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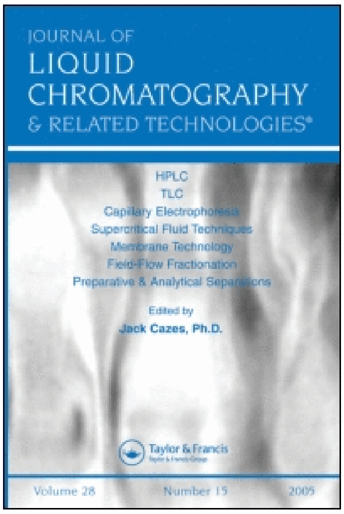

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The Chromatographic Efficiency of Several Commercially Available Ion Chromatography Columns

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THE CHROMATOGRAPHIC EFFICIENCY OF SEVERAL COMMERCIALLY AVAILABLE ION CHROMATOGRAPHY COLUMNS

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ABSTRACT

The influence of mobile phase flow rate on the efficiency of six commercially available ion chromatography columns was examined. Optimum performance was achieved at flow rates between 0.3 and 0.7 mL/min. For all but one of the columns studied, the column efficiency versus reduced velocity relationship was similar to the classical Knox-type behavior. Operation at typical use conditions for all the columns examined results in performance which is only 50 to 75% as good as when the columns are operated at the flow rates optimized in terms of efficiency. Such changes in the column efficiency are directly related to the column's ability to effectively resolve sample components.

INTRODUCTION

The tremendous popularity of the general class of methodologies termed ion chromatography (IC) is due, at least in part, to the advantage they posses, in terms of speed of analysis, over potential alternates. The intrinsic advantage of speed which a multi-analyte per

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injection chromatographic method has over other approaches requiring a separate multi-step procedure for each individual analyte has been amplified in IC by the development of stationary phase materials and column configurations which offer either high efficiencies or may be operated with high mobile phase flow rates. Indeed, one can find numerous examples of high speed IC separations in the chemical literature. (1-4) In many applications, however, analytical speed is not the primary optimization variable; this is especially true in those cases wherein optimum chromatographic performance is required to insure adequate peak purity in a complex matrix or to promote accurate and reproducible analyte quantitation. From both a practical and theoretical perspective, one expects that the chromatographic conditions favoring speed or efficiency will be quite different. Attempts to generalize the relationship between flow rate and efficiency in IC are complicated by the significant differences in the nature of the stationary phases available commercially. Thus, for example, one column type is reported to exhibit minimal efficiency dependance on flow rate under normal operating conditions (5) while another exhibits a 3-fold change in reduced plate height as the reduced velocity is increased by a factor of 10 (6). In this research, the efficiency versus flow rate relationship was examined for six commercially available IC columns.

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EXPERIMENTAL

Apparatus. The chromatographic system consisted of the following components: ABI (Ramsey, NJ) Model 400 pump and 757 UV detector, Micromertics (Norcross, GA) Model 728 Autosampler, Rheodyne (Cotati, CA) Model 7010 electronically actuated injector and a Linear (Reno, NV) stripchart recorder. Columns examined are described in

TABLE I. COLUMNS EXAMINED

DESIGNATION	SUPPLIER	BACKBONE TYPE	LENGTH (mm)	ID (mm)	PARTICLE Size (um)
269-013	Wescan	Silica	100	4.6	5
269-031	Wescan	Polymer	100	4.1	10
301TP	Vydac	Silica	250	4.6	10
PRP-X100	Hamilton	Polymer (1)	150	4.1	10
AS-5A	Dionex	Latex (2)	150	4.0	5
IC-Pak A	Waters	Gel (3)	50	4.6	10

(1) co-polystyrene divinylbenzene
(2) agglomerated
(3) polymethacrylate

NOTE: The functional group on these stationary phases is the quarternary amine.

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Table I. All components between the injector and detector were connected with the minimum possible length of 0.007 in. ID stainless steel tubing. The chromatographic system was unchanged in any respect over the entire course of this experimentation.

Operating Conditions. The mobile phase used in all experiments was 2 mM potassium hydrogen phthalate at pH 6; analytes were detected indirectly using a "vacancy" chromatographic approach at wavelengths of either 270 or 250 nm. The test article used throughout contained 100 ppm each of chloride, nitrate and sulfate and was prepared from their sodium salts. Sample injection size was 10 microliters.

Design. Each column evaluated was used as received by the vendor and was equilibrated with mobile phase for a period of not less than eight hours (to insure that equilibration was indeed complete) prior to the initiation of the efficiency evaluation. After equilibration, each column was "conditioned" by making five injections of the test article while the system was operating at a flow rate of 1 mL/min. After conditioning, the individual columns were equilibrated to a particular flow rate (ranging from 0.1 to 4.0 mL/min) and the test article was injected in replicate. The flow rate was then changed, the column re-equilibrated and more injections were made. Flow rate changes were made in a random order for each column tested. Appropriate properties of the resultant chromatograms were then measured from the stripchart recordings. Under the chromatographic conditions used, the peak asymmetry was less than 1.1 in all cases and thus deviations from quassian peak shape were not so pronounced as to greatly influence the accuracy of the efficiency calculations (7).

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Calculations. The following equations were used to calculate chromatographic performance and operating parameters:

$$N = 5.545\ (t_a/w_{1/2})^2 \tag{1}$$

$$R = 2(t_b - t_a)/w_b + w_a \tag{2}$$

$$h = L/N\ dp \tag{3}$$

$$\nu = L\ dp/D_m\ t_m \tag{4}$$

where: N = number of theoretical plates
R = resolution
h = reduced plate height
ν = reduced velocity
t = retention time or distance
$w_{1/2}$ = peak width at half peak height
w = peak width at baseline
L = column length
dp = particle size of the stationary phase

t_m = retention time of an unretained solute

D_m = solute diffusion coefficient in the mobile phase [taken as 5 x 10^{-6} $cm^{-2}sec^{-1}$ as being typical of low molecular weight solutes in water (8)]

RESULTS AND DISCUSSION

Classically, the Knox equation has been used to describe the relationship between reduced performance parameters (h and v) in liquid chromatography. (9-10) This equation takes the general form:

$$h = B/v + Av^{1/3} + Cv \qquad (5)$$

where B, A and C are constant unique to a particular chromatographic separation mechanism and (usually) unique to a specific stationary phase type. The various components summarize the contributions of longitudinal diffusion of the solute in the mobile phase (B), flow dispersion in the stationary phase (A) and rate of mass transport in both phases (C) to the overall chromatographic efficiency. As evidenced by the Knox-type curves generated for the columns evaluated (Figures 1 through 6), the efficiency of the exchange process in these columns is influenced almost exclusively by mass transfer kinetics. Over the flow rate range of 0.1 to 1.5 mL/min (producing somewhat different reduced velocities in the different columns, see Table III for typical values of v at a flow rate of 1 mL/min) only the 301TP column exhibits a strong influence of v on

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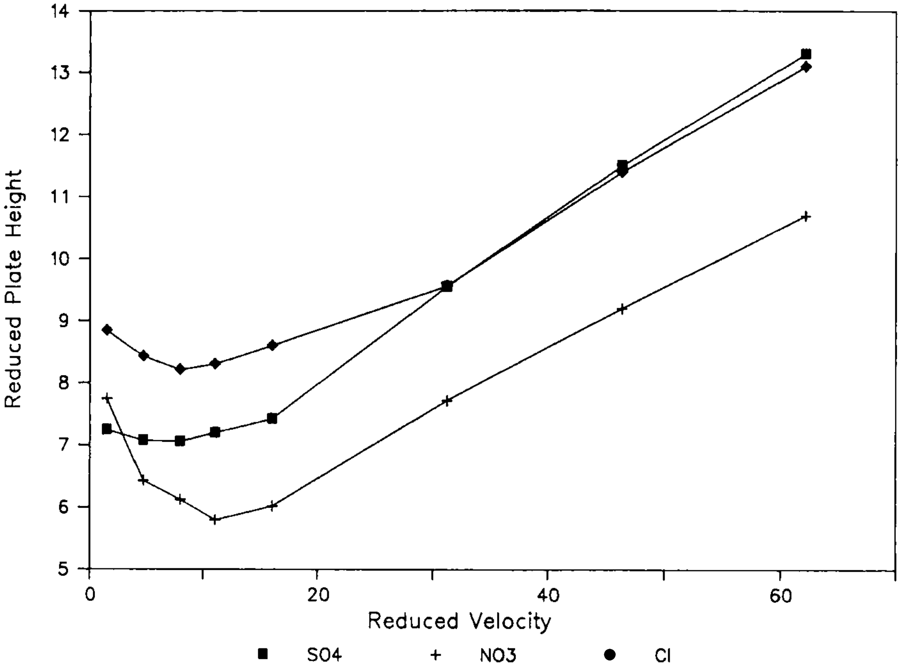

Figure 1. Efficiency Versus Reduced Velocity, 269-013 Column.

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efficiency. Thus in general over this flow rate range, the influence of *v* on efficiency is not greatly influenced by the nature of the stationary phase for modern IC packings. For the AS-5A and IonPak A columns, this range represents the entire practical operating range (the backpressure in the AS-5A column at a flow rate of 1.5 mL/min is sufficiently high that column leaking is imminent and the vendor recommends against using the IC-Pak A column at flow rates greater than 1.2

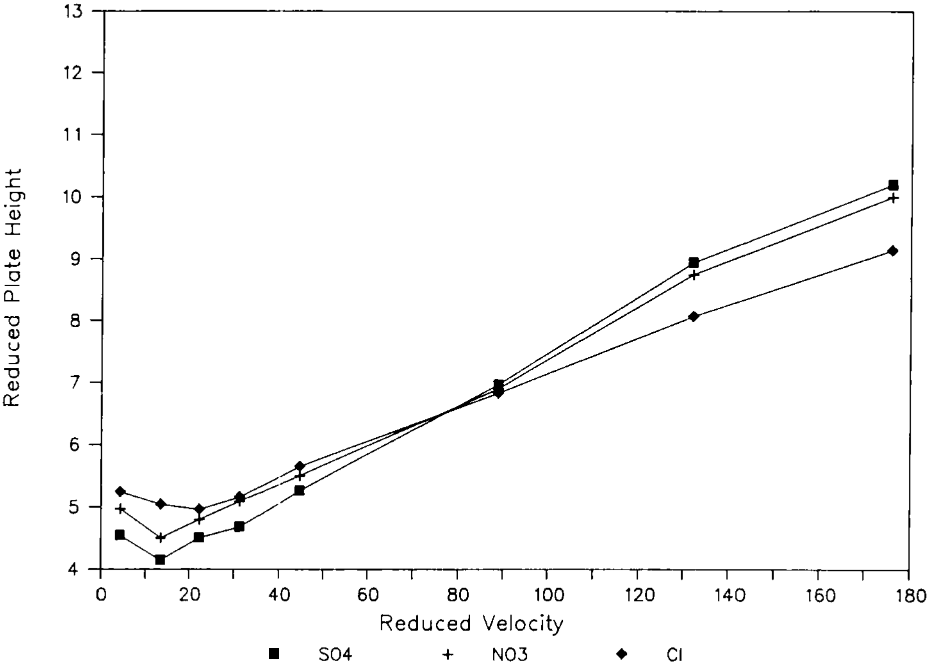

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Figure 2. Efficiency Versus Reduced Velocity, 269-031 Column.

mL/min). For the other columns, efficiency degrades noticeably at flow rates in excess of 1.5 mL/min which is where the columns produce their most time efficient separations. Thus, for example, operating the 269-013 column at a flow rate of 3 mL/min (which is the flow rate used in the test chromatograms provided by the vendor) results in a 40% loss of efficiency from the optimum (achieved at a flow rate between 0.5 and 0.7 mL/min). Similar efficiency losses at higher flow rates are also observed in the 269-031, PRP-X100 and 301TP columns.

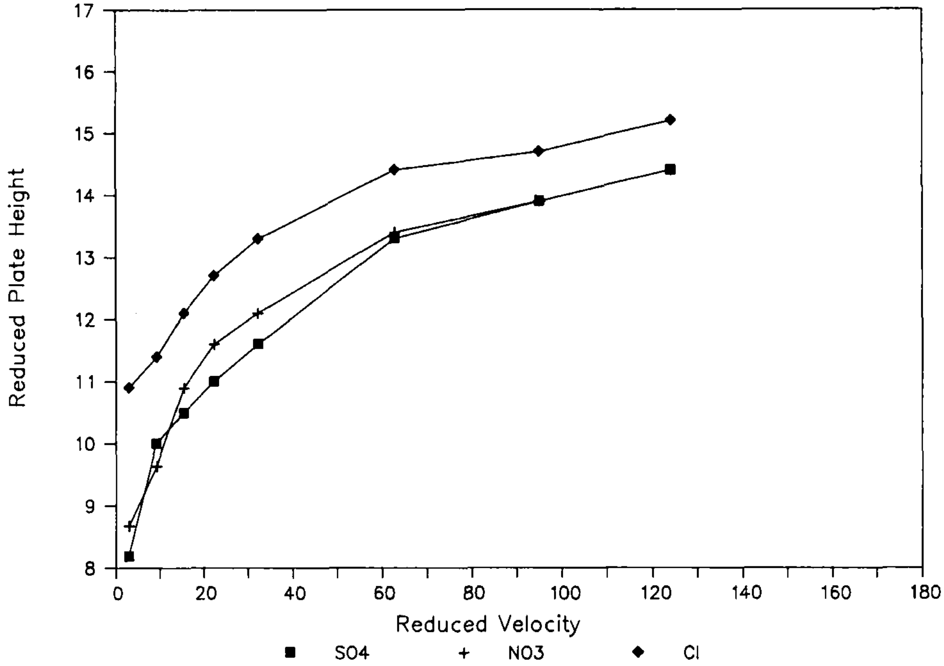

Figure 3. Efficiency Versus Reduced Velocity, 301TP Column.

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Some of the trends observed in terms of inter- and intra-column efficiencies can be understood in the context of the capacity factor's influence on efficiency. Qualitatively, one recognizes that efficiency is improved as the amount of time during which the solute interacts with the stationary phase (i.e., the capacity factor) is increased; thus it is not surprising that the columns with the lowest and highest capacity factors (301TP and IC-Pak A respectively) for the analytes studied also exhibit the lowest and highest absolute efficiencies,

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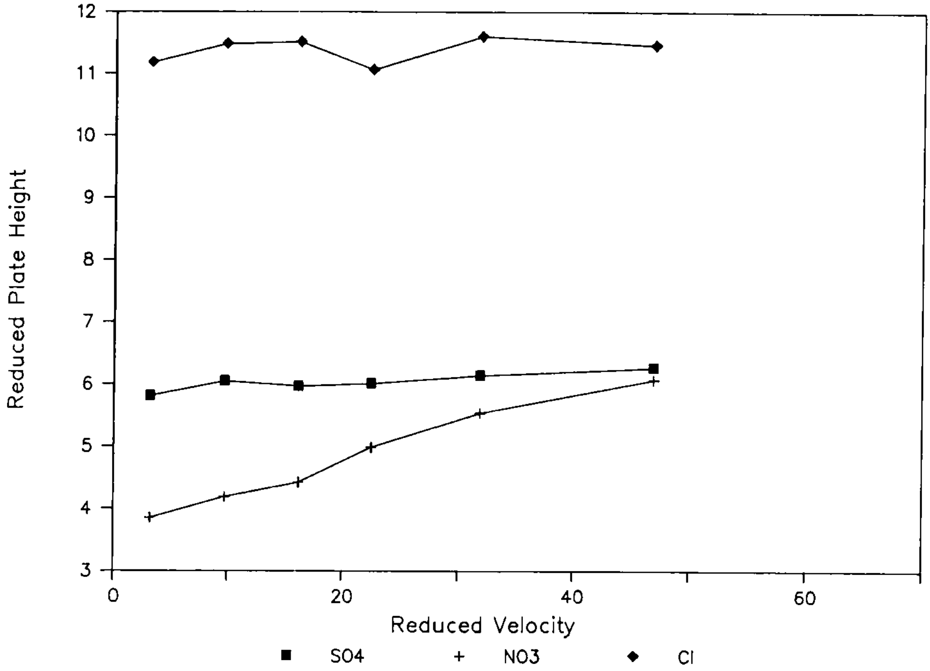

Figure 4. Efficiency Versus Reduced Velocity, AS-5A Column.

regardless of flow rate (see Table II). Additionally, for a given column, the measured efficiency for each solute typically tracks capacity factor to some degree. Thus in all cases the chloride ion, with the lowest capacity factor, is characterized by the poorest efficiency. For columns in which the capacity factors for all the analytes is large (greater than 1.5) and roughly similar, the efficiencies observed for all the analytes is roughly similar as well. The most notable

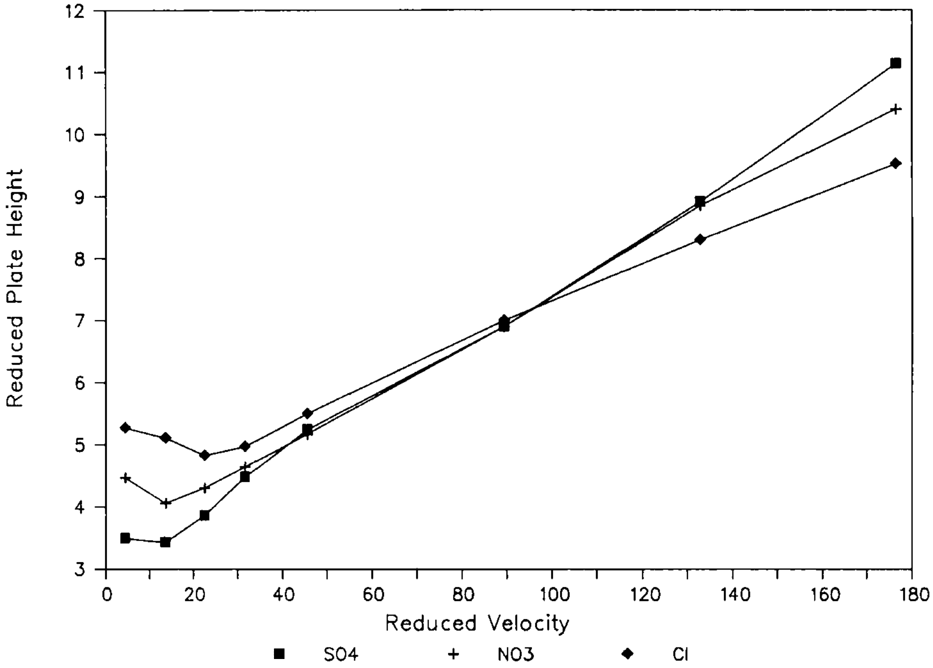

Figure 5. Efficiency Vesus Reduced Velocity, PRP-X100 Column.

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TABLE II. Capacity Factors and Selectivities at 1 mL/min

Column	Capacity Factor			Selectivity (*)	
	Cl	NO3	SO4	NO3	SO4
269-013	1.29	2.36	4.23	1.83	3.36
269-031	1.62	3.46	6.06	2.14	3.74
301TP	0.70	0.90	1.90	1.29	2.71
PRP-X100	1.45	2.97	5.42	2.05	3.74
AS-5A	0.67	2.22	4.42	3.31	6.60
IC-Pak A	4.98	12.4	14.3	2.49	2.87

(*) versus Cl

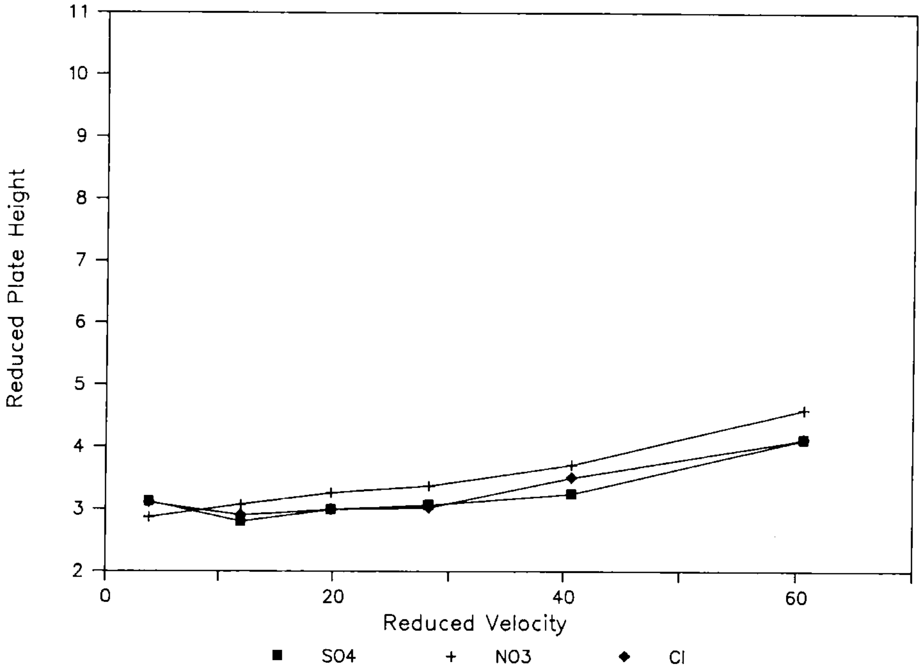

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Figure 6. Efficiency Vesus Reduced Velocity, IonPak A Column.

exception is the AS-5A column; in this column the poorly retained chloride ion has a much lower efficiency than does the strongly retained nitrate and sulfate ions.

Table III provides a means of correlating column performance in terms of flow rate, reduced properties and total analysis time. This type of information is useful in terms of providing a means of choosing an appropriate column for a particular application. Thus, for example, if the analyst is efficiency constrained and desires to use the mobile phase used herein at a flow rate of 1

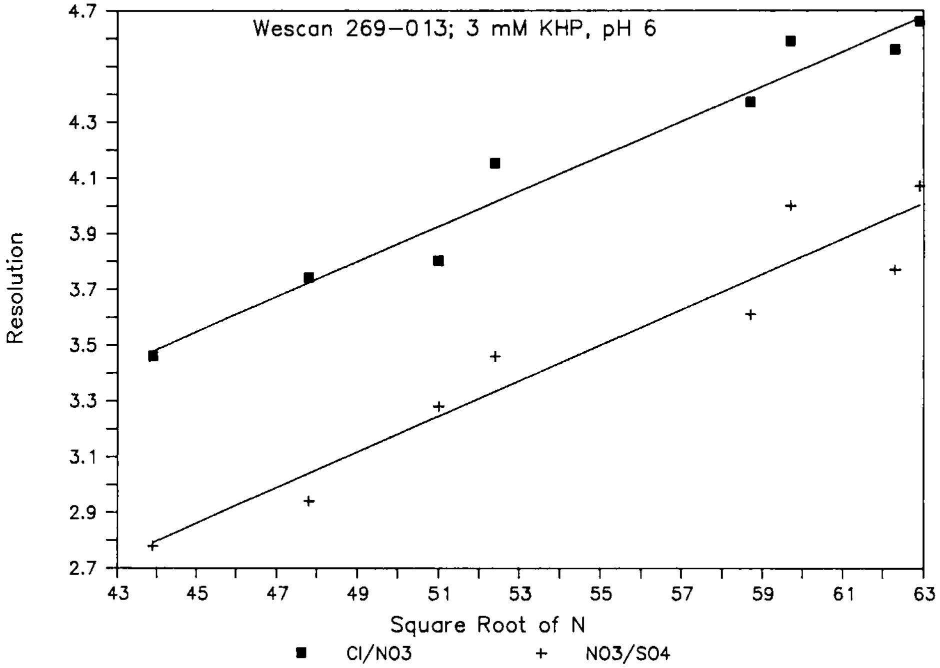

Figure 7. Experimental Relationship between Resolution and Column Efficiency. Data shown is for the 269-013 column operated over the entire (0.1 to 4.0 mL/min) flow rate range. The x axis represents the efficiency of the nitrate ion.

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TABLE III. Typical Operating Properties at 1 mL/min

Column	Reduced Velocity	Total Analysis Time (min)	Reduced Plate Height Cl	NO3	SO4
269-013	16.0	6.0	8.70	6.02	7.42
269-031	44.6	6.2	5.65	5.50	5.26
301TP	32.2	9.0	13.0	11.8	10.6
PRP-X100	45.5	8.0	6.00	5.17	5.24
AS-5A	31.9	4.8	11.6	5.54	6.14
IC-Pak A	40.7	7.4	3.5	3.71	3.24

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mL/min, the IC-Pak A column is most appropriate. On the other hand, analysis time constraints would favor the use of the AS-5A column. In point of fact, all the columns evaluated (with the exception of the 301TP which is not a classical IC stationary phase) exhibit operationally effective efficiencies and reasonable total analysis times at the nominal flow rate of 1 mL/min.

As noted in the Introduction, the need to optimize resolution (for example in order to insure peak specificity or to optimize precision) implies that efficiency should be optimized. Resolution is directly related to column efficiency by the equation:

$$R = 1/4\ ((N)^{1/2}\ (a-1/a)\ (k'/k'+1) \qquad (6)$$

where a is the selectivity coefficient for the solute of interest and k' is the capacity factor. As shown in Figure 7, this relationship is typically obeyed by the IC columns evaluated. Thus, for example, improving the efficiency of the 269-013 column by changing the flow rate from its typical operating value (3 mL/min) to its optimum efficiency value (0.5 to 0.7 mL/min) results in a 20 to 30% increase in resolution. Similar R versus N relationships were observed for the other columns studied.

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