average electron population within an ECD cell decreases with increasing pulse frequency, the pulsed modes result in greater numbers of electrons within the cell than the d-c operation and hence, provide for increased sensitivity. Whereas the coulometric detector has greater inherent detectability for those compounds with large rate constants for electron attachment (such as SF_6, CCl_4, etc.), the constant-current ECD has the larger linear-response range. At the present stage of

development, the coulometric detector should only be considered when the chromatographic analysis is dealing with strongly electron-attaching compounds.

5.4 *Carrier Gas*:

5.4.1 The carrier gas must fulfill the basic functions of reducing the electron energy to thermal levels and quenching unwanted side reactions, particularly metastable atom formation, where possible. In pulsed-mode operation, electron mobility should also be high. For these reasons, a mixture of argon with 5 to 10 % methane, or helium with 5 % methane, is often recommended for use with pulse-operated detectors. Carbon dioxide can also be substituted for the methane in either case. For d-c operation, nitrogen is recommended as long as it is reasonably free of water and oxygen (prepurified or oil-pumped grade). However, the gas mixture cited above for pulsed operation can also be used for d-c operation. Similarly, nitrogen carrier gas can also be used for pulsed ECD operation. In fact, several of the constant-current ECDs can operate with either argon/methane or nitrogen. The use of nitrogen carrier gas with certain designs of the constant-current ECD can actually increase the overall sensitivity, but the corresponding linear range decreases by a factor of approximately three. However, at least one commercial ECD employs a displaced coaxial-cylinder cell geometry to obtain both picogram detectability and equivalent 10^4linearity with nitrogen carrier gas.

5.4.2 When a capillary column is being used, the low gas flowrate through the ECD must be increased with a post-column make-up gas to ensure proper detector operation. It is recommended that helium or hydrogen be used as the capillary column carrier gas for optimum chromatographic performance and that nitrogen or argon/methane be used as the make-up gas for optimum detector response. Other types of make-up gases have been used to give enhanced sensitivities to specific functional groups over other function groups that may be present in a sample matrix **(55)**. The make-up gas must meet the requirements listed in 5.4.1.

NOTE 1—In an ECD where tritium is used as the ionization source, hydrogen may not be suitable for use in the carrier or make-up gas. Refer to the detector's manufacture for recommendations.

5.4.3 Since the electron capture response can be affected markedly by contaminants in the carrier gas, the analyst should use high purity gases. Additionally, gas scrubbers to remove residual oxygen and water from the carrier and make-up gases should be installed on the gas lines. It is preferred that the scrubbers be mounted vertically and located as close to the GC system as possible. The potentially damaging role of oxygen is due to its electron absorbing ability **(48, 49)**. Several reports have shown that levels of oxygen below 10 ppm can reduce the standing current to less than half its maximum value. Besides absorbing the detector electrons, oxygen can form ions such as $O_2^-$and $(H_2O)_nO_2^-$, which can in turn undergo ion-molecule reactions with the chromatographic solutes. This situation complicates the response mechanism and is undesirable for analytical purposes. Contamination of the carrier gas by compounds desorbed from elastomeric parts of pressure and flow regulators, lubricants in metal tubing, compounds derived from unconditioned injection port septa, etc. must also be eliminated **(57)**. Therefore, the use of metal diaphragm diffusion-resistant pressure regulators, the use of cleaned metal tubing for all gas connections, the avoidance of flow regulators with plastic diaphragms, and the use of thoroughly baked injection port septa are recommended for good performance.

5.5 *Detector Temperature and Flow Rate*— The temperature of the detector and flow rate through it are two variables that can affect detector response. Most of the time the choice of these conditions is limited by the application at hand and the analytical conditions chosen for the gas-chromatographic column system. However, certain electron-capturing compounds show a marked dependence of response on detector temperature and this dependency can be used to increase significantly the response for compounds with a dissociative mechanism **(50-52)**. The detector flow rate can be utilized to shift the entire linear range of a noncoulometric ECD by approximately an order of magnitude since this type of ECD is a concentration-sensitive device. When a post column make-up gas is used, its flowrate can be adjusted for optimum detector response without changing the column efficiency. It should be recognized that changing the detector temperature and flowrate will affect detector operation. When they are altered, steps to regain optimum response, such as voltage or pulse-cycle adjustment, as cited in 5.3.1, should be taken.

5.6 *Detector Contamination*:

5.6.1 Contamination of the ECD occurs if various substances that elute from the chromatographic column are condensed within the detector cell. These deposited films are usually derived from a combination of column bleed, septum bleed, and impurities in the carrier gas, solvent, and the actual sample. The observable symptoms that indicate a contaminated detector include a reduced baseline current or an increased base frequency (f_o), a decreased dynamic range, a reduced sensitivity and an increased baseline drift.

5.6.2 To minimize contamination of the ECD, the detector should always be maintained at a temperature at least 10°C above the injector, column, and interface temperatures. It is also advisable to employ chromatographic columns prepared from high-temperature, low-bleed stationary phases which are coated with low percentages (1.0 to 5 %) of the liquid phase. All columns should be thoroughly conditioned at a temperature of about 25°C above the maximum oven temperature to be employed in the chromatographic analyses. Always disconnect the column from the ECD during conditioning to prevent contamination. Traces of water and oxygen impurities in the carrier gas can also affect the performance of the ECD. Therefore, molecular sieve filters of the 5 A or 13 X type should be used in combination with the commercially available filters to remove water and oxygen, respectively, from the carrier gas. Problems due to septum bleed can be minimized by several approaches including the use of TFE-fluorocarbon-coated septa, solvent-extracted septa which have been thermally conditioned, and injection ports which reduce the contact between the carrier gas and the septum. Since certain analytical samples may contain relatively large amounts of contaminants in the natural sample matrix, it may be necessary to perform a sample cleanup procedure before the actual GC/ECD analysis.

5.6.3 Recent data suggest that the contaminants deposited on the inside of the detector inhibit charge collection by means

of polarization effects. The electrical polarization effects of an insulating film can be diagnosed by operating the ECD a sufficient time to obtain a stable baseline. Then, reverse the anode and cathode connections on the ECD and continue the reversed operation for several minutes. Finally, reconnect the ECD leads to their normal positions and observe the recorder baseline as a function of time. If the above procedure lowers the baseline to a stable position which persists for 2 to 4 min and then slowly returns to the pretest, high baseline, the test indicates a contamination film within the ECD. Another experimental indication of a contaminated detector is the appearance of negative peaks subsequent to positive sample peaks.

5.6.4 Recommended Procedures for Cleaning a Contaminated ECD:

5.6.4.1 The tritium radioactive foils and cell bodies can be cleansed by immersion for 1 to 2 h in 5 % KOH in methanol, followed by a thorough rinse with pure methanol. The detector foil and cells are allowed to dry. Then the foil is inserted into the detector cell body and the ECD can be used for further analyses after equilibration in the GC for 1 h at normal operating temperatures. Always allow the ECD cell to warm up in the GC before connecting the detector to the column. This latter procedure will prevent condensation of column effluents on the cold ECD.

5.6.4.2 The ^{63}Ni ECD contains a radioactive source which normally should not be opened for cleaning except by the manufacturer. However, the ^{63}Ni detector can sometimes be decontaminated by either purging the ECD at 350 to 400°C for 12 to 24 h while maintaining carrier gas flow, or by injecting several 100-µL aliquots of distilled water into a 300°C chromatographic system by means of an empty column. Another method of cleaning a ^{63}Ni ECD is to pass hydrogen gas through the detector at high temperatures for 30 min or more. However, after cleaning, diminished response is observed toward oxygen and some chlorinated compounds for periods up to several hours. The procedure recommended in the manufacturer's manual should be consulted when detector contamination is suspected **(53)**.

5.7 *Detector Maintenance*:

5.7.1 All ECD manufacturers sell their detector under a general low level radioactive material license. In accordance with this license, the owner or operator of the detector is required to perform a wipe test on the detector's body to check for the event of a radioactivity leak. This test in most cases, is required once every six months. Wipe test kits are available from the manufacturer of the detector and companies licensed to interpret the radioactive wipe test swabs. In the case of the ^{63}Ni ECD, the detector should not be disassembled to remove the radioactive foil.

TERMS AND RELATIONSHIPS

6. Sensitivity (Response)

6.1 *Description*—The noncoulometric ECD generally acts as a concentration-sensitive detector rather than a mass-sensitive detector. Therefore, the sensitivity (response) of the normal ECD is the signal output per unit concentration of a test substance in the carrier gas. In addition to the concentration of the electron-capturing eluant, the signal of a noncoulometric ECD also depends on the electron-capture characteristics of each component. For quantitative analyses it is necessary to calibrate the ECD separately for every relevant compound. A simplified relationship for the sensitivity of an ECD is:

$$S = \frac{A_i F_c}{W_i} \tag{2}$$

where:

S = sensitivity (response) in A·mL/pg or Hz·mL/pg (for constant-current mode),

A_i = peak area for substance, i, in A·min or Hz·min (for constant-current mode),

F_c = carrier-gas flow rate in mL/min (corrected to detector temperature, refer to Appendix X1), and

W_i = mass of test substance, i, in the sample, pg.

Specificity of the detector for an analyte of interest is stated as the ratio of the sensitivity of the detector for the test substance to the sensitivity of a potential interfering solute. An unsubstituted hydrocarbon that elutes close to test sample is generally used for this purpose. The ECD signal measured in the absence of an electron capturing chromatographic species is called the detector background or baseline current. This background signal is established by the sum of the signals for the carrier gas, make-up gas and other impurities. The sensitivity of the ECD for a sample is defined as the change in the measured ECD signal resulting from a change in the concentration of the sample within the detector volume.

6.2 *Test Conditions*:

6.2.1 Since individual substances have widely different electron-capture rates, the test substance may be selected in accordance with the expected application of the detector. The test substance should always be well-defined chemically. When specifying the sensitivity of the ECD, the test substance used must be stated.

6.2.1.1 The recommended test substance is lindane (1,2,3,4,5,6-hexachlorocyclohexane), with dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo-exo-1,4:5,8-dimethanonaphthalene) as an alternative.

6.2.1.2 The ECD can also be calibrated for halogenated compounds using permeation tubes.

6.2.2 The measurement must be made within the linear range of the detector, at a signal level between 10 and 100 times greater than the minimum detectability, and 20 and 200 times greater than the noise level at the same conditions.

6.2.3 The rate of drift of the base current for the detector at the same conditions must be stated.

6.2.4 The conditions under which the detector sensitivity is measured must be stated. These should include but not necessarily be limited to the following:

6.2.4.1 Geometry of detector, radioactive source, and source activity,

6.2.4.2 Mode of operation,

6.2.4.3 For the d-c mode: applied voltage; for the constant-frequency mode: duration and interval of pulses, and pulse height in volts; for the constant-current mode: the pulse duration, pulse amplitude, and the reference detector current, *I*ref,

6.2.4.4 Detector temperature,

6.2.4.5 Carrier gas, and if a capillary column is used, the make-up gas must be specified,

6.2.4.6 Carrier gas flow rate, and if a capillary column is installed, the total gas flow rate which includes the column flow and make-up gas flow (in either case the flow must be corrected to the detector temperature) (Note 2), and

6.2.4.7 Specific test substance.

NOTE 2—For the method of correction, see Annex A1.

6.2.5 Linearity and response speed of the recording system or other data acquisition device used should be such that it does not distort or otherwise interfere with the ouput of the detector. Recorders should have a maximum 1-s response time corresponding to 90 % of full scale deflection. If additional amplifiers are used between the detector and the final readout device, their characteristics should be established, their time constants should be noted, and their possible overall effect on peak shape of early eluted peaks determined. It should be noted that manipulation of integrator and computer parameters to reduce noise can distort the observed peaks **(54)**.

6.3 *Data Handling*:

6.3.1 All manufacturers supply an integral electrometer to allow the small electrical current changes to be coupled to recorder/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 microvolt-seconds. These data can then be readily used to calculate the linear range.

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

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

6.3.2 *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 manufacturers' devices but may include accurate constant voltage supplies or pulsegenerating equipment. The instruction manual should be studied and thoroughly understood before attempting to use electronic integration for peak area or peak height measurements.

7. Minimum Detectability

7.1 *Description*—Minimum detectability (Note 3) is the concentration of test substance in the carrier gas that gives a detector signal equal to twice the noise level and is calculated from the measured sensitivity and noise:

$$D = \frac{2N}{S} \tag{3}$$

where:

D = minimum detectability, pg test substance/mL carrier gas,

N = noise, A or Hz, and

S = sensitivity of the ECD, A·mL/pg or Hz·mL/pg.

NOTE 3—Although the minimum detectable amount is frequently used to express the limits of detection for a specific analytical method, the proper term for testing the detector is minimum detectability. It is the intention of Committee E-19 to delete reference to the term of minimum detectable amount in this practice on using detectors. By definition the minimum detectability is independent of the peak width; the minimum detectable amount for a specific analytical method is not.

$$D' = Dt_bF_c = \frac{2Nt_bF_c}{S} \tag{4}$$

where:

D' = minimum detectable amount, pg,

D = minimum detectability, pg/mL,

N = noise, A or Hz

S = sensitivity of the ECD, A·mL/pg or Hz·mL/pg,

F_c = corrected carrier-gas flow rate in mL/min, and

t_b = time corresponding to the width at base, min.

7.2 *Test Conditions*—Measure sensitivity in accordance with Section 6. Measure noise in accordance with Section 11. Both measurements must be carried out at the same conditions (see 6.2.4) and, preferably, at the same time. State the test substance and conditions in accordance with Section 6. Also state the noise level upon which the calculation was based.

8. Linear Range

8.1 *Description*—The linear range of an ECD is the range of concentrations of test substances in the carrier gas passing through the detector over which the sensitivity of the detector is constant to within ± 5.0 % as determined from the linearity plot specified below in 8.2.1. The linear range of the ECD may be expressed in three different ways:

8.1.1 As the ratio of the upper limit of linearity obtained from the linearity plot to the minimum detectability (or to the lower limit, if it is greater), both measured for the same test substance:

$$L.R. = \frac{c_{\max}}{D} \text{ or } L.R. = \frac{c_{\max}}{c_{\min}} \tag{5}$$

where:

$L.R.$ = linear range of the detector,

$c_{\max}$ = concentration of the test substance corresponding to the upper limit of linearity obtained from the linearity plot, pg/mL,

D = minimum detectability of the detector, pg/mL, and

$c_{\min}$ = concentration of the test substance in carrier gas corresponding to the lower limit of linearity obtained from the linearity plot, pg/mL.

If the linear range is expressed by this ratio, the minimum detectability or lower limit must be stated.

8.1.2 By giving the minimum detectability or the lower limit of linearity (whichever is greater) and the upper limit of linearity, for example, 1×10^{-2}pg/mL to 30 pg/mL.

8.1.3 By presenting the linearity plot itself, with the minimum detectability indicated on the plot.

8.2 *Method of Measurement*:

8.2.1 Analyze various amounts of the test substance and calculate the peak area sensitivity for each case in accordance with Section 5. Plot the values of sensitivity as the ordinate

versus the log of the sample concentration. Draw a smooth line through the data points. The limits of linearity are given by the intersection of the line with values of $0.95 \cdot S_{const}$ and $1.05 \cdot S_{const}$ where: S_{const} is the constant value of sensitivity on the graph, and the lower limit of linearity cannot be less than the minimum detectability. The linearity plot for an ECD is illustrated in Fig. 1.

8.2.2 Express the linear range according to 8.1.1. It should be noted that the usable linear range of an ECD for quantitative work may be less than the calculated linearity which is based on a lower limit determined by the minimum detectability.

8.2.3 In giving the linear range or the linearity plot, the test substance and the test conditions must be specified in accordance with 6.2.4. Since the noncoulometric ECDs are concentration detectors, it is especially important to state the total detector gas flow rate and detector temperature. In addition, the detector sensitivity usually varies with the composition of detector reagent gas; thus, it is necessary to identify the GC column carrier gas, and if a capillary column is being used, the make-up gas must also be stated.

9. Dynamic Range

9.1 *Description*—The dynamic range of the ECD is that range of concentrations of the test substance in the carrier gas over which an incremental change in concentration produces a change in detector signal. The lower limit of the dynamic range is given by the minimum detectability as described in Section 7. The upper limit of the dynamic range is the highest concentration at which a slight further increase in concentration will give an observable increase to the detector signal/noise response. The dynamic range is the ratio of the upper and lower limits. The dynamic range is larger than or equal to the linear range, but obviously cannot be smaller.

9.2 *Method of Measurement*—The necessary data for plots of the dynamic range are obtained by determining the signal/noise ratios as a function of the amounts of the test substance. Refer to 11.2 for the description of noise measurement. The signal/noise values are plotted against their corresponding sample concentrations on log-log graph paper. The best smooth line is drawn through these data points. The lower limit of the dynamic range is defined by the minimum detectability of the test substance. The upper limit of the dynamic range is the sample concentration corresponding to the point where the slope of the dynamic-response plot first becomes zero. Typical dynamic-response plots for both the constant-current and d-c modes of ECD operation are shown in Fig. 2. This particular graph also illustrates the greater linear-response and dynamic-response ranges of the constant-current mode as compared to the d-c mode.

10. Relative Electron-Capture Rate

10.1 *Description*—The relative electron-capture rate (K_{rel}) is a useful expression of the difference in ECD response for two substances of different electron-capture cross sections. It is calculated from the detector sensitivity (S) or minimum detectability (D) values for the two substances:

$$K_{rel} = \frac{S_2}{S_1} = \frac{D_1}{D_2} \tag{6}$$

where: subscripts 1 and 2 refer to the two substances. K_{rel} expresses the electron-capture rate of the second substance relative to the first. If the relative electron-capture rates of a number of substances are to be expressed, a standard test

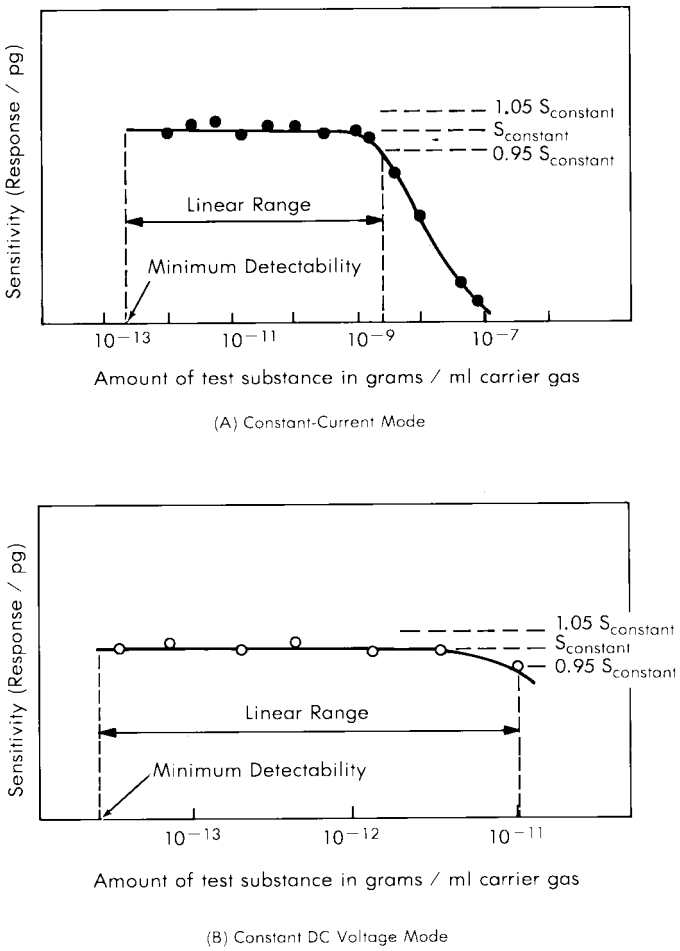

FIG. 1 Example of a Linearity Plot for an Electron-Capture Detector

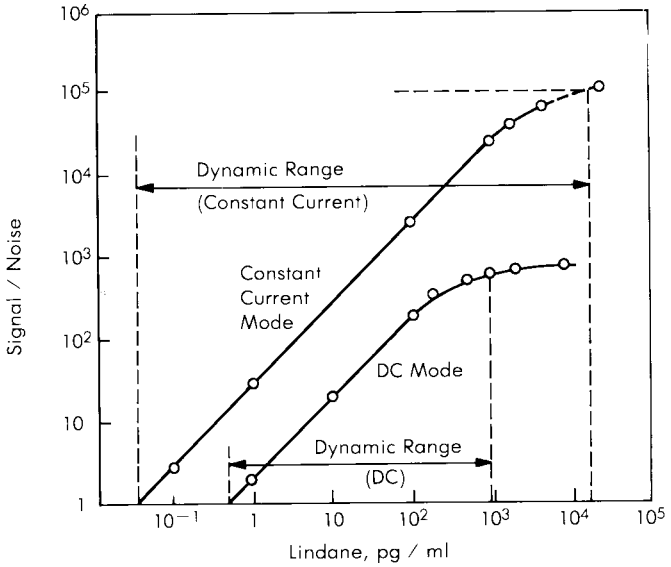

FIG. 2 Example of a Plot to Determine the Dynamic Range of an Electron-Capture Detector

substance is selected as the first substance (see Table 1). Then, detector sensitivities for subsequent substances are determined on the same detector under identical conditions.

11. Noise and Drift

11.1 *Descriptions:*

11.1.1 *Noise*—Noise is the amplitude expressed in amperes or Hertz of the baseline envelope which includes all random variations of the detector signal of the frequency on the order of 1 cycle/min or greater (see Fig. 3). This noise corresponds to the observed noise only. The actual amount of noise is a function of the whole system, including the detector, signal cables, and the instrument monitoring the signal (recorder, integrator, or computer). Modern integrators and computers may contain electronic filters that selectively remove some types of noise and reduce the apparent amount of detector noise. To effectively use the filtering capacity, the user must have a basic understanding of how the electronic device monitors the detector output. A lack of understanding of the device's operation may lead to poor analytical results. Both noise measurements and sensitivity measurements should be made under the same conditions.

11.1.2 *Drift*—Drift is the average slope of the noise envelope expressed in amperes per hour or Hertz per hour as measured over a period of ½ h (see Fig. 3).

11.2 *Methods of Measurement*:

11.2.1 With the detector output set at maximum sensitivity and adjusted with the zero-control to read near midrange on the recorder, allow at least ½ h of baseline to be recorded.

11.2.2 Draw two parallel lines to form an envelope that encloses the random excursions of a frequency of approximately 1 cycle/min and greater. Measure the distance perpendicular to the time axis between the parallel lines and express the values as amperes or Hertz of noise.

11.2.3 Measure the net change in amperes or Hertz of the envelope over ½ h and multiply by two. Express the value as amperes per hour or Hertz per hour of drift.

11.2.4 In specifications giving the measured noise and drift of the ECD, the conditions stated in 6.2.4 must be given.

12. Typical Values

12.1 Typical values for the various parameters of both pulse-modulated and d-c ECD systems are listed below. The proper way to express these values for both ECD modes is also presented. A maximum of two significant figures is sufficient in reporting these ECD values.

TABLE 1 Typical Values for Electron-Capture Rate Constants and Constant-Current Sensitivities

Compound	Sensitivity, Hz·mL/pg	Electron-Capture Rate Constant, (mL/molecule·s) $\times 10^7$
Aldrin	69.5	4.55
Dieldrin	65.7	4.49
Decachlorobiphenyl	28.4	4.32
Lindane	69.2	3.61
p,p′-DDE	62.4	3.55
p,p′-DDT	48.9	3.10
Trichloroacetyl amphetamine	57.0	2.86
CCl_4	...	2.81
CF_2Br_2	...	2.61
SF_6	...	2.20
$CFCl_3$	...	1.14

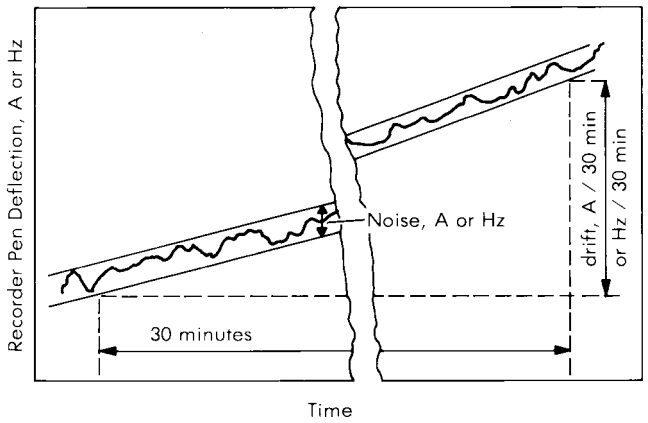

FIG. 3 Example for the Measurement of the Noise and Drift of an Electron-Capture Detector

12.2 *Standing Current*—For suitable performance in the d-c mode, the standing current (I_o), also called base current or background current, should be within the range of 1×10^{-9} to 3×10^{-8}A. These standing current values for a d-c cell are characteristic for operation with pure nitrogen carrier gas. In the constant-current mode, the base frequency values (f_o) are the analogs of standing current values for d-c operation. The base frequencies may vary somewhat depending upon the particular design specifications for different ECD systems. For example, f_o values are dependent upon the magnitude of the external reference current (I_{ref}), the radioactive source activity, the composition of the carrier gas (nitrogen or argon/methane), the actual cell design and relative location of the anode, the pulse width, the pulse amplitude, etc. However, the range for the base frequencies of different commercial ECD systems, which are of constant-current design, should be from 1×10^3 to 5×10^3Hz. Constant-current ECDs with pulse widths of approximately 0.5 to 1.0 μs and pulse amplitudes of 50 V should yield baseline frequencies from 0.25 to 3 kHz depending upon the particular ECD design.

12.3 *Noise and Drift*—A noise range of 10^{-12} to 10^{-11}A is to be expected from most d-c systems. ECD noise of these magnitudes is caused by statistical fluctuations in the emission of β rays and by temperature instabilities in the detector block. Typical noise in constant-current ECDs ranges from approximately 0.1 to 1.0 Hz. For both the d-c and constant-current modes, the drift or short-term baseline instability can be as much as five to ten times the noise level per hour.

12.4 *Sensitivity*—As previously discussed, the actual ECD sensitivity is very dependent on the specific chemical compound and its electron capturing rate. Values for sensitivity of 2×10^{-12} to 200×10^{-12}A·ml/pg are typical for compounds of high to moderate electron-capture rate constants whose detection is by an ECD in the d-c mode. Highly electrophilic compounds such as lindane, dieldrin, DDT, and carbon tetrachloride have electron-capture rate constants from 2.5 to 4.6×10^{-7}mL/molecule·s. The constant-current ECD sensitivity for a compound like lindane varies from approximately 65

Hz·mL/pg to 500 Hz·mL/pg. These constant-current ECD sensitivities are dependent on the frequency-to-voltage conversion factor employed by the various commercial designs. Specificity of response against hydrocarbons can range from (approximately) 10^6 for polyhalogenated compounds to $10^3$for dichlorinated compounds and $10^1$for esters or ethers.

12.5 *Minimum Detectability*—The minimum detectability of an ECD is also dependent upon the relative electroncapture rate for the concomitant chemical species. However, the minimum detectability for lindane, which has a relatively large electron-capture rate, should be in the 0.1 to 1.0-pg/mL range. For maximum detectability, the optimum detector temperature should be experimentally determined by observing the ECD response as a function of detector temperature for each particular analyte of interest. Response changes of several orders of magnitude are not uncommon when the detector temperature is varied over a range of 300°C.

12.6 *Linear Range*—A linear range of about 100 should be expected for both the d-c and constant-frequency modes. This also means that, in order to make measurements within the linear range, the value for the current decrease corresponding to the peak height (*I*) should not be more than about 25 % of the value of the standing current (I_o). The linearity for the constant-current type of ECD is usually within ± 5 % over a working range of 1000 to 5000. For most compounds, this value drops to ± 10 % or more at a range of 10 000 to 20 000.

12.7 *Range of Electron-Capture Rate Constants*—Relative responses of the ECD have been shown to vary over a range of about 7 decades. However, those compounds with practical relative responses are usually clustered with 4 decades. Table 1 lists the electron-capture rate constants and corresponding constant-current ECD sensitivities for some selected compounds.

13. Evaluation of the Total GC/ECD System

13.1 The analyst who uses the electron-capture detector in gas chromatography must be aware of the operational characteristics and the enigmas of both the ECD and the corresponding gas chromatograph. Routine analysis with a GC/ECD system can involve a number of pitfalls and tradeoffs. For example, the choice of chromatographic column stationary phase and the construction of the actual column as it relates to the inertness of the tubing to the solute molecules has a crucial influence on final quantitative results. Although some compounds produce a relatively large ECD response, their quantification can be hindered by catalytic and adsorption losses in the injection port, the column and poorly swept areas of the detector flow path of the GC. The possibility of significant analyte losses due GC system activity and dead volume is suggested when a compound exhibits a nonlinear response as a function of sample weight. In addition, the occurrence of chromatographic peaks which tail excessively or the appearance of several different components (for example, analyte breakdown products) for a pure, single-component sample are indicative of undesirable sample interactions. If chromatographic losses are discovered, then corrective modifications in the system are imperative. Several practical guides have been published that can provide help in troubleshooting a GC system **(58-60)**.

13.2 Other complications in the analytical applications of GC/ECD systems can arise from a high liquid-phase bleed, septum bleed, oxygen and water impurities in the carrier gas, leaks, and the analysis of“ dirty” samples. The ECD problems due to excessive bleed and contamination by oxygen and water are characterized by a reduction in baseline current or frequency, a reduced dynamic range, and a reduced sensitivity. Besides the preceding effects, ECD contamination problems due to the analysis of dirty samples are indicated by an irregular baseline. Once a specific GC/ECD problem has been correctly diagnosed, the chromatographer can usually find a solution by referring to the appropriate articles in the list of references or by discussing the problem with a technical representative of the GC/ECD manufacturer.

14. Keywords

14.1 electron-capture detector (ECD); gas chromatography (GC)

ANNEXES

(Mandatory Information)

A1. CORRECTION OF FLOW RATE TO DETECTOR TEMPERATURE

A1.1 Since carrier-gas flow rate is usually measured at ambient (room) temperature, it has to be corrected to express conditions at the temperature of the detector.

A1.2 The correction is made according to the following formula:

$$F_d = F\left(\frac{T_d}{T_a}\right)\left(1 - \frac{p_w}{p_a}\right) \quad \text{(A1.1)}$$

where:

F_d = gas flow rate from the detector corrected to the detector temperature, mL/min,
F = gas flow rate measured from the column (or detector) outlet at ambient temperature and pressure with a wet flowmeter, ml/min,
T_d = detector temperature, K,
T_a = ambient temperature, K,

p_w = partial pressure of water at ambient temperature, Pa, and
p_a = ambient pressure, Pa.

A1.3 The factor $(1 - p_w/p_a)$ is to be applied only if a wet (for example, soap bubble) flow meter is used for the measurement. If a digital (for example, dry) flowmeter is used, then correction to detector temperature is calculated as follows:

$$F_d = F_a(T_d/T_a) \quad \text{(A1.2)}$$

where:
F_a = volumetric dry gas flow rate from the detector, mL/min.

A2. LIST OF SYMBOLS AND ABBREVIATIONS

A_i = peak area for substance, *i*, in A·min or Hz·min
A = current, in amperes
c_{max} = concentration corresponding to upper limit of linearity, pg/mL
c_{min} = concentration corresponding to lower limit of linearity, pg/mL
C = Coulomb or A·s
D = minimum detectability, pg/mL
D' = minimum detectable amount, pg
f = frequency
F = gas flow rate from the column or detector as measured using a bubble (wet) flowmeter
F_c = carrier gas flow rate corrected to the temperature of the detector, mL/min
F_a = carrier gas flow rate measured at the outlet of the column or detector at ambient temperature, mL/min
F = Faraday, 9.65×10^4C/mole
g = mass, in grams
Hz = frequency, in Hertz
I = peak height, A
I_{ref} = external reference current, A
I_o = standing current, A
K_{rel} = relative electron-capture rate
L.R. = linear range of the detector
M = Molecular weight, g
mCi = millicurie
N = noise, A or Hz
p_a = ambient pressure, Pa
p_w = partial pressure of water at ambient temperature, Pa
S = detector sensitivity (response), A·mL/pg or Hz·mL/pg
S_{const} = constant value of sensitivity on the fitted curve when plotting sensitivity versus concentration of test substance passing the detector on a semilog paper, A·mL/pg or Hz·mL/pg
s = time, second
t_b = time corresponding to the peak width at base, min
T_a = ambient temperature, in Kelvin
T_d = detector temperature, in Kelvin
V = volt
W = mass of the test substance corresponding to a peak, g

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