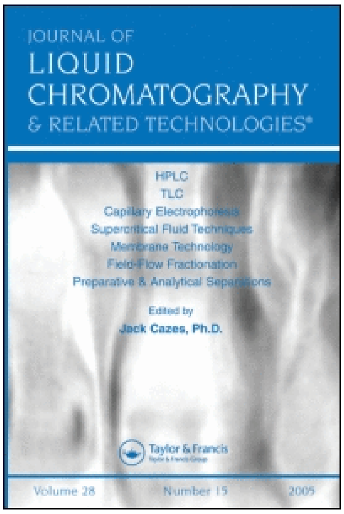

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OPERATION OF AN IMPROVED, CONTINUOUS ANNULAR CHROMATOGRAPH*

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ABSTRACT

A rotating annular chromatograph has been demonstrated to have utility in the continuous separation of solutes in a feed stream. Recent modifications to the system have resulted in a more efficient separation. Design of the inlet and the exit has been significantly changed to improve chromatograph performance. Refinements have also been made to the method of gradient elution. The effects of changing superficial velocity and initial resin loading on the height equivalent to a theoretical plate are shown for the ternary nickel-cobalt carbonate amine system. A continuous separation of this ternary mixture utilizing pH gradient elution is presented.

INTRODUCTION

Most preparative chromatographic columns are presently limited by resolution losses resulting from excessive mixing and flow variations as well as by the batch nature of large column operation. Several attempts have been made to develop a continuous chromatographic system for use in large-scale, preparative work. These include the use of an annular array of individual columns by Svensson et al.(1), and a rotating annulus used by Fox et al.(2). Other work has been summarized by Scott et al.(3),

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and the developments presented in this paper are an extension of Scott's research.

Our work utilizes a pressurized rotating chromatograph with a stationary feed stream and stationary eluate collection devices. Recent modifications have resulted in a much more operable system with a high degree of resolution.

EQUIPMENT DESCRIPTION

The improved chromatograph is the result of refinements made to an original basic prototype system that was described previously(3). The chromatographic section is an annulus 1.25 cm wide by 50 cm long with an outside diameter of 28.4 cm. The rotating annulus receives solutes from stationary feed entries and is sealed to allow pressurized operation. The slow rotation subjects the resin to the feed stream for a relatively short time, followed by a much longer period of elution. The result is a series of helical bands of the separated species. The Plexiglas body remains basically unchanged with the exception of removal of the entry segmenters. The associated instrumentation and the remainder of the chromatograph system have been extensively changed.

Inlet Distributor

A new inlet distributor has been fabricated to provide more flexibility of operation. This distributor (Fig. 1) is a stainless steel tube with nine entry points. Eight are evenly spaced around the tube, whereas the ninth entry point is through the center and allows placement of a conductance-type level controller, The remaining entries consist of two feed entries, four eluent nozzles, an air inlet for pressurized operation, and a pressure tap. Four manifolds (Fig. 2), each with six nozzles attached, have been fabricated for operation in the gradient elution mode. The nozzles are made of capillary tubing so that all flows are automatically matched.

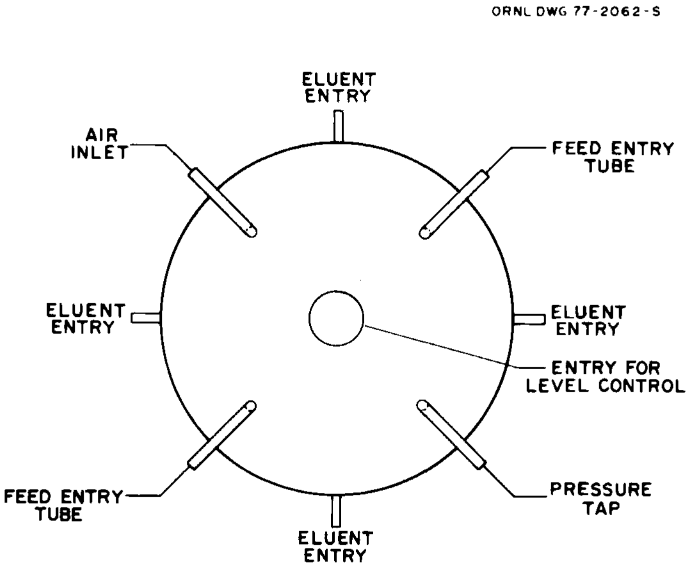

FIGURE 1
Inlet distributor (end view).

Feed System

The feed system was modified to reduce concentration variations in the radial direction (i.e., the variation of bandwidth with position across the annulus). Problems in reproducibility had been encountered with a single feed nozzle in the center of the annulus; these problems have been eliminated by the use of a two-nozzle system. The nozzles are located approximately 0.62 cm apart and 0.31 cm from each annulus wall.

The cone-shaped feed stream that occurs at the nozzle exit also caused problems when the nozzle was buried in the resin. The initial bandwidths could not be defined under those circumstances because interaction with the resin began immediately and occurred simultaneously with hydrodynamic band spreading. This problem has been overcome by placing two layers of glass beads above the resin (Fig. 3). The nozzles are placed about 2 cm beneath the surface.

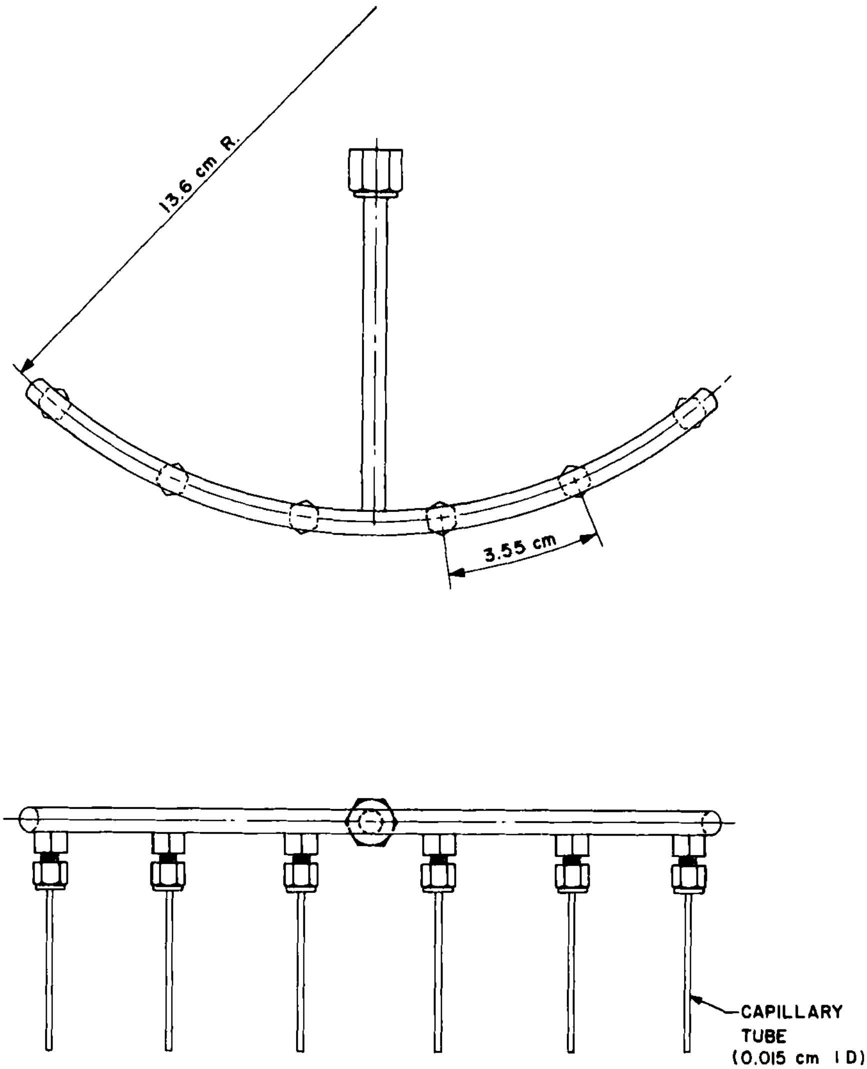

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FIGURE 2
Gradient elution manifold.

The glass beads allow time for the feed band to spread until its velocity matches the eluent velocity. At this point, hydrodynamic spreading ceases and an initial bandwidth is developed.

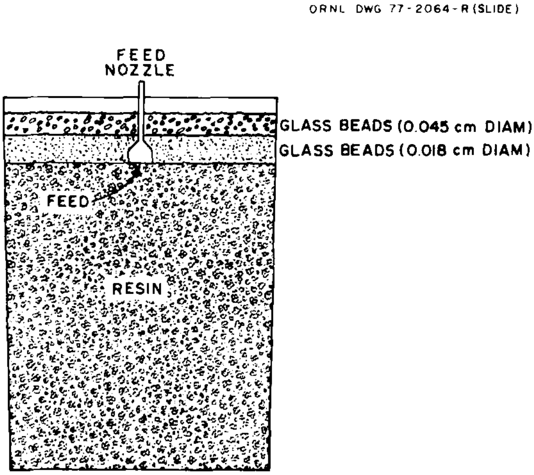

FIGURE 3
Composition of chromatograph bed.

Chromatograph Exit

The continuous chromatograph has always experienced significant circumferential mixing near the exit. Use of porous Teflon and wire mesh with spacers, as described by Scott(3), were successful in reducing mixing but did not eliminate it. The triangular exit spacers at the exit were located at 2-cm intervals on the circumference. This wide spacing prevented a differential scan of the eluate. A new support-exit assembly has been installed (Fig. 4). A v-groove was machined into the plate below the annulus and 180 exit holes were drilled through the plate at the bottom of the groove. Stainless steel tubes (3.2 mm OD by 5 cm long) were gold soldered into each hole from below, and porous Teflon plugs (porosity "D") were driven in from above. This provided an integrated bed support and exit system with very little mixing. There are 180 discrete exit tubes located 2° (∿0.47 cm) apart. This makes it possible to draw samples at close intervals or to attach an analytical instrument directly to the chromatograph exit.

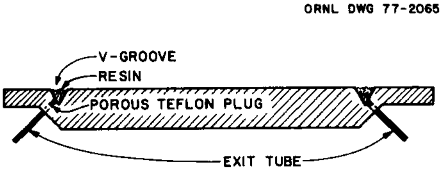

FIGURE 4
Exit assembly section.

OPERATION

The continuous annular chromatograph (CAC) can be operated in the isocratic mode with a single eluent or in the gradient elution mode with multiple eluent streams. The column itself is the same in either mode, but the control system and method, as well as the eluent entry system, are radically different for the two modes of operation. The rotation rate can be varied between 10°/hr and 600°/hr and is maintained by a digitally set drive with feedback control.

Isocratic Operation

Pressurized operation of the CAC with a single eluting agent has been improved by the addition of a layer of glass beads above the sorbent. This layer has allowed operation with a very simple and reliable control system. Since the feed nozzle was buried below the surface, a liquid head above the bed can be tolerated. A two-probe conductivity controller was used to maintain the liquid level by operating a positive displacement pump. A constant gas overpressure was used to force the liquid through the bed. The feed material was continuously injected below the surface of the glass beads, and the gas overpressure forced a single eluent straight down through the column as it rotated.

A Perkin Elmer spectrophotometer has been used as an in-line instrument to measure the separation achieved. The spectrophotometer flow cell was connected directly to one of the 3.2-mm tubes at the chromatograph exit. Since the bands appear to be stationary as the column rotates, each exit tube passes through the bands. This method has been used to obtain a chromatogram of the separation.

Gradient Elution

Operation with gradient elution requires the use of several eluent entries and a control system to maintain equal flows to all areas of the column. Several manifolds have been used to obtain this equal distribution of eluent. These eluent manifolds (Fig. 2) were installed, each covering 90° of the chromatograph. The nozzles have an inside diameter of 0.15 mm, resulting in a pressure drop of about 414 kPa for a flow rate of 8 cm^3/min. Each manifold is supplied from its own positive displacement pump. The pumps have been calibrated so that all can be set to deliver the same flow. The nozzles have also been matched so that each gives one-sixth of the manifold flow. Assembly of the manifolds results in 24 nozzles, evenly spaced at 3.55 cm around the column and centered in the annulus. The result is that each nozzle supplies eluent to an annular segment with an area approximately equal to that of a 1.25-cm by 3.55-cm rectangle. There is no noticeable mixing between adjacent nozzles. The glass beads are used as a buffer space to allow room for the eluent to spread out to cover that area before reaching the ion exchange resin. The system presently allows use of as many as four different eluents simultaneously.

In order to use two or more eluents, a method of operation had to be developed which would not require a liquid head of eluent. If the liquid level is maintained inside the glass-bead layer, very little circumferential mixing occurs, and a wet resin is still maintained. We have used an optical device attached to the side of the column to control the liquid level. This device looks at the meniscus in a side glass and, through the use of special electronics, controls the gas overpressure in the chromatograph to maintain a constant liquid level. Our procedure is to first set all eluent pumps to give equal flows, and then to allow the controller to seek the equilibrium pressure that will prevent liquid accumulation or depletion. The controller can be trimmed so that pressure fluctuations, and therefore flow pulses, are as low as 1%. We intend to replace the optical detector with a differential pressure transmitter to eliminate disturbances caused by ambient light fluctuations.

EXPERIMENTAL RESULTS

Although the CAC is not limited to ion exchange, most experiments to date have been performed using Dowex 50W-X8 ion exchange resin (50 to 60 μm). The bed depth is approximately 46 cm. This ion exchanger has been used to separate a synthetic ore leach liquor⁽⁴⁾ containing nickel and cobalt carbonate amine complexes.

The transparent Plexiglas chromatograph and the vivid color of both the cobalt and nickel amines make possible observations that could not ordinarily be made. Visual examination of the cobalt and nickel bands has revealed that a slope change occurs at the point of the nickel-cobalt split. The change is the result of high solute concentrations that overload the sorptive capacity of the resin in the vicinity of the feed. In order to avoid the problems caused by this discontinuity, several experiments were performed with a single species in the feed. The elution position ($\bar{\theta}$) of the band peak has been found to be inversely related to the superficial eluent velocity (U) and yields a linear relationship, as shown in Fig. 5. These data can be used to calculate distribution coefficients via the following relationship(3).

$$K = \frac{(\bar{\theta}/L)(\frac{U}{\omega}) - \varepsilon}{1 - \varepsilon} , \qquad (1)$$

where

L is the column length, cm,
ω is the rotation rate, °/hr, and
ε is the bed void fraction, ($\sim$0.4).

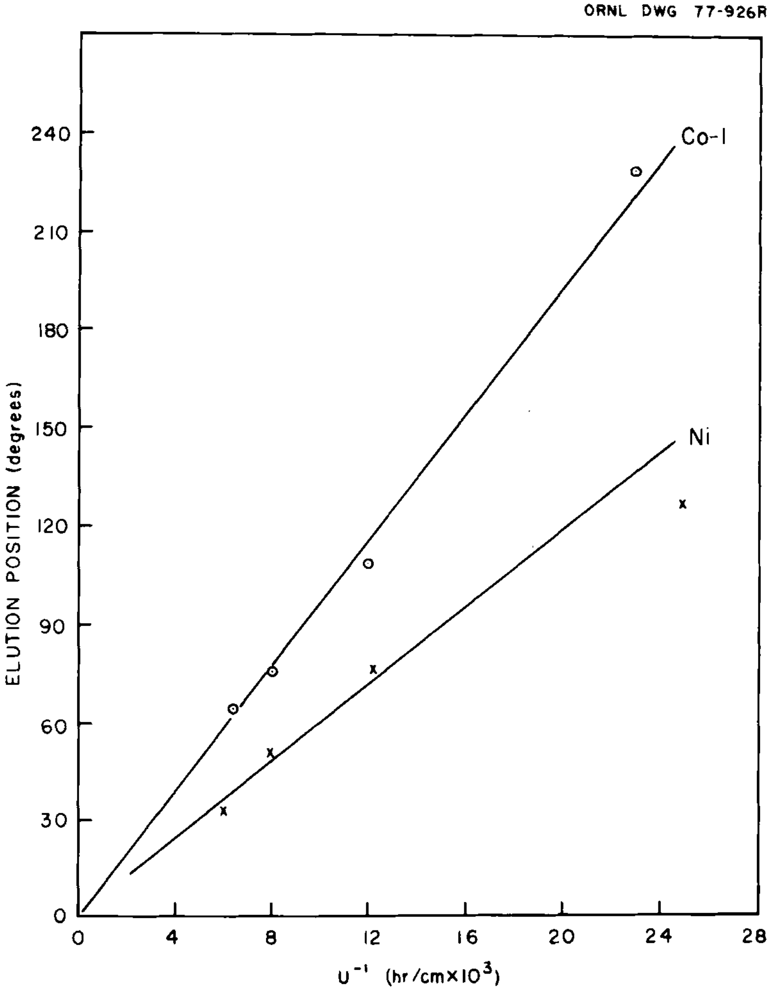

FIGURE 5
Relationship between elution position and superficial eluent velocity for nickel and cobalt-1. Rotation rate = 50°/hr; pH = 8.0.

Location of the area of peak concentration position at various lengths down the chromatograph allows calculation of $\overline{\theta}/L$ for several measurements by regression analysis. Distribution coefficients are then calculated by Eq. (1). Measurement of the bandwidth (W_G) at the same locations permits calculation of the height equivalent of a theoretical plate (HETP) with $^{(3)}$

$$\text{HETP} = \frac{(W_G^2 - W_o^2)/L}{16(\overline{\theta}/L)^2} \qquad (2)$$

where W_o is the bandwidth in degrees at the feed point.

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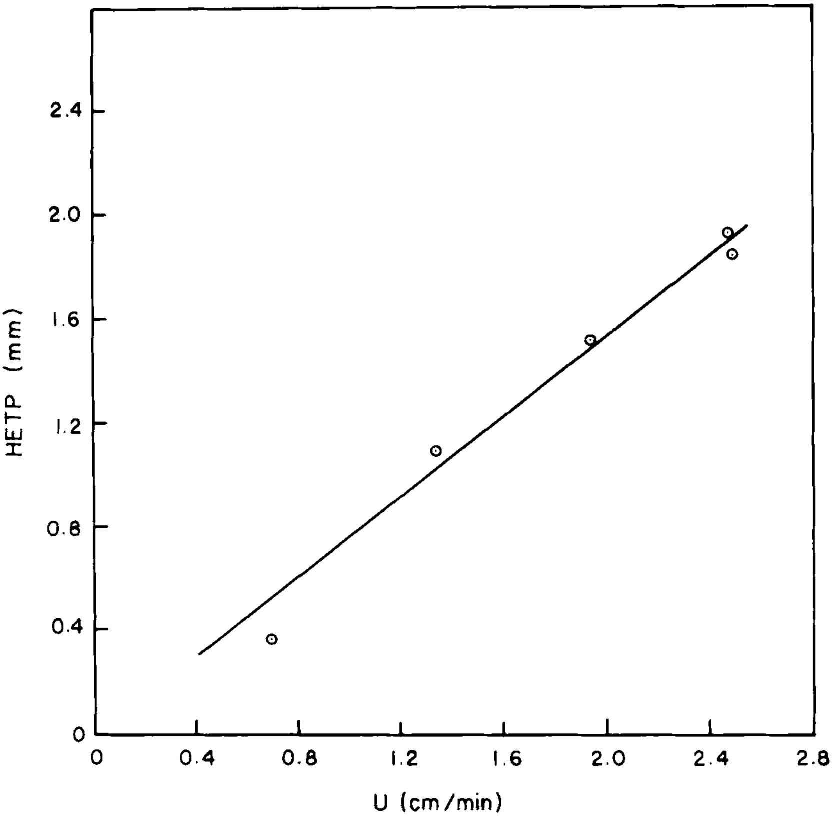

FIGURE 6
Effect of superficial eluent velocity on the height equivalent of a theoretical plate (HETP) for cobalt-1 with 1 $\underline{M}$ $(NH_4)_2CO_3$.

Figure 6 shows the relationship of HETP to superficial velocity for cobalt, and Table 1 contains the distribution coefficients and HETP values for cobalt and nickel at various eluent velocities.

Preliminary investigations have been made to determine the bed capacity. Calculated values of HETP are seen to increase with increased initial resin loading (W_f^o), as shown in Fig. 7 for cobalt. This effect is also present with nickel, but it is less noticeable due to the lower distribution coefficient.

The continuous annular chromatograph (CAC) has been operated in the gradient elution mode with the cobalt-nickel system. This separation can also be made without gradient elution; however, a comparison between the two modes of operation proved instructive (Fig. 8). One molar ammonium carbonate was introduced as the eluent in all four quadrants. The feed nozzle was located between quadrants 4 and 1, both of which received eluent at pH = 9.68. Quadrants 2 and 3 received eluent of pH = 8.01. The rotation rate was 35°/hr and the eluent velocity was 1.37 cm/min in all quadrants. The feed consisted of 4 g per liter of nickel, 1 g per liter of Co-1, and 1 g per liter of Co-2 in 1 $\underline{M}$ $(NH_4)_2CO_3$ at 3 cm^3/min. The distribution coefficient for nickel is a strong function of pH, but the pH variations have very little affect on the cobalt complexes. At pH 9.68, nickel has the highest coefficient and is therefore highest on the chromatograph in quadrant 1, as shown at the left of the picture. A drastic change in the nickel-band slope occurs at the interface, because nickel has the lowest distribution coefficient at pH 8.01; it therefore exhibits the steepest slope in quadrant 2. The sharpness of the slope change demonstrates that little eluent mixing occurs at the interface. Proper adjustment of the pH in quadrants 2 and 3 will result in any bandwidth separation desired, which is indicative of the power of this method. For instance, nickel and cobalt could be eluted 180° apart. Since the operation is continuous, separation time is not a factor for preparative work with this device.

TABLE 1
Distribution Coefficients and Theoretical Plate Heights for the Nickel and Cobalt Amine Complexes from Continuous Chromatograph Data with Dowex 50W-X8 Resin and 1 M $(NH_4)_2CO_3$ as Eluent

Run	pH	Feed Rate (cc/min)	Eluent Velocity (cm/min)	Distribution Coefficient		Height Equivalent to Theoretical Plate (HETP) (cm)
				Ni	Co-1	
A1	8.07	2.00	1.33	3.43		0.168 ± 0.031
A2	8.07	2.00	2.67	3.17		0.224 ± 0.022
A3	7.94	2.00	0.65	2.81		0.208 ± 0.022
A4	7.97	2.00	2.00	3.29		0.300 ± 0.087
B1	8.02	2.00	0.71		6.38	0.037 ± 0.007
B2	7.86	2.00	1.34		5.45	0.098 ± 0.028
B3	8.05	2.00	1.95		5.25	0.151 ± 0.077
B4	7.94	2.00	2.49		4.66	0.164 ± 0.075

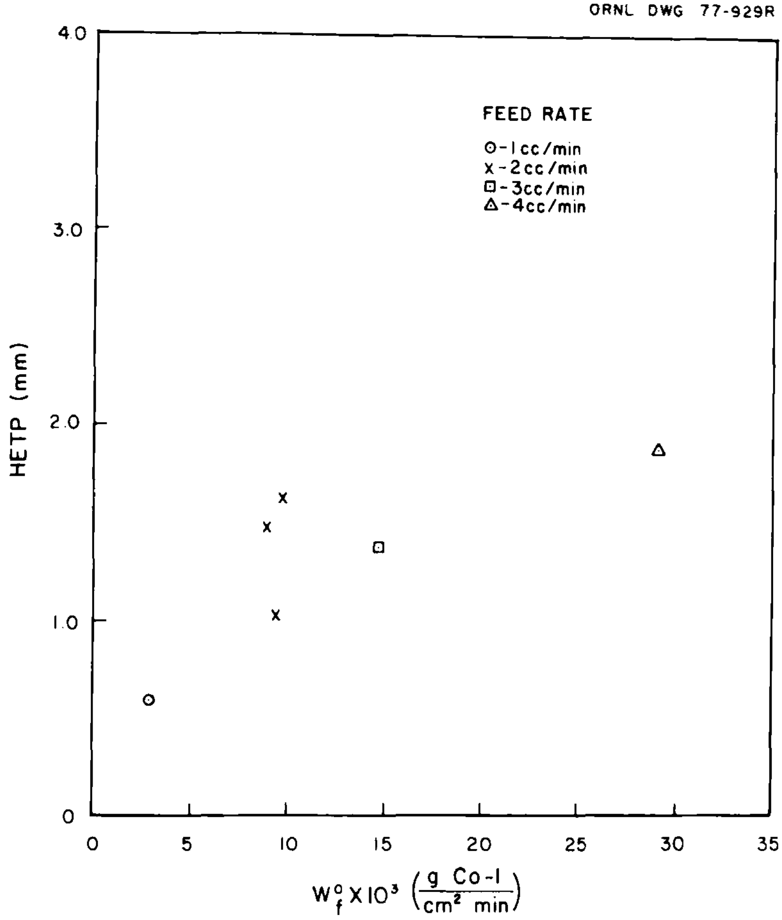

FIGURE 7

Effect of initial loading on the height equivalent of a theoretical plate (HETP) for 3.80 g of cobalt per liter of feed at various feed rates.

CONCLUSIONS

The rotating continuous annular chromatograph has been shown to be an effective device for performing the cobalt-nickel separation. Improvements to the original prototype have resulted in

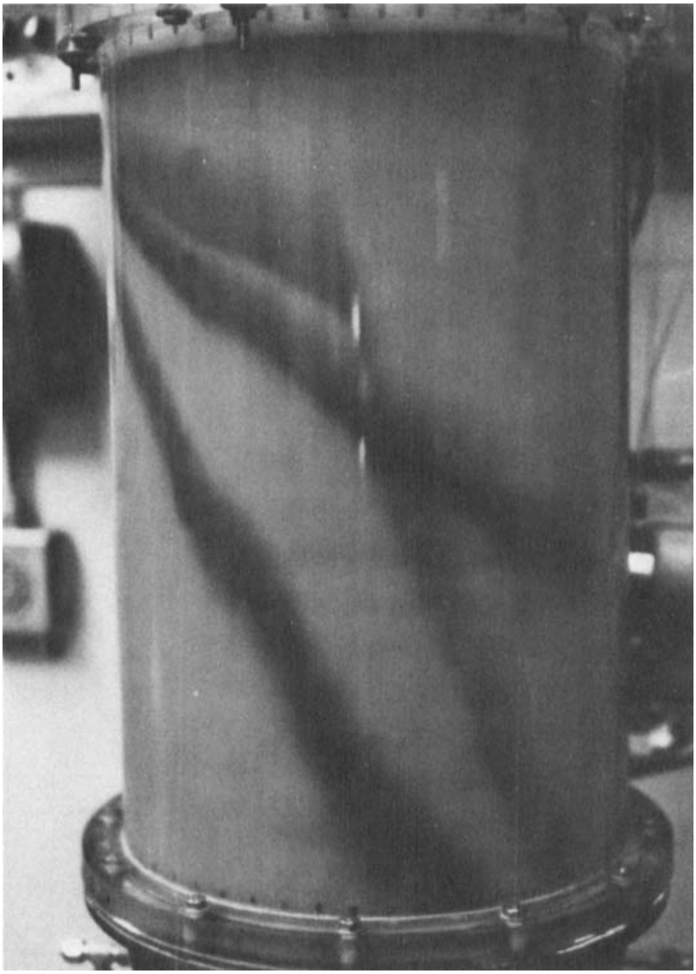

FIGURE 8
Continuous separation of the nickel-cobalt amine system utilizing pH gradient elution with 1 $\underline{M}$ $(NH_4)_2CO_3$.

more consistent and reliable data, particularly in the determination of bandwidth. Modifications have been made which allow gradient elution operation, thus multiplying the potential for application.

Development of a differential model of the system is underway and further experiments with other systems are planned. A second-generation device is now in the design stage and is expected to produce marked improvement, especially in gradient elution operation.

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