Designation: E 1151 – 93

Standard Practice for Ion Chromatography Terms and Relationships[1]

This standard is issued under the fixed designation E 1151; 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 deals primarily with identifying the terms and relationships of those techniques that use ion exchange chromatography to separate mixtures and a conductivity detector to detect the separated components. However, most of the terms should also apply to ion chromatographic techniques that employ other separation and detection mechanisms.

1.2 Because ion chromatography is a liquid chromatographic technique, this practice uses, whenever possible the terms and relationships identified in Practice E 682.

1.3 *This standard does not purport to address all of the safety problems, 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:*

E 682 Practice for Liquid Chromatography Terms and Relationships[2]

3. Descriptions of Techniques

3.1 *Ion Chromatography,* (IC)—a general term for several liquid column chromatographic techniques for the analysis of ionic or ionizable compounds. Of the many useful separation and detection schemes, those most widely used have been the two techniques described in 3.2 and 3.3 in which ion exchange separation is combined with conductimetric detection. By describing only these two techniques, this practice does not mean to imply that IC is tied only to ion exchange chromatography or conductimetric detection.

3.2 *Chemically Suppressed Ion Chromatography, (Dual Column Ion Chromatography)*—In this technique, sample components are separated on a low capacity ion exchanger and detected conductimetrically. Detection of the analyte ions is enhanced by selectively suppressing the conductivity of the mobile phase through post separation ion exchange reactions.

3.3 *Single Column Ion Chromatography, (Electronically Suppressed Ion Chromatography)*—In this technique sample components are separated on a low capacity ion exchanger and detected conductimetrically. Generally, lower capacity ion exchangers are used with electronic suppression than with chemical suppression. Mobile phases with ionic equivalent conductance significantly different from that of the sample ions and a low electrolytic conductivity are used, permitting analyte ion detection with only electronic suppression of the baseline conductivity signal.

4. Apparatus

4.1 *Pumps*—Any of various machines that deliver the mobile phase at a controlled flow rate through the chromatographic system.

4.1.1 *Syringe Pumps*, having a piston that advances at a controlled rate within a cylinder to displace the mobile phase.

4.1.2 *Reciprocating Pumps*, having one or more chambers from which mobile phase is displaced by reciprocating piston(s) or diaphragm(s). The chamber volume is normally small compared to the volume of the column.

4.1.3 *Pneumatic Pumps*, employing a gas to displace the mobile phase either directly from a pressurized container or indirectly through a piston or collapsible container. The volume within these pumps is normally large as compared to the volume of the column.

4.2 *Sample Inlet Systems*, devices for introducing samples into the column.

4.2.1 *Septum Injectors*—The sample contained in a syringe is introduced directly into the pressurized flowing mobile phase by piercing an elastomeric barrier with a needle attached to a syringe. The syringe is exposed to pressure and defines the sample volume.

4.2.2 *Valve Injectors*—The sample contained in a syringe (or contained in a sample vial) is injected into (or drawn into) an ambient-pressure chamber through which the pressurized flowing mobile phase is subsequently diverted, after sealing against ambient pressure. The displacement is by means of rotary or sliding motion. The chamber is a section (loop) of tubing or an internal chamber. The chamber can be completely filled, in which case the chamber volume defines the sample volume, or it can be partially filled, in which case the syringe calibration marks define the sample volume.

4.3 *Columns*, tubes, containing a stationary phase and through which the mobile phase can flow.

4.3.1 *Precolumns*, positioned before the sample inlet system and used to condition the mobile phase.

---

[1] This practice is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and is the direct responsibility of Subcommittee E 13.19 on Chromatography.

Current edition approved July 15, 1993. Published September 1993.

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

4.3.2 *Concentrator Columns*, installed in place of the sample chamber of a valve injector and used to concentrate selected sample components.

4.3.3 *Guard Columns*, positioned between the sample inlet system and the separating columns and used to protect the separator column from harmful sample components.

4.3.4 *Separating Columns*, positioned after the sample inlet system and the guard column and used to separate the sample components.

4.3.5 *Suppressor Columns*, positioned after the separating column and a type of post column reactor where the conductivity of the mobile phase is selectively reduced to enhance sample detection.

4.4 *Postcolumn Reactors*, reaction systems in which the effluent from the separating columns is chemically or physically treated to enhance the detectability of the sample components.

4.4.1 *Conductivity Suppressors*, post column reactors in which the conductivity of the mobile phase is reduced through reactions with ion exchangers. Conductivity suppressors are differentiated by their type (cationic or anionic), by their form (H^+, Na^+, etc.), and by their method of regeneration (batch or continuous).

4.4.2 *Suppressor Columns*—Tubular reactors packed with ion exchangers. Suppressor columns require batch regeneration when the breakthrough capacity of the column is exceeded.

4.4.3 *Membrane Suppressors*—Reactors made from tubular shaped ion exchange membranes. On the inside of the tube flows the mobile phase; a regenerative solution surrounds the tube. These membrane suppressors can be in the form of an opened tube, hollow fiber suppressors, or a flattened tube for higher capacity. Tubular membranes can be packed with inert materials to reduce band broadening.

4.4.4 *Micromembrane Suppressor*—Reactors made from two sizes of ion-exchange screen. A fine screen is used for the mobile phase chamber and a coarse screen is used for the regenerant chambers. The mobile phase screen is sandwiched between ion-exchange membranes, and on either side of each membrane is a regenerant screen. The stack is laminated by pressure, causing intimate contact between screens and membranes. Mobile phase passes through a hole in the upper regenerant screen and membrane. It enters the screen-filled mobile phase chamber and passes through it. It then exits through a second set of holes in the upper membrane and regenerant screen. The regenerant flows countercurrent to the mobile phase through the screen-filled regenerant chamber.

4.5 *Detectors*—Devices that respond to the presence of eluted sample components. Detectors may be divided either according to the type of measurement or the principle of detection.

4.5.1 *Bulk Property Detectors*, measuring the change in a physical property of the liquid phase exiting the column. Thus a change in the refractive index, conductivity, or dielectric constant of a mobile phase can indicate the presence of eluting sample components. Conductimetric parameters, symbols, units and definitions are given in Appendix X1.

4.5.2 *Solute Property Detectors*, measuring the physical or chemical characteristics of eluting sample components. Thus, light absorption (ultraviolet, visible, infrared), fluorescence, and polarography are examples of detectors capable of responding in such a manner.

5. Reagents

5.1 *Mobile Phase*—Liquid used to sweep or elute the sample components through the chromatographic system. It may consist of a single component or a mixture of components.

5.2 *Stationary Phase*—Active immobile material within the column that delays the passage of sample components by one of a number of processes or their combination. Inert materials that merely provide physical support for the stationary phase are not part of the stationary phase. The following are three types of stationary phase:

5.2.1 *Liquid Phase*—A stationary phase that has been sorbed (but not covalently bonded) to a solid support. Differences in the solubilities of the sample components in the liquid and mobile phase constitute the basis for their separation.

5.2.2 *Interactive Solid*—A stationary phase that comprises a relatively homogeneous surface on which the sample components sorb and desorb effecting a separation. Examples are silica, alumina, graphite, and ion exchangers. In ion chromatography the interactive material is usually an ion exchanger that has ionic groups that are either ionized or capable of dissociation into fixed ions and mobile counter-ions. Mobile ionic species in an ion exchanger with a charge of the same sign as the fixed ions are termed “co-ions.” An ion exchanger with cations as counter-ions is termed a “cation exchanger,” and an ion exchanger with anions as counter-ions is termed an “anion exchanger.” The ionic form of an ion exchanger is determined by the counter-ion, for example, if the counter-ions are hydrogen ions then the cation exchanger is in the acid form or hydrogen form, or if the counter-ions are hydroxide ions then the anion exchanger is in the base form or hydroxide form. Ionic groups can be covalently bonded to organic polymers (for example, styrene/divinylbenzene) or an inorganic material (for example, silica gel). Ion exchange parameters, symbols, units and definitions are given in Appendix X2. Separation mechanisms on ion exchangers are described in Appendix X3.

5.2.3 *Bonded Phase*—A stationary phase that comprises a chemical (or chemicals) that has been covalently attached to a solid support. The sample components sorb onto and off the bonded phase differentially to effect separation. Octadecylsilyl groups bonded to silica represent a typical example for a bonded phase.

5.3 *Solid Support*—Inert material to which the stationary phase is sorbed (liquid phases) or covalently attached (bonded phases). It holds the stationary phase in contact with the mobile phase.

5.4 *Column Packing*—The column packing consists of all the material used to fill packed columns. The two types are as follows:

5.4.1 *Totally Porous Packing*—One where the stationary phase is found throughout each porous particle.

5.4.2 *Pellicular Packing*—One where the stationary phase is found only on the porous outer shell of the otherwise impermeable particle. Surface agglomerated packings are considered to be a type of pellicular packing.

6. Readout

6.1 *Chromatogram*—Graphic representation of the detector response versus retention time or retention volume as the sample components elute from the column(s) and through the detector. An idealized chromatogram of an unretained and a retained component is shown in Fig. X1.1.

6.2 *Baseline*—Portion of a chromatogram recording the detector response when only the mobile phase emerges from the column.

6.3 *Peak*—Portion of a chromatogram recording detector response when a single component, or two or more unresolved components, elute from the column.

6.4 *Peak Base (CD in* Fig. X1.1*)*—Interpolation of the baseline between the extremities of a peak.

6.5 *Peak Area (CHFEGJD in* Fig. X1.1*)*—Area enclosed between the peak and the peak base.

6.6 *Peak Height (EB in* Fig. X1.1*)*—Distance measured in the direction of detector response, from the peak base to peak maximum.

6.7 *Peak Widths*—Represent retention dimensions parallel to the baseline. Peak width at base or base width, (KL in Fig. X1.1) is the retention dimension of the peak base intercepted by the tangents drawn to the inflection points on both sides of the peak. Peak width at half height, (HJ in Fig. X1.1) is the retention dimension drawn at 50 % of peak height parallel to the peak base. The peak width at inflection points, (FG in Fig. X1.1), is the retention dimension drawn at the inflection points (= 60.7 % of peak height) parallel to the peak base.

7. Retention Parameters, Symbols, and Units

7.1 Retention parameters, symbols, units, and their definitions or relationship to other parameters are listed in Table X3.1.

NOTE 1—The adjusted retention time, capacity ratio, number of theoretical plates, and relative retention times are exactly true only in an isocratic, constant-flow system yielding perfectly Gaussian peak shapes.

7.2 Fig. X1.1 can be used to illustrate some of the following most common parameters measured from chromatograms:

Retention time of unretained component, $t_M = OA$

Retention time, $t_R = OB$

Adjusted retention time, $t_R = AB$

Capacity factor, $k' = (OB - OA)/OA$

Peak width at base, $w_b = KL$

Peak width at half height, $w_h = HJ$

Peak width at inflection points, $= FG = 0.607(EB)$

Number of theoretical plates, $N = 16[(OB)/(KL)]^2 = 5.54[(OB)/(HJ)]^2$

Relative retention, r (Note 2) $= (AB)_i/(AB)_s$

Peak resolution, R_s(Note 2 and Note 3) $= 2[(OB)_j - (OB)_i]/(KL)_i + (KL)_j \simeq (OB)_j - (OB)_i/(KL)_j$

NOTE 2—Subscripts *i, j*, and *s* refer to some peak, a following peak, and a reference peak (standard), respectively.

NOTE 3—The second fraction may be used if peak resolution of two closely spaced peaks is expressed; in such as case $(KL)_i = (KL)_j$.

APPENDIXES

(Nonmandatory Information)

X1. Separation Mechanisms

X1.1 *Ion Exchange Chromatography*—Sample and mobile counter-ions compete to form neutral ion pairs with the fixed ions of an ion exchanger. When paired, the sample ions do not move through the ion exchange column. Separation is achieved because the fixed ions have different thermodynamic complexation constants resulting in chromatographic selectivity between ions.

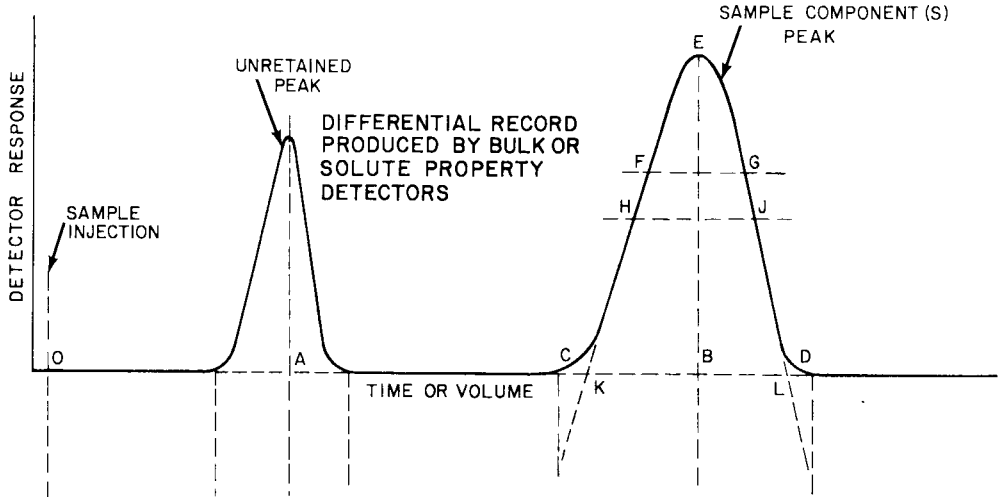

FIG. X1.1 Idealized Chromatogram

TABLE X1.1 Conductometric Parameters

Parameter	Symbol	Unit[A]	Definition or Relation to Other Parameters
Conductance		S	The reciprocal of a measured resistance
Electrolytic conductivity	κ	$S \cdot cm^{-1}$	The reciprocal of the resistance of a 1-cm cube of liquid at a specified temperature.
Equivalent conductivity	Λ	$S \cdot cm^2 \cdot equivalents^{-1}$	$\Lambda = \kappa/C$, where C is the total concentration (equivalents/cm^3) of positive or negative charge produced on dissociation of an electrolyte.
Ionic equivalent conductivity	λ	$S \cdot cm^2 \cdot equivalents^{-1}$	The contribution of an individual ion to the equivalent conductivity of an electrolyte, for example, $\Lambda = \lambda_c + \lambda_a$, where λ_c is the ionic equivalent conductance of the cations and λ_a is the ionic equivalent conductance of the anions of an electrolyte.
Cell constant	θ	cm^{-1}	$\theta = \kappa R\ R_{solv}/R_{solv} - R$ R is the resistance measured when the cell is filled with a standard electrolyte solution and R_{solv} is the resistance when the cell is filled with solvent at the same temperature.

[A] The SI unit siemens (S) was formerly called mho (Ω^{-1}).

X1.2 *Ion Exclusion Chromatography* (or *Donnan exclusion chromatography*)—Sample co-ions are excluded from entering the ion exchanger pore structure (or Donnan membrane) by electrostatic repulsion from the fixed ions while neutral and partially ionized sample components can enter and be retained by a partition or adsorption mechanism. Separation of partially ionized sample components, such as weak acids, is achieved because of their differences in ionization and their distribution constants.

X1.3 *Partition Chromatography*—Separation is based on differences between the solubilities of the sample components in the mobile and stationary phases.

X1.4 *Adsorption Chromatography*—Separation is based on differences between adsorption affinities of the sample components for the surface of an active solid.

X1.5 *Ion Pair Chromatography*—Sometimes called mobile phase ion chromatography, an ionic reagent is added to the mobile phase to interact with sample ions so as to influence their chromatographic partition or adsorption behavior. Separating columns which are generally used for partition chromatography are employed for separation of the resultant species.

X2. Ion Exchange Parameters, Symbols, Units, and Definitions

TABLE X2.1 Ion Exchange Parameters, Symbols, Units, and Definitions

Parameter	Quantity Symbol	Unit	Definition or Relation to Other Parameters
Theoretical specific ion exchange capacity	Q_0	meq/g	(milliequivalent of ionogenic groups)/(weight of dry ion exchanger) If not otherwise stated, the capacity should be reported per gram of the H-form of a cation exchanger and Cl-form of an anion exchanger.
Volume ion exchange capacity	Q_V	meq/cm^3	(milliequivalent of ionogenic groups)/(volume of swollen ion exchanger) The ionic form of the ion exchanger, the medium, and the temperature should be specified.
Practical specific ion exchange capacity	Q_A	meq/g	(total milliequivalent of ions taken up)/(weight of dry ion exchanger) The conditions under which the ions are taken up by the ion exchanger should be specified
Break-through capacity of ion exchange column	Q_B	meq/cm^3	The practical capacity of an ion-exchanger column obtained experimentally by passing a solution containing a particular ionic species through the column under specified conditions, and measuring the amount of that species which has been taken up when the species is first detected in the effluent or when the concentration in the effluent reaches some arbitrarily defined value.

X3. Retention Parameters, Symbols, Units and Definitions

TABLE X3.1 Retention Parameters, Symbols, Units and Definitions

Parameter	Quantity Symbol	Unit	Definition or Relationship to Other Parameters
Time	t	min	
Temperature of mobile phase	T	K	°C + 273.15 at the point where mobile phase flow is measured
Temperature of column	T_c	K	
Ambient temperature	T_a	K	
Column inlet pressure	P_i	Pa	
Column outlet pressure	P_o	Pa	
Pressure drop along the column	P	Pa	$P = P_i - P_o = Lu/B_o$
Relative column pressure	P		$P = P_i / P_o$
Ambient (atmospheric) pressure	P_a	Pa	
Column length	L	cm	
Column inside diameter	d_c	cm	
Average diameter of solid particles in the column	d_p	cm	
Pore radius	r_p	cm	
Interparticle porosity	ϵ		fraction of column cross section available for the moving phase
Column cross-sectional area	A_c	cm^2	$A_c = (d_c)^2\pi/4$
Volume of mobile phase in column + system	V_M	cm^3	$V_M = F_c\ t_M$
Interstitial volume of column	V_I	cm^3	In ideal case, assuming no extracolumn volume in system: $V_M = V_I$ In actual systems: $V_M = V_I + V_{ext} = V_I + V_i + V_d$ where V_{ext} is the extra column volume, V_1 is the volume between the effective injection point and the column inlet and V_d is the volume between the column outlet and the effective detection point
Geometric volume of column	V_c	cm^3	$V_c = d_c^2\pi L/4 = A_c L$
Molar volume	V_m	cm^3/mol	
Phase Ratio	β		$\beta = V_I/V_S$ V_S = volume of the stationary phase
Specific column permeability	B_o	cm^2	$B_o = \frac{d_p^{\,2}\epsilon^3}{180(1-\epsilon)^2} \simeq \frac{d_p^{\,2}}{1000}$
Flow rate of the mobile phase from the column	f_a	cm^3/min	measured at ambient temperature and pressure
Flow rate of mobile phase from the column, corrected to column temperature	f_c	cm^3/min	$F_c = F_a/T_c;T_a$
Linear velocity of mobile phase	u	cm/s	$u = \frac{L}{60t_M} = \frac{F_a}{60_\epsilon A_c}$
Optimum linear velocity of mobile phase	u_{opt}	cm/s	the value of u at the minimum of the HETP versus u plot; the value of u where the measured HETP is the smallest
Viscosity of mobile phase	η	P [g/(cm·s)]	expressed at column temperature
Reduced mobile phase velocity	ν	...	$\nu = \frac{ud_p}{D_M}$
Diffusion coefficient of solute in mobile phase	D_M	cm^2/s	
Diffusion coefficient of solute in stationary phase	D_S	cm^2/s	
Retention time (total retention time)	t_R	min	time from sample injection to maximum concentration (peak height) of eluted compound
Mobile phase holdup time	t_M	min	observed elution time of an unretained substance
Adjusted retention time	t_R'	min	$t_R' = t_R - t_M$
Retention volume (total retention volume)	V_R	cm^3	$V_R = t_R F_c$
Adjusted retention volume		cm^3	$V_R' = t_R' F_c$
Peak width at inflection points	w_i	cm	retention dimension between the inflection points (representing 60.7 % of peak height) of any single-solute peak
Peak width at half height	w_h	cm	retention dimension between the front and rear sides of any single-solute peak at 50 % of its maximum height
Peak width at base	w_b	cm	retention dimension between intersections of baseline with tangents to the points of inflection on the front and rear sides of any single-solute peak
Peak area	A	cm^2	

TABLE X3.1 *Continued*

Parameter	Quantity Symbol	Unit	Definition or Relationship to Other Parameters
Distribution constant (partition coefficient)	K		$K = \frac{\text{solute concentration in the stationary phase}}{\text{solute concentration in the mobile phase}}$
Capacity factor (partition ratio, mass distribution ratio)	k		$k = t_R'/t_M = (t_R - t_M)/t_m$ $= V_R'/V_M = (V_R - V_M)/V_M$ $= (1 - R)R$
	κ		$\kappa = \log k$
Number of theoretical plates	n		$n = 16(t_R/w_b)^2 = 5.54(t_R/w_h)^2 = 4(t_R/w_l)^2$
Number of effective plates	N		$N = 16(t_R'/w_b)^2 = 5.54(t_R'/w_h)^2 = 4(t_R'/w_l)^2$ $= n\left(\frac{k}{k+1}\right)^2$
Height equivalent to one theoretical plate	h, HETP	cm	$H = L/n$
Height equivalent to one effective plate	H, HEETP	cm	$H = L/N$
Reduced plate height	h_r		$h_r = h/d_p$ a term used in paper and thin-layer chromatography
Retention factor	R_F		$R_F = \frac{\text{distance moved by solute}}{\text{distance moved by mobile phase}}$ $HR_F = 100 \times R_F$
R value	R		$R = 1/(k + 1)$
R_M value	R_M		$R_M = \log[(1/R_f) - 1]$
R_s value	R_s		$R_s = R_f/R_{f(s)}$
Peak resolution	R_s		$R_s = \frac{2(t_{Rj} - t_{Ri})}{w_{bi} + w_{bj}} \simeq \frac{t_{Rj} - t_{Ri}}{w_{bj}}$ where $t_{Rj} > t_{Ri}$
Relative retention	$r_{i,s}$		$r_{i,s} = t_{Ri}'/t_{Rs}' = K_i/K_s = k_i/k_s$
Relative retention (separation factor, separation ratio)	α		$\alpha = t_{R2}'/t_{R1}' = K_2/K_1 = k_2/k_1$ The symbol r is used to designate relative retention of a peak relative to the peak of a standard while the symbol α is used to designate the relative retention of two consecutive peaks. By agreement, $t_{R2}' > t_{R1}'$ and thus, the value of α is always larger than unity while the value of r can be either larger or smaller than unity, depending on the relative position of the standard peak.
Number of theoretical plates required for a given resolution of peaks 1 and 2	n_{req}		$n_{req} = 16\,R_s^2\left(\frac{\alpha}{\alpha - 1}\right)^2\left(\frac{k_2 + 1}{k_2}\right)^2$
Number of effective plates required for a given resolution of peaks 1 and 2	N_{req}		$N_{req} = 16\,R_s^2\left(\frac{\alpha}{\alpha - 1}\right)^2$
Weight-average molecular weight	M_W	g/mol	second moment of a polymer distribution
Number-average molecular weight	M_N	g/mol	first moment of a polymer distribution
Molecular weight distribution	MWD		weight (or number) fractions as a function of molecular weight
Integral molecular weight distribution	∫MWD		sum of weight fractions as a function of molecular weight
Differential molecular weight distribution	d(MWD)		relative abundance of a fraction as a function of molecular weight
Dispersity	d		a measure of the breadth of a molecular weight distribution
Hydrodynamic volume	V_h	cm^3/mol	a polymer molecular property proportional to M
Exclusion limit	$V_{h,max}$	cm^3/mol	maximum V_h that entered into pore
Solute designations (subscripts)	i		any solute
	j		a solute eluting after solute i
	s		a standard or reference solute
	1, 2		two consecutive solutes from which solute 2 elutes later than solute 1