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## PRESSURIZED, ANNULAR CHROMATOGRAPH FOR CONTINUOUS SEPARATIONS

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### SUMMARY

The concept for a continuous chromatograph utilizing a rotating annulus was presented over 25 years ago. Such a system with a stationary feed point and stationary effluent ports can accept a continuous feed stream and separate it into a series of constituent streams that appear as separate helical bands in the annulus. A theoretical plate concept can be used to mathematically describe the system. Recent developments for continuous liquid chromatography include the addition of gas overpressure for higher pressure operation and the use of segmenting spacers at the feed entry to allow gradient elution. Molecular sieves and ion-exchange systems are being investigated for utility in several specific separations.

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### INTRODUCTION

Preparative, large-scale chromatographic separations are usually achieved by increasing the diameter of the analytical-scale sorption column. This expanded size allows larger amounts of feed material to be introduced in a batch mode without seriously overloading the column. Unfortunately, the increase in the dimension normal to the eluent flow contributes to a loss of resolution due to radial flow variations and other mixing effects. As a result, the scale-up of conventional columns beyond about 2.5 cm diameter leads to a measurable loss of resolution.

Much consideration has been given to the technique of continuous liquid chromatography and to various systems designed to take advantage of its capabilities. One system would contain provisions for the solid sorbent phase to move counter-current to the eluent stream and have intermediate takeoff points for the various different solutes; however, the design problems associated with such a scheme would be quite difficult. A variation of the technique developed by Arehart *et al.*<sup>1</sup>, which is the closest approach to this concept, would still not be adequate since it contributes to extensive backmixing. In any case, the bulk sorbent phase must have the capability of moving past the feed entry point and various product takeoff points in order for the chromatograph to be truly continuous.

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An annular chromatograph rotating with respect to a feed stream and eluate collection points was proposed by Martin<sup>2</sup> over 25 years ago. Later, it was considered on a theoretical basis by Giddings<sup>3</sup>. Several other workers have developed and evaluated various versions of this concept during the past 20 years, but apparently were not able to circumvent the operational problems. For example, Svensson *et al.*<sup>4</sup> utilized an annular array of individual columns while Fox *et al.*<sup>5</sup> used a rotating annulus. On the other hand, Dunnill and Lilly<sup>6</sup> carried out experiments to determine the effectiveness of a stationary annulus with rotating feed nozzle and fraction collector. In these cases, the designs of the various systems resulted in relatively simple biochemical separations; however, such systems used only gravity or low-pressure flow, making it difficult to take advantage of high-resolution separations and the designs of the systems were not compatible with gradient elution techniques.

We are now considering an extension of this concept in which a rotating annulus will be used with stationary feed and elution streams as well as stationary eluate collection ports. Further, the feed and eluent streams will be introduced through appropriate seals to permit pressurized operation with an overpressure of gas, and segmenting vanes will be included at the top of the annular bed to reduce feed back-mixing and to allow gradient elution.

A more complete theoretical analysis of the system utilizing a theoretical plate concept has also been completed, and a photometric monitor has been developed for measuring elution position and band spreading.

#### THEORETICAL CONSIDERATIONS\*

##### *Principle of operation*

In our approach, operation of the continuous, annular chromatograph involves moving an annular bed of sorbent past a stationary feed entry point and stationary effluent recovery ports (Fig. 1). As the annulus rotates, it is subjected to a short feed introduction time followed by a relatively long period of elution from a series of eluent nozzles. During this operational sequence, the initial entry point completes a revolution.

As elution proceeds, the eluted substances progress down the annulus, giving the appearance of helices as the annulus rotates. The more strongly sorbed species exit from the rotating annulus at a greater distance from the feed point, thus providing a continuous separation of species with differing sorption characteristics.

##### *Mathematical description*

The annular chromatograph can be described mathematically by a theoretical plate approach similar to that developed by Martin and Synge<sup>7</sup> and amplified by Said<sup>8</sup> for stationary columns. The mathematical description should result in algebraic expressions for the elution position (as measured from the feed point) of each solute and for the bandwidth as a function of elution position or other system parameters.

*General considerations.* The following simplifying assumptions are made: (1) The annulus consists of a series of equally sized segments arranged circumferentially. (2) Each of these annular segments is made up of a series of theoretical plates,

\* See also List of symbols at the end of the article.

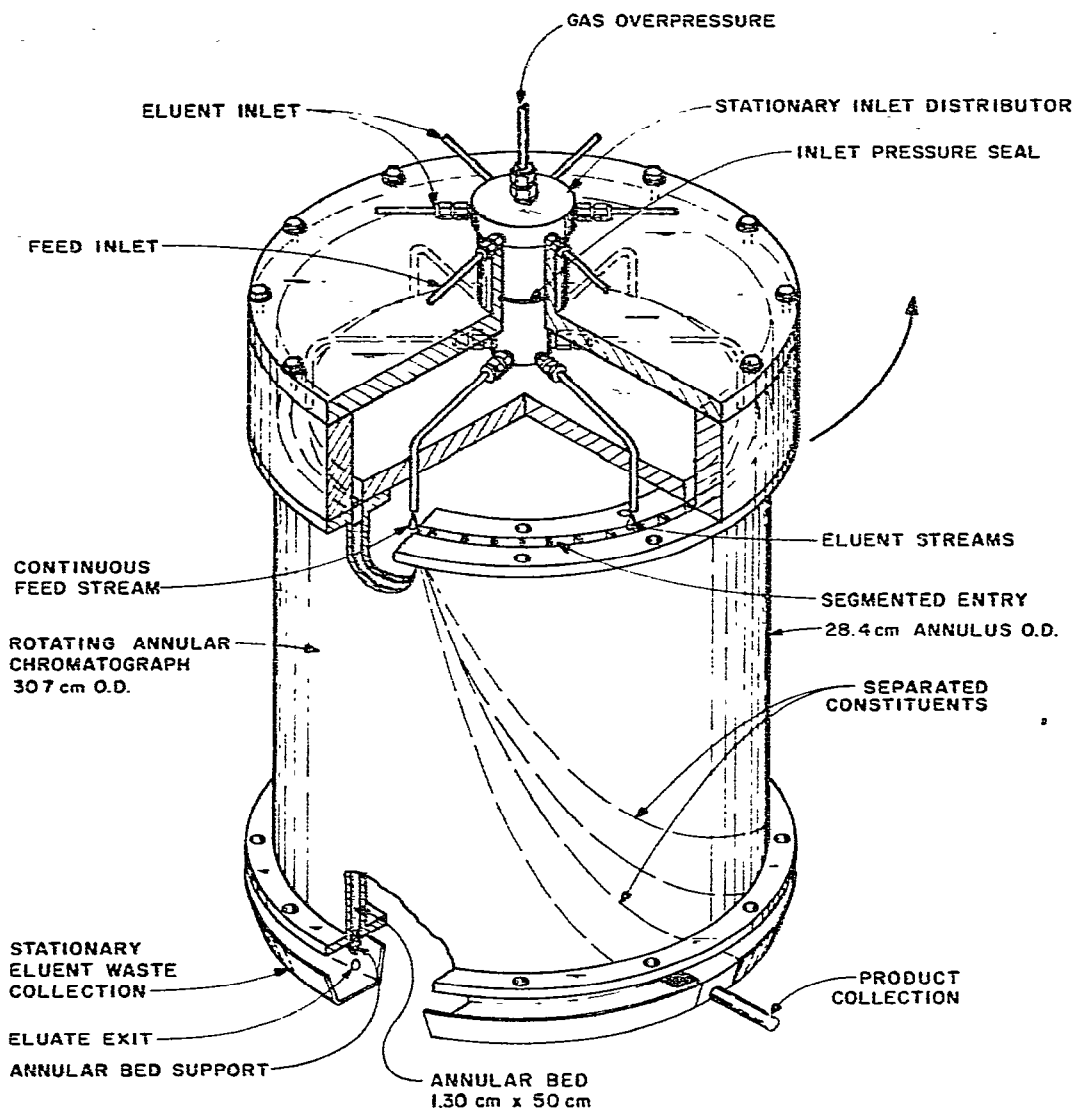


Fig. 1. Pressurized, continuous annular chromatograph.

progressing from the top to the bottom, that have identical fixed heights. (3) The concentration of a solute as it leaves the theoretical plate is at equilibrium with the average concentration of the solute sorbed in the stationary phase. (4) There is no lateral mass transport of the solute or solvent to adjoining annular segments. (5) No radial variation exists in either the fluid or the sorbent phase. (6) The superficial velocity of the eluent is constant throughout the annulus.

One of the problems encountered in mathematically describing the annular chromatograph is the establishment of a usable point of reference. This is somewhat difficult since the feed and eluate recovery points are stationary while the annular

sorbent phase is in motion. In fact, it is convenient to use two references, viz. the stationary feed point and a specific point in the rotating annulus (e.g., the top). For the sake of simplicity, the following additional assumptions were made in an attempt to circumvent this problem: (1) A single annular segment as it rotates will be one reference point for the mathematical treatment and the feed point will be the other. (2) All of the solute is assumed to be in the first theoretical plate at the end of the feed introduction period.

The actual chromatographic process begins at  $t = 0$ , when the reference annular segment just leaves the feed zone. Thereafter, the elution sequence occurs and the annular position of the reference segment, in terms of the stationary feed point, is dependent on the time and angular speed of the annulus. The steady-state chromatographic patterns can be established by following the chromatographic process in a single columnar segment as it makes a complete circuit.

The mathematical description of the process with the above assumptions can be generated by considering a series of material balances of the solute around each of the theoretical plates of the reference segment. For example, at plate 1, after the feed stage during the time lapse of  $\Delta t$  (or an eluent flow through the segment of  $\Delta v$  and an angular displacement of  $\Delta\theta$  from the feed point), the material balance would be (Fig. 2)

$$\text{solute in} - \text{solute out} = \text{change in solute inventory} \quad (1)$$

If  $\Delta t$ ,  $\Delta v$ , and  $\Delta\theta$  become vanishingly small, the differential form of the material balance becomes

$$0 - c_1 dv = d \left[ \frac{V}{N} \varepsilon c_1 + \frac{V}{N} (1 - \varepsilon) K c_1 \right] \quad (2)$$

where

$c_1$  = concentration of solute in the fluid phase leaving the first theoretical plate, moles/cm<sup>3</sup>

$v$  = total eluent flow through an annular segment during time  $t$  and displacement  $\theta$ , cm<sup>3</sup>

$V$  = total volume of an annular segment, cm<sup>3</sup>

$N$  = total number of theoretical equilibrium plates in the annular segment

$K$  = distribution coefficient,  $\frac{\text{moles solute/cm}^3 \text{ sorbent phase}}{\text{moles solute/cm}^3 \text{ fluid phase}}$

$\varepsilon$  = void fraction in chromatograph,  $\frac{\text{cm}^3 \text{ fluid phase}}{\text{cm}^3 \text{ annular volume}}$

Rearrangement yields

$$\frac{dc_1}{c_1} = -B dv \quad (3)$$

where

$$B = \frac{N}{V} \left[ \frac{1}{\varepsilon + (1 - \varepsilon) K} \right]$$

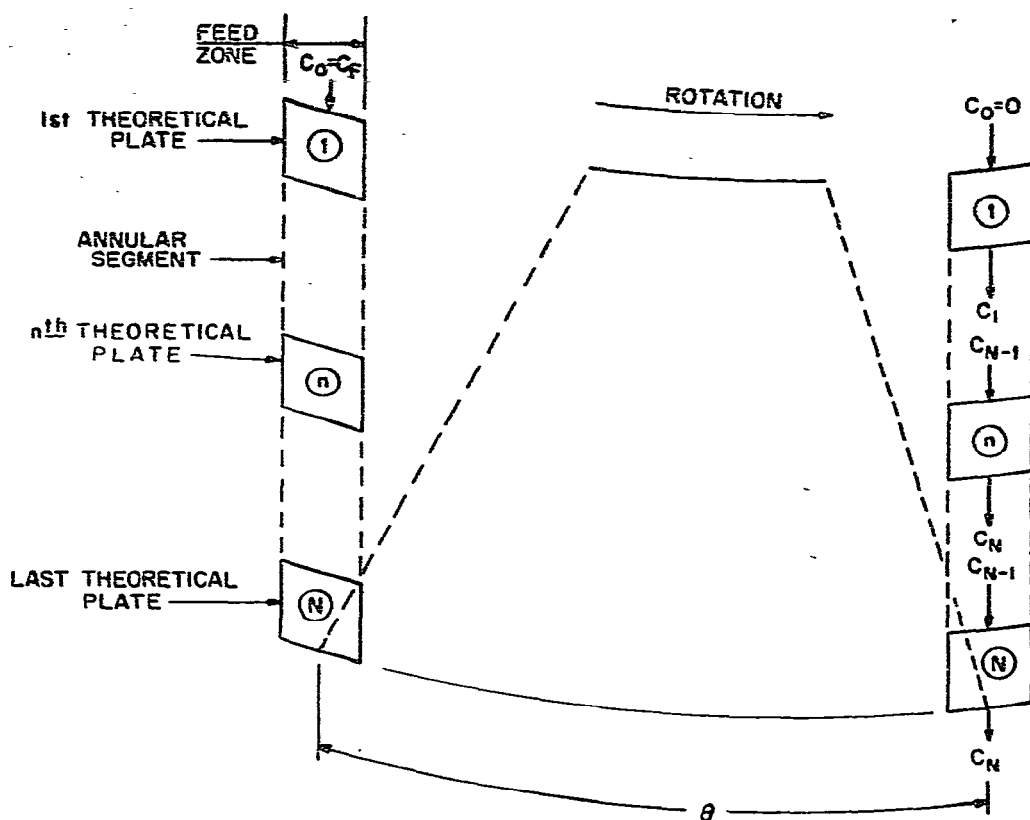


Fig. 2. Movement of an annular segment in the continuous annular chromatograph.

Here the boundary conditions are

$$v = 0, t = 0, c_1 = c_f$$

where  $c_f$  = solute concentration in the feed, moles/cm<sup>3</sup>. The solution of eqn. 3 results in the fluid phase solute concentration in plate 1 of the annular segment after the flow of a volume,  $v$ , of the eluent

$$c = c_f e^{-Bv} \quad (4)$$

During the time required for the flow of  $v$  through the annular segment, the segment has rotated away from the feed point by an angle of

$$\Theta = \omega t = \frac{\omega v}{uA} \quad (5)$$

where

$A$  = cross-sectional area of the annular segment, cm<sup>2</sup>

$t$  = time for the reference annular segment to be displaced by an angle of  $\Theta$  from the feed point, sec

$u$  = eluent superficial velocity, cm/sec

$\omega$  = angular velocity, rad/sec

Therefore, the concentration of the solute as it leaves the first theoretical plate at a position  $\Theta$  from the feed point is given by eqn. 4.

Similarly, the mobile phase concentration can be represented at any theoretical plate,  $n$ , in the annular segment at any point around the annulus by

$$\frac{c_n}{c_f} = e^{-Bv} \frac{(Bv)^{n-1}}{(n-1)!} = e^{-B'\theta} \frac{(B'\theta)^{n-1}}{(n-1)!} \quad (6)$$

where

$$B' = \frac{Nu}{\omega L} \left[ \frac{1}{\varepsilon + (1 - \varepsilon)K} \right]$$

$L$  = vertical distance from feed point to exit, cm. In the case of the system exit, this equation becomes

$$\frac{c_N}{c_f} = \frac{e^{-B'\theta} (B'\theta)^{N-1}}{(N-1)!} \quad (7)$$

This is a Poisson distribution, which can be approximated by a Gaussian distribution for large values of  $B'\theta$  (ref. 9)

$$\frac{c_N}{c_f} = \frac{1}{\sqrt{2\pi B'\theta}} \exp - \left\{ \frac{[B'\theta - (N-1)]^2}{2B'\theta} \right\} \quad (8)$$

*Elution position.* The maximum value of solute concentration at the exit will occur at a specific angular location,  $\bar{\theta}$ , and can be determined by allowing the differential of eqn. 7 with respect to  $\theta$  to approach zero:

$$\left[ \frac{e^{-B'\theta} (B'\theta)^{N-2}}{(N-2)!} \right] \left( 1 - \frac{B'\theta}{N-1} \right) = 0 \quad (9)$$

Eqn. 9 indicates that the first derivative is zero at

$$B'\theta = N-1, \quad B'\theta = 0, \quad B'\theta = \infty$$

or at

$$\theta = \frac{N-1}{B'}, \quad \theta = 0, \quad \theta = \infty$$

The maximum exit concentration or "elution position",  $\bar{\theta}$ , of the solute must then be at the point where

$$\bar{\theta} = \frac{N-1}{B'} \quad (10)$$

or, for large values of  $N$

$$\bar{\theta} = \frac{N}{B'} \quad (11)$$

Minimum values will be found at

$$\Theta = 0 \text{ and } \Theta = \infty$$

From eqns. 8 and 11 the maximum concentration will then be

$$\left(\frac{c_N}{c_f}\right)_{\max.} = \frac{1}{\sqrt{2\pi B' \Theta}} = \frac{1}{\sqrt{2\pi(N-1)}} \approx \frac{1}{\sqrt{2\pi N}} \quad (12)$$

If we introduce the expression for  $B'$  into eqn. 11, the elution position is defined by

$$\bar{\Theta} = \frac{\omega L}{u} [\varepsilon + (1 - \varepsilon) K] \quad (13)$$

Thus, eqn. 13 should predict the radial exit location of the maximum concentration of a solute (elution position) as a function of system length ( $L$ ), angular velocity or rotational speed ( $\omega$ ), superficial velocity ( $u$ ), void fraction ( $\varepsilon$ ), and the distribution coefficient ( $K$ ).

**Bandwidth.** In order to establish conditions for separating two or more solutes, both the elution position and the width of solute bands must be predictable. The solute band is defined as the solute concentration in the circumferential or horizontal direction. Disregarding circumferential diffusional effects and mixing, there are two major contributions to the width of the helical bands as they exit the chromatograph: the initial width of the feed stream and longitudinal diffusional and mixing effects. The first of these is easily measured and thus predictable at the feed introduction point, while the second can be estimated with the assumptions inherent in the theoretical plate theory.

As indicated by the mathematical treatment of Van Deemter *et al.*<sup>10</sup>, the various band spreading phenomena in combination can be represented by a simple addition of the variances of each of the mechanisms. Thus, the total variance,  $\sigma_t^2$ , would be a linear combination of the two effects noted above

$$\sigma_t^2 = \sigma_f^2 + \sigma_l^2 \quad (14)$$

or

$$\sigma_t = \sqrt{\sigma_f^2 + \sigma_l^2} \quad (15)$$

where the subscripts  $t$ ,  $f$ , and  $l$  represent total, feed, and longitudinal, respectively.

It is most convenient to express band spreading by angular displacement since this fits in with the angular elution position. In this case, the standard deviation of band spreading,  $\sigma$ , will be expressed as the angle of displacement from the midpoint of the band.

The contribution of the feed bandwidth is rather straightforward since it is defined by the distance between spacers at the top of the chromatograph. On the other hand, band spreading in the longitudinal direction,  $\sigma_l$ , can be approximated by modifying the expression developed for the concentration profile given by eqn. 6. As

previously mentioned, this expression for large values of  $B'\theta$  can be approximated by a Gaussian distribution which, when put in the standard form, could be used to determine the standard deviation.

As before, we have considered a reference segment of the annulus rotating sequentially through the feed zone and the elution zone. The total quantity of solute,  $Q$ , leaving the segment during the course of the elution would be

$$Q = \int_{-\infty}^{\infty} c_N dv \text{ or } Q = \frac{uA}{\omega} \int_{-\infty}^{\infty} c_N d\theta \quad (16)$$

(Note: Because all of the material is eluted in a single revolution after which feed is again introduced, the limits of integration,  $-\infty$  and  $\infty$ , are actually "dummy" limits, relating only to a single sample input pulse.)

The total quantity of feed introduced to the first plate was:

$$Q = c_f \frac{AL}{N} [\varepsilon + (1 - \varepsilon) K] \quad (17)$$

Normalizing eqn. 16 by dividing by eqn. 17 results in

$$\int_{-\infty}^{\infty} B' \frac{c_N}{c_f} d\theta = 1 \quad (18)$$

which is a necessary criterion for a standard Gaussian distribution of the function

$$\left( B' \frac{c_N}{c_f} \right)$$

From eqn. 12 it can be seen that

$$\left( \frac{B' c_N}{c_f} \right)_{\max.} = \frac{B'}{\sqrt{2\pi N}} \quad (19)$$

But, for a standard Gaussian distribution, the maximum value will also be

$$\left( \frac{B' c_N}{c_f} \right)_{\max.} = \frac{1}{\sigma_t \sqrt{2\pi}} \quad (20)$$

Combining eqns. 19 and 20 and substituting eqn. 11 results in

$$\sigma_t = \frac{\bar{\theta}}{\sqrt{N}} \quad (21)$$

The total bandwidth at the exit of the chromatograph can then be approximated by

$$\sigma_t = \sqrt{\sigma_f^2 + \frac{\bar{\theta}^2}{N}} \quad (22)$$

#### EXPERIMENTAL EQUIPMENT

An annular chromatograph and a photometric monitoring device were developed and fabricated for this study.



### *Annular chromatograph*

The annular chromatograph (Fig. 1) was fabricated from Plexiglas®. The annulus was formed from two concentric open cylinders and appropriately sealed at the top and the bottom by flanges. The annulus was 1.30 cm wide and 50 cm long, with an outside diameter of 28.4 cm. The top of the cylinder forming the inner annulus wall was also sealed. The enclosed head space above the annulus was created by bolting another open cylinder with sealed top to the flange on the outside annulus wall. A Teflon® flow distributor fit into a special port provided in the top of the chromatograph with a double O-ring seal. Inlet holes drilled through this distributor allowed access of the feed line and six eluent lines, while an air line provided constant overpressure. The head space in the top of the chromatograph provided a gas blanket over the annulus which could be pressurized to a maximum of 25 p.s.i.g., while the O-ring seal allowed the distributor to remain stationary during rotation of the annulus.

Forty-eight spacers were placed across the annulus at regular intervals at the top and the bottom of the annulus. These spacers not only served to maintain a constant annulus width, but also segmented the top of the column into different regions for gradient elution.

The sorbent bed was held in place by a plastic fabric over a wire mesh, which was clamped in place between two plastic gaskets, and the entire chromatograph was bolted onto a support plate. The eluate stream tended to contact solid surfaces at the system exit which could result in flow over the surfaces, extensive mixing, and separation into a few, discrete eluate streams. To circumvent this problem, a series of 1/8-in.-thick spacers was also placed in the annular exit just below the stationary phase support. Each spacer extended across the annulus exit, and had a triangular cross section whose apex extended below the chromatograph. This arrangement, which resulted in channeling of the eluate stream onto each spacer, with eluate dripping from each apex, prevented gross backmixing. The spacers were placed at 2-cm intervals around the annulus exit.

A slow-speed drive system allowed the support plate (and the annular chromatograph) to rotate at speeds of approximately 0.1 to 20 rph. Metering pumps were available to introduce the feed and eluent streams through the stationary distributor; for nongradient elution, an electrical feedback level control was available to maintain a constant eluent level above the surface of the sorbent.

### *Monitoring device*

A device for monitoring the concentration of solute in the helical bands was developed. It included a light source that imposed light through the outer chromatograph wall into the eluting band and a photo detector that measured reflected light. These were enclosed in an aluminum body (see Fig. 3). Light from the source was focused with a lens into the sorbent phase, and the reflected light was then focused onto a photovoltaic silicon detector. The signal from the silicon detector was amplified and subsequently recorded on a strip-chart recorder.

### *Operation*

For gradient elution, the top of the sorbent bed was just above the lower edge of the top spacers. This separated the top of the annulus into a series of "segments" with a small amount of contained headspace above each. During operation, the feed

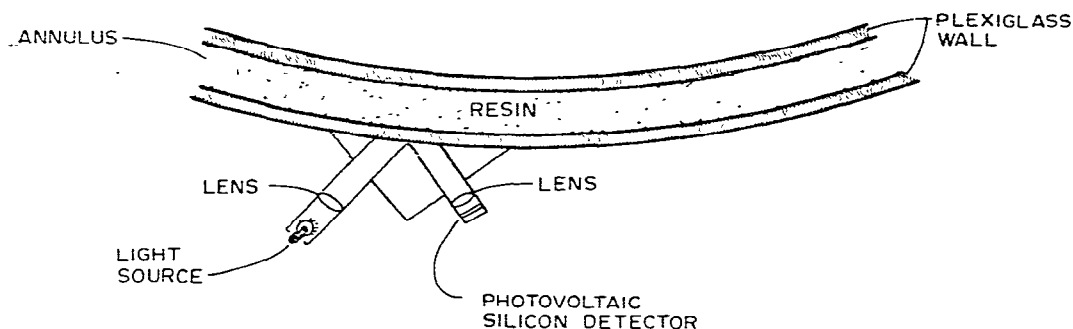


Fig. 3. Schematic of solute monitoring device.

stream was introduced sequentially into each segment as the annulus rotated past the feed nozzle. The separation process was actually begun before the solute had progressed below the bottom of the spacer. The feed rate was controlled so that the head space in each segment was not exceeded during the time that the feed point was above the segment. With this mode of operation, the eluent streams were introduced into each segment as it passed sequentially under the individual eluent nozzles. The eluent flow-rates were also adjusted so that the segment head space was not exceeded. The spacing of the eluent nozzles was such that the eluent in the segment head space was exhausted just as the segment progressed to the next nozzle.

For isocratic elution, the sorbent level was maintained above the top of the spacers and the feed nozzle tip was adjusted so that it was below the surface of the sorbent bed. This resulted in the feed nozzle plowing through the top portion of the bed. In most cases, the packed sorbent material had enough fluidity to prevent any permanent trace from the feed nozzle; however, an overlay of a nonadsorbing gel could be used to circumvent this problem. With such an approach, feed convective mixing was retarded and the initial feed bandwidth was about half that when the segments were used. A constant head of eluent fluid was maintained above the entire bed by a simple liquid-level feedback controller and the gas overpressure forced the eluent through the sorbent.

*Solute monitor.* Band eluting position was simply determined visually as the midpoint of the exiting solute band. However, the concentration across the solute band was determined by the monitoring device. Since the helical band appeared to be stationary while the annulus rotated, band monitoring was achieved by attaching the monitoring device to the outer surface of the chromatograph and allowing it to scan across the band with the motion of the annulus (Figs. 4 and 5).

## EXPERIMENTAL RESULTS

Two different types of separation were studied: (1) a system using cross-linked dextran gels for separation by molecular size, and (2) a system using ion-exchange resins. The former would be typically applied to biochemical separations, while the latter would normally be used for separation of inorganic solutes. The primary experimental parameters measured were the elution position and the bandwidth as a function of bed depth. These data were correlated by the expressions developed

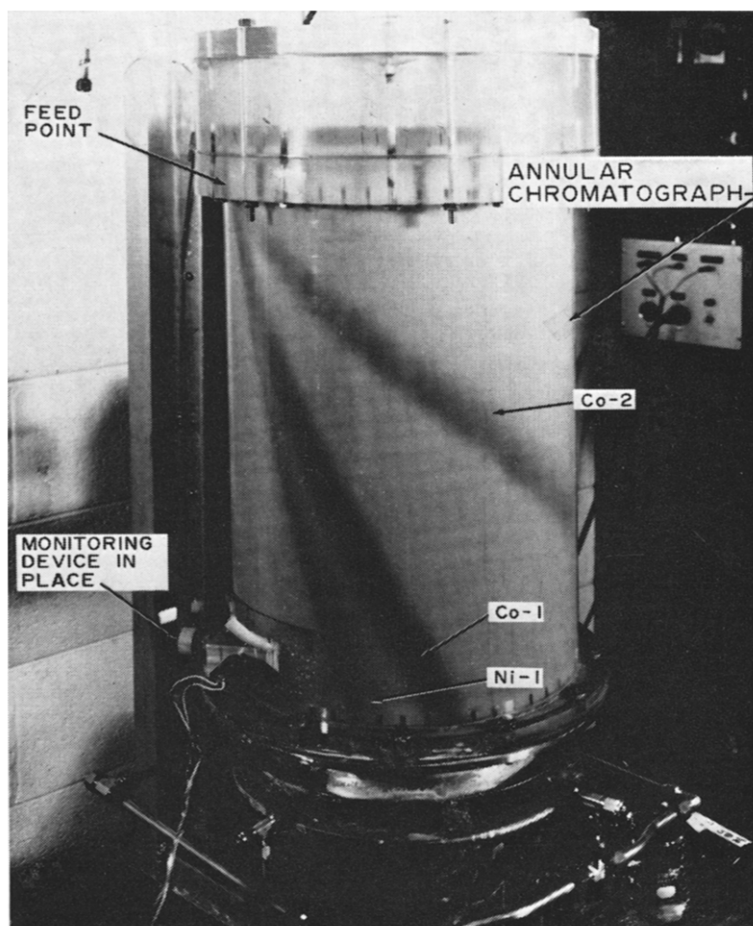


Fig. 4. Separation of a nickel and two cobalt complex ions in a simulated ammonia process liquor by the continuous annular chromatograph.

by the mathematical model, and the resulting correlations were used to verify the validity of that mathematical interpolation.

#### *Molecular sieve separations*

Cross-linked dextran gels can be used to separate mixtures of biological macromolecules by difference in molecular size. This molecular sieving operation is one of the most important separation tools used in biochemical research.

In order to evaluate the continuous annular chromatograph for such applications and, at the same time, to verify the mathematical model, a series of tests was made with various Sephadex<sup>\*</sup> gels as the stationary phase. Typically, Sephadex G-25 in the size range of 100–300  $\mu\text{m}$  was used with a test feed stream containing Blue Dextran 2000<sup>\*</sup> (a high-molecular-weight, soluble dextran) either as a single solute or in

\* Trademark of Pharmacia Fine Chemicals, Uppsala, Sweden.

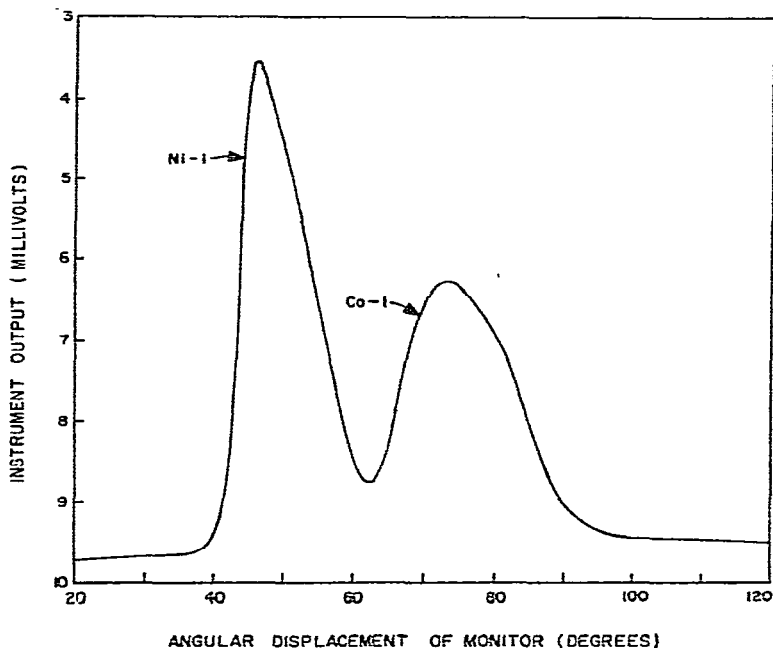


Fig. 5. Typical output of monitoring device as it scans across the elution bands in the ion-exchange separation of nickel and cobalt complex ions. Scanning wavelength, 620 mm; scanning speed, 49°/h.

combination with  $\text{CoCl}_2$ . In the latter case, the significant difference in the molecular size of the two solutes (the Blue Dextran molecule was much too large to penetrate the gel matrix) gave a clear indication of the molecular sieving action. Since both solutes were highly colored materials, they were easily detected and quantified in the experimental apparatus. Distilled water was used as the eluent.

#### *Ion-exchange separation*

The separation of nickel and cobalt from a synthetic process liquor was investigated as an ion-exchange separation of potential utility. In the preferred process for nickel recovery from oxide ores<sup>11</sup>, an ammonia-rich process liquor is produced that contains a nickel complex ion and as many as three cobalt complex ions. Hurst<sup>12</sup> recently identified these complexes as  $[\text{Ni}(\text{NH}_3)_{6-x}(\text{H}_2\text{O})_x]^{2+}$ ,  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$ ,  $[\text{Co}(\text{NH}_3)_5\text{CO}_3]^+$ , and  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , referred to hereafter as Ni-1, Co-1, Co-2, and Co-3 and he proposed that a high-resolution ion-exchange separation could be used for the final purification step in this process with recovery of both nickel and cobalt. In such a process, a continuous chromatograph would be most useful.

Dowex 50W-X8 ion-exchange resin (50–60  $\mu\text{m}$ ) was used to separate the components in a synthetic feed liquor containing Ni-1, Co-1, and Co-2. The third cobalt species was not included since it represents a relatively simple separation. The eluent was 1 M  $(\text{NH}_4)_2\text{CO}_3$  buffered to a pH of 7.8, and the elution sequence was Ni-1 followed by Co-1 and Co-2 (Fig. 4). Since all three solutes are colored substances with useful light absorption properties, the separation could be easily followed by the monitor.

### Calibration of the solute monitor

In order to measure the bandwidths of the eluting solutes, it was necessary to measure the concentration profile across the eluting band. Thus, the output of the solute monitoring device had to be related to solute concentration. In this context, the measurement of actual concentration was not as important as determining the relative concentration across the band.

Calibration of this device was accomplished by fabrication of a stationary section of the chromatographic annulus divided into segments, which allowed the stationary phase to be introduced with several different solute concentrations. Each segment could then be scanned by the monitor and the instrument reading compared to actual solute concentration.

This procedure was followed for several solutes in various sorbents in a variety of concentration ranges. The solute concentration was found to be related to the instrument output by an inverse log relationship similar to that expected for the dependence of absorbance on transmittance measurements:

$$c = C \ln \frac{1}{R} \quad (23)$$

where

$R$  = ratio of the instrumental reading at a solute concentration of  $c$  to the instrument reading for zero solute

$C$  = calibration constant

A typical plot of such data for Blue Dextran in the Sephadex G-25 is shown in Fig. 6. Such a relationship was used in subsequent tests to determine the bandwidth at half the maximum band concentration.

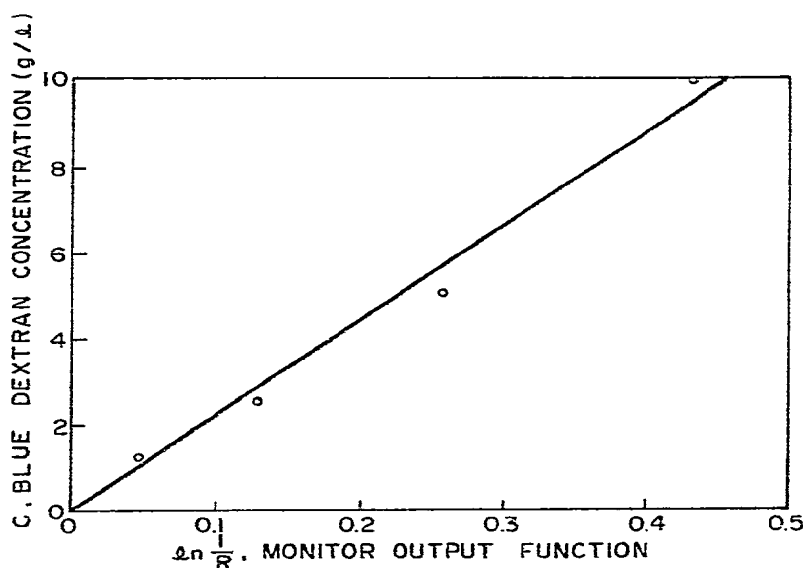


Fig. 6. Relationship between Blue Dextran concentration in a bed of Sephadex G-25 and the output from the solute monitor. Measurement at 620 nm.

### Void fraction

The elution position of a specific solute, measured as the angular displacement of the band from the feed point, should be dependent on the length of the chromatograph, speed of rotation, superficial velocity, void fraction, and distribution coefficient, as indicated in eqn. 13. Blue Dextran 2000 has such a large molecular weight that it should not penetrate the pores of Sephadex gels, and minimal surface sorption phenomena are expected. Thus, it could be used to measure the efficiency of the chromatographic system.

Since no interaction of the solute with the stationary phase is expected, the distribution coefficient should be zero and the mathematical expression for elution position should be

$$\bar{\theta} = \frac{\omega L \varepsilon}{u} \quad (24)$$

Since  $\varepsilon$  should be relatively constant at a given elution rate (where  $u$  is constant), we would expect a plot of  $\bar{\theta}$  vs.  $L$  to produce a straight line at a given rotational speed. This was found to be true at rotational speeds of 0.0013–0.0044 rad/sec, where the band displacement was measured vertically down the annulus (Fig. 7).

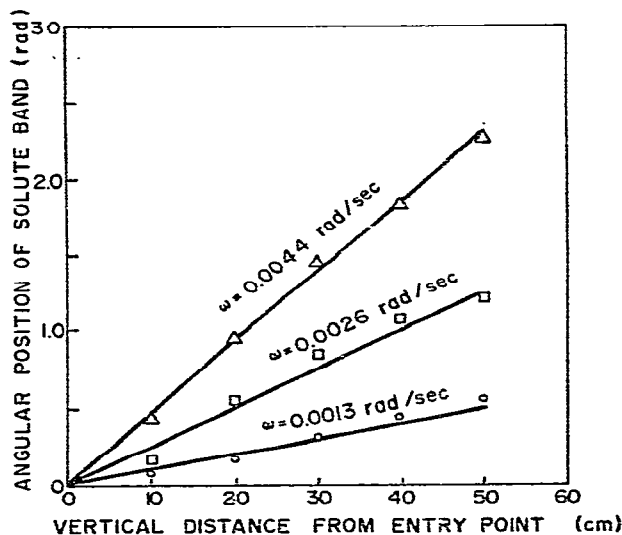


Fig. 7. Effect of vertical distance and rotational speed on elution position of the Blue Dextran band eluting through Sephadex G-25 (100–300  $\mu$ m) in the continuous annular chromatograph. Eluent, distilled water; feed, 20 g/l Blue Dextran at 1 ml/min.

Further, it would be expected that, upon measurement of the elution position of Blue Dextran at specific operating conditions, eqn. 24 after rearrangement could be used to establish the void fraction,  $\varepsilon$ . If this value was found to be relatively constant over a range of operating conditions, the mathematical interpretations of the system would prove to be useful. Using this approach, the void fraction was found to be essentially constant for all runs, that is, it was independent of flow-rate (Table I).

TABLE I

VOID FRACTION AND DISTRIBUTION COEFFICIENTS CALCULATED FROM ELUTION POSITIONS FOR SEPARATION OF BLUE DEXTRAN AND  $\text{CoCl}_2$  IN A CONTINUOUS ANNULAR CHROMATOGRAPH USING SEPHADEX G-25 AS THE SORBENT PHASE

Operating conditions: temperature,  $25 \pm 2^\circ$ ; gas overpressure, 5–7 p.s.i.; eluent, distilled water; sorbent phase, Sephadex G-25; particle size, 100–300  $\mu\text{m}$ .

Annular velocity, $\omega$ (rad/sec $\times 10^3$ )	Superficial velocity, $u$ (cm/sec $\times 10^2$ )	Elution position, $\bar{\Theta}^*$ (rad)		Calculated value of $\epsilon^{**}$ for Blue Dextran	Calculated value of $K^{**}$ for $\text{CoCl}_2$
		Blue Dextran	$\text{CoCl}_2$		
1.05	1.37	1.38	2.21	0.36	0.34
1.05	1.63	1.11	1.77	0.34	0.32
1.01	1.95	0.94	1.58	0.36	0.39
1.02	1.93	0.97	1.60	0.37	0.37
1.03	1.92	0.93	1.58	0.35	0.37
1.05	2.15	0.93	1.54	0.38	0.40
1.03	2.41	0.69	1.16	0.32	0.33
1.05	2.68	0.74	1.19	0.38	0.37
1.05	3.40	0.58	0.92	0.38	0.35
1.11	2.10	1.01	1.64	0.38	0.39
2.60	1.89	2.41	3.98	0.35	0.35
Mean (standard deviation)				0.36 (0.02)	0.36 (0.026)

\* Measured at 50 cm below the feed point.

\*\* Calculated using eqn. 13.

### Distribution coefficient

After the void fraction is known, eqn. 13 can also be used to determine the distribution coefficient for eluting substances which have an affinity for sorption. In the molecular sieve separation,  $\text{CoCl}_2$  does not penetrate the gel pores, where it undergoes a weak ionic interaction with the stationary phase. This causes the solute to elute after Blue Dextran. The elution position can be used to establish a distribution coefficient. As shown in Table I, this distribution coefficient was reasonably constant over the range of operating conditions, thus further showing the utility of the mathematical interpretation. As expected, the Blue Dextran and  $\text{CoCl}_2$  were well separated in all tests.

All of the measured ionic constituents in the ion-exchange separation were sorbed more strongly by the solid phase than was  $\text{CoCl}_2$  by the Sephadex G-25. Using an externally measured void fraction ( $\epsilon = 0.40$ ) and the elution positions of the three constituents, distribution coefficients were again determined. The calculated distribution coefficients were relatively constant over a minimal range of operating conditions (Table II), but were up to 25% less than those measured by stationary analytical columns. The distribution coefficients were quite dependent on pH and it is expected that variations in pH within the annular chromatograph caused the difference.

### Theoretical plates

In a few of the runs, the solute monitoring device was used to measure the width of the  $\text{CoCl}_2$  band just prior to the elution exit (at 45 cm from the feed point) in the molecular sieve separation and the width of the Ni-1 band in the ion-exchange

TABLE II  
SEPARATION OF NICKEL AND COBALT COMPLEX IONS BY CATION-EXCHANGE RESIN IN THE CONTINUOUS ANNULAR CHROMATOGRAPH

Operating conditions: temperature,  $25 \pm 2^\circ$ ; gas overpressure, 9–10 p.s.i.; eluent, 1 M  $(\text{NH}_4)_2\text{CO}_3$  buffered to pH 7.8; sorbent phase, Dowex 50-X8; particle size, 50–60  $\mu\text{m}$ .

Annular velocity, $\omega$ ( $\text{rad}/\text{sec} \times 10^3$ )	Superficial velocity, $u$ ( $\text{cm}/\text{sec} \times 10^3$ )	Bed length of measurement, $L$ (cm)	Initial bandwidth for Ni-I, $W_0$ (rad)	Final bandwidth for Ni-I, $W^*$ (rad)	Elution position, $\bar{\Theta}^*$ (rad)			Distribution coefficient, $K^{**}$			Number of theoretical plates, $N^{***}$
					Ni-I	Co-1	Co-2	Ni	Co-1	Co-2	
2.43	2.52	44.5	0.119	0.162	0.942	1.38	2.98	4.69	403		
2.35	2.43	43.8	0.131	0.164	0.838	1.24	2.63	4.21	393		
2.11	2.25	43.8	0.035	0.110	0.942	1.45	3.15	5.20	451		
					Mean			2.92	4.70	11.62	416
					Measured on analytical column			3.98	5.57	14.80	

\* Measured at bed length,  $L$ .

\*\* Calculated using eqn. 13.

\*\*\* Calculated from bandwidth data using eqn. 28.



separation. These data, coupled with the feed bandwidth and elution position, will allow determination of the number of theoretical plates.

Band spreading due to longitudinal dispersion should be approximated by eqn. 21. That expression rearranged for determining the number of theoretical plates,  $N$ , will be

$$N = (\bar{\Theta}/\sigma_t)^2 \quad (25)$$

From the relationship for total band spreading, eqn. 15, it can be shown that

$$\sigma_t = \sqrt{\sigma_t'^2 - \sigma_f^2} \quad (26)$$

The width of the band at half the maximum concentration,  $W$ , is much easier to measure than the standard deviation. This parameter can be related to the standard deviation by

$$\sigma^2 = W^2/8 \ln 2 \quad (27)$$

Recognizing the contribution of the initial feed bandwidth,  $W_0$ , to total band spreading and incorporating eqns. 26 and 27 into eqn. 25 result in

$$N = \frac{8 \ln 2 \bar{\Theta}^2}{W^2 - W_0^2} \quad (28)$$

This relationship was used to determine the number of theoretical plates in the vertical section of the annular chromatograph from elution and bandwidths data.

The number of theoretical plates in the annular chromatograph using the molecular sieve separation was calculated from  $\text{CoCl}_2$  bandwidths to be 646, with a standard deviation of 109, over four different tests (Table III). The Ni-1 bandwidth was used to determine the number of theoretical plates in the ion-exchange separation. The results of three tests gave a mean value of 416, with a standard deviation of

TABLE III

NUMBER OF THEORETICAL PLATES FOR  $\text{CoCl}_2$  ELUTION IN THE CONTINUOUS CHROMATOGRAPH

Operating conditions: temperature,  $25 \pm 2^\circ$ ; gas overpressure, 5–7 p.s.i.; eluent, distilled water; sorbent phase, Sephadex G-25; particle size, 100–300  $\mu\text{m}$ .

Angular velocity, $\omega$ (rad/sec $\times 10^3$ )	Superficial velocity, $u$ (cm/sec $\times 10^2$ )	Initial bandwidth, $W_0$ (rad $\times 10^2$ )	Bandwidth at 45 cm, $W^*$ (rad $\times 10^2$ )	Elution position $\bar{\Theta}^*$ (rad)	Number of theoretical plates, $N^{**}$
1.05	1.37	0.7	17.6	1.90	645
1.01	1.95	3.8	13.3	1.41	687
1.02	1.93	6.8	16.8	1.45	497
2.60	1.89	7.9	31.1	3.51	755
Mean (standard deviation)					646 (109)

\* Measured at 45 cm below the feed point.

\*\* Calculated with eqn. 28.

31 (Table II). Neither of these systems constitutes a high-resolution system; however, the number of theoretical plates are probably in the expected range for the type of solid phase used.

#### *Effect of feed rate on bandwidth*

The feed rate was 3 ml/min in each of the tests with ion-exchange resin. This represented a superficial velocity of 0.024 cm/sec, about equal to the average elution rate around the chromatograph. Obviously, as the feed rate was increased, additional mixing and band spreading would be expected. Indeed, it was found that the bandwidth increased at feed rates which resulted in a superficial velocity greater than twice the average eluting superficial velocity (Table IV). This effect will have to be taken into account when studying or designing for a specific separation.

TABLE IV

#### EFFECT OF FEED RATE ON Ni-1 BANDWIDTH

Operating conditions: temperature,  $25 \pm 2^\circ$ ; gas overpressure, 5 and 10 p.s.i.; eluent, 1 M  $(\text{NH}_4)_2\text{CO}_3$  buffered to pH 7.8; sorbent phase, Dowex 50-X8; particle size, 50–60  $\mu\text{m}$ .

<i>Eluent superficial velocity (cm/sec)</i>	<i>Feed superficial velocity (cm/sec)</i>	<i>Bandwidth, W*</i> (rad)
0.24	0.24	0.11
0.24	0.53	0.12
0.24	0.78	0.20
0.24		0.23
0.12	0.78	0.30

\* Bandwidth measured at 40 cm below the feed point.

#### CONCLUSIONS

The rotating annular chromatograph has been shown to represent a potentially useful concept for continuous chromatography. The use of gas overpressure allows pressurized operation, which is usually required in modern chromatography, and the use of segmenting spacers at the chromatograph top allows gradient elution. A monitoring device, measuring reflected light, can be used to detect band positions and bandwidth when a transparent annulus is used.

The system can be mathematically described by a modified theoretical plate model, and the resulting correlations can be used for design purposes. Future experiments will be required to completely define the effects of feed stream concentration and flow-rate.

#### LIST OF SYMBOLS

$A$  = cross-sectional area of the annular segment,  $\text{cm}^2$

$$B = \frac{N}{V} \left[ \frac{1}{\epsilon + (1 - \epsilon) K} \right]$$

$$B' = \frac{Nu}{\omega L} \left[ \frac{1}{\epsilon + (1 - \epsilon) K} \right]$$

$c$  = concentration of solute in the fluid phase, moles/cm<sup>3</sup>

$C$  = calibration constant

$K$  = distribution coefficient,  $\frac{\text{moles solute/cm}^3 \text{ sorbent phase}}{\text{moles solute/cm}^3 \text{ fluid phase}}$

$L$  = vertical distance from feed point to exit, cm

$n$  = general designation for theoretical plate number

$N$  = total number of theoretical equilibrium plates in the annular segment

$Q$  = total quantity of solute introduced to an annular segment, mole.

$R$  = ratio of solute monitor reading at a solute concentration of  $c$  to the instrument reading for zero solute

$t$  = time for the reference annular segment to be displaced an angle of  $\Theta$  from the feedpoint, sec

$u$  = eluent superficial velocity, cm/sec

$v$  = total eluent flow through an annular segment during time  $t$  and displacement  $\Theta$ , cm<sup>3</sup>

$V$  = total volume of an annular segment, cm<sup>3</sup>

$W$  = width of solute band at half the maximum solute concentration, rad

$\epsilon$  = void fraction in chromatograph,  $\frac{\text{cm}^3 \text{ fluid phase}}{\text{cm}^3 \text{ annular volume}}$

$\omega$  = angular velocity or rotational speed, rad/sec

$\sigma$  = standard deviation of the solute concentration across a solute band, rad

$\Theta$  = angular displacement of the solute band measured from the feed point, rad

$\bar{\Theta}$  = angular displacement of the maximum solute concentration at the chromatograph exit, rad

### Subscripts

1 = first theoretical plate

$f$  = feed point

$l$  = longitudinal

$n$  =  $n$ th theoretical plate

$N$  =  $N$ th theoretical plate

0 = initial

$t$  = total

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