Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Distillation vs. Chromatography: A Comparison Based on the Purity Index

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To cite this Article Cloete, C. E. and De Clerk, K.(1972) 'Distillation vs. Chromatography: A Comparison Based on the Purity Index', Separation Science and Technology, 7: 4, 449 — 455
To link to this Article: DOI: 10.1080/00372367208055588
URL: http://dx.doi.org/10.1080/00372367208055588

SEPARATION SCIENCE, 7(4), pp. 449–455, 1972

NOTE

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Abstract

The ratio of the number of theoretical distillation plates to chromatographic plates needed to achieve the same separation is shown to depend on the proposed purity index I, the relative volatility α, and k_1, the mass distribution coefficient of component 1.

Rony (*1*) recently compared distillation and chromatography in terms of his extent of separation (*2*). A more general measure of separation, based on the entropy of separation, has since been proposed (*3*). This measure, termed the purity index I, will be used in the present note as the basis of a comparison of the analytical efficiencies of distillation and chromatography, and it will be shown to differ significantly from Rony's results in that it shows a marked dependence on the mass distribution coefficient.

The purity index I is defined by

$$I = -0.25 \log \eta_1\eta_2 \tag{1}$$

where η_i is the impurity ratio (*4*) for the ith component. Since (see

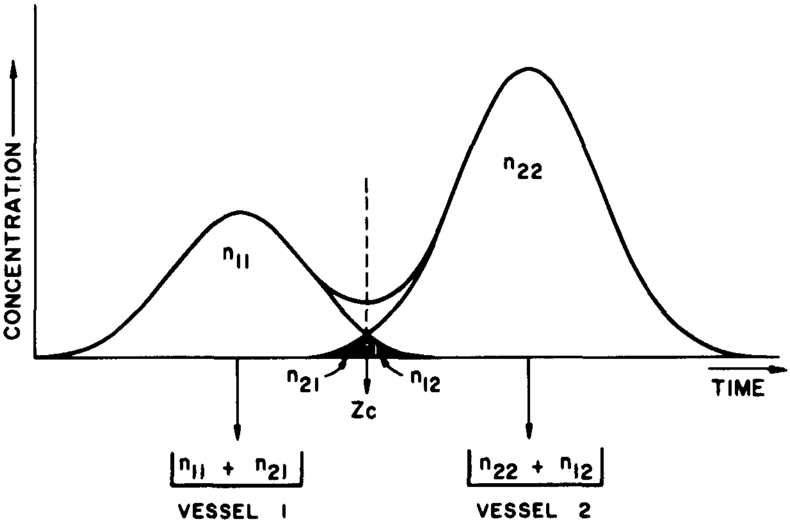

FIG. 1. Illustration of fraction separation in relation to cutpoint z_c.

Fig. 1)

$$\eta_1 = n_{21}/n_{11} \tag{2}$$

and

$$\eta_2 = n_{12}/n_{22} \tag{3}$$

the purity index I for a single binary equilibrium stage is obtained as

$$\begin{aligned} I_{ss} &= -0.25 \log \frac{n_{21}}{n_{22}} \frac{n_{12}}{n_{11}} && (4) \\ &= 0.25 \log k_2/k_1 && (5) \\ &= 0.25 \log \alpha && (6) \end{aligned}$$

where α is the relative volatility.

Consider the countercurrent multistage system shown in Fig. 2. The stages are numbered in the direction of flow of Component 1; for distillation Component 1 will be the more volatile and Component 2 the less volatile component.

Analogous to Rony's use of Klinkenberg's (*5*) procedure for obtaining the conservation-of-mass equations, the material balances and equilibrium conditions yield the following expression for the general case of partial reflux

$$I_{d\ \text{partial reflux}} = -0.25 \log \frac{[(k_2^m - 1) + (r_w/r_{w+1})(k_2 - k_2^m)]}{[(k_1^m - 1) + (r_w/r_{w+1})(k_1 - k_1^m)]}$$

$$\times \frac{(k_1^m - k_1^{n+m}) + (r_e/r_{e+1})(k_1^{n+m-1} - k_1^m)}{(k_2^m - k_2^{n+m}) + (r_e/r_{e+1})(k_2^{n+m-1} - k_2^m)} \qquad (7)$$

The reflux ratios r for the extraction section and washing section are defined by

$$\frac{r_e + 1}{r_e} = \frac{n_{11}(n + m - 1)}{n_{12}(n + m)} \qquad (8)$$

and

$$\frac{r_w + 1}{r_w} = \frac{n_{12}(1)}{n_{11}(0)} \qquad (9)$$

respectively.

At total reflux ($r_e = r_w = 0$) and equal numbers of washing and extraction stages ($n = m$), Eq. (7) reduces to

$$I_{d\ \text{total reflux}} = 0.25(2n - 1) \log \alpha \qquad (10)$$

For no reflux ($r_e = r_w = 0$) and $n = m$, $I_{d\ \text{no reflux}}$ is obtained as

$$I_{d\ \text{no reflux}} = 0.25n \log \alpha \qquad (11)$$

The elution curve in linear chromatography is given by the Gaussian distribution

$$C_i(z, t) = \frac{m_i}{(2\pi)^{1/2}\sigma_i} \exp\left[-\frac{(z - z_i)^2}{2\sigma_i^2}\right] \qquad (12)$$

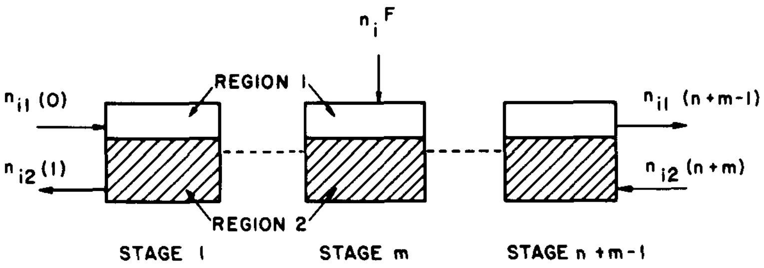

Fig. 2. Definition of terms for a countercurrent multistage system.

where C_i = concentration of ith component, z = axial distance coordinate, z_i = position of distribution mean of ith component, m_i = area of peak, and σ_i = standard deviation of the ith peak.

The impurity fractions η_1 and η_2 then follow as

$$\eta_1 = \frac{m_2[1 - \operatorname{erf}(Z_2/\sqrt{2})]}{m_1[1 + \operatorname{erf}(Z_1/\sqrt{2})]} \tag{13}$$

and

$$\eta_2 = \frac{m_1[1 - \operatorname{erf}(Z_1/\sqrt{2})]}{m_2[1 + \operatorname{erf}(Z_2/\sqrt{2})]} \tag{14}$$

where

$$Z_1 = \frac{z_c - z_1}{\sigma_1} \tag{15}$$

and

$$Z_2 = \frac{z_2 - z_c}{\sigma_2} \tag{16}$$

It has not been possible to determine an analytical expression for the cut point z_c which would maximize the purity function I, and a numerical analysis appears to be indicated. For the present purpose, however, it is deemed sufficient to determine z_c from a simpler condition which promises at least qualitative agreement with the above requirement, viz., that cut point which yields equal impurity fractions for both regions, i.e.,

$$\eta_1 = \eta_2 \tag{17}$$

The extent of separation I_c can then be written as

$$I_c = -0.5 \log \frac{\{1 - \operatorname{erf}[z_2 - z_1/\sigma(8)^{1/2}]\}}{\{1 + \operatorname{erf}[z_2 - z_1/\sigma(8)^{1/2}]\}}\,. \tag{18}$$

The dimensionless parameter $(z_2 - z_1)/\sigma(8)^{1/2}$ can be written more conveniently in terms of time units as (*6*)

$$\frac{z_2 - z_1}{\sigma(8)^{1/2}} = \frac{t_2 - t_1}{\sigma_{t_1}(8)^{1/2}} \tag{19}$$

where t_1 and t_2 are the retention times of the two components and σ_{t_1} the standard deviation of component, measured in time units.

From the relations

$$t_i = l(1 + k_i)/u \tag{20}$$

$$\sigma_{t_i} = \sigma_i(1 + k_i)/u, \tag{21}$$

$$H_c = \sigma_1^2/l \tag{22}$$

and

$$N_c = l/H_c \tag{23}$$

it follows that

$$I_c = -0.5 \log \frac{[1 - \text{erf } (N_c/8)^{1/2}][(\alpha - 1)k_1/(1 + k_1)]}{[1 + \text{erf } (N_c/8)^{1/2}][(\alpha - 1)k_1/(1 + k_1)]} \tag{24}$$

For close separations, i.e., α close to unity,

$$\text{erf} \left(\frac{N_c}{8}\right)^{1/2} \frac{(\alpha - 1)k_1}{(1 + k_1)} \sim \left(\frac{N_c}{2\pi}\right)^{1/2} \frac{(\alpha - 1)k_1}{(1 + k_1)} \tag{25}$$

since (7)

$$\text{erf } x \underset{0}{\overset{x}{\longrightarrow}} \frac{2x}{(\pi)^{1/2}} \tag{26}$$

Equation (24) becomes

$$I_c = -0.5 \left[\log\left\{1 - \left(\frac{N_c}{2\pi}\right)^{1/2} \frac{(\alpha - 1)k_1}{(1 + k_1)}\right\} - \log\left\{1 + \left(\frac{N_c}{2\pi}\right)^{1/2} \frac{(\alpha - 1)k_1}{(1 + k_1)}\right\}\right] \tag{27}$$

By using the approximation $\ln x \sim x - 1$ for $x \sim 1$, Eq. (27) reduces to

$$I_c = \frac{1}{2.303} \left(\frac{N_c}{2\pi}\right)^{1/2} \frac{(\alpha - 1)k_1}{(1 + k_1)} \tag{28}$$

To the same approximation Eqs. (11) and (10) become, respectively,

$$I_{d \text{ no reflux}} = \frac{0.25}{2.303} n(\alpha - 1) \tag{29}$$

and

$$I_{d \text{ total reflux}} = \frac{0.25}{2.303} (2n - 1)(\alpha - 1) \tag{30}$$

Equations (28), (29), and (30) now make possible the comparison of chromatography and distillation for the case where the purity index I is taken as a measure of the analytical efficiency. For analytical purposes, yield is, per definition, of trivial importance, and the appropriate index for distillation would therefore be the one which corresponds to maximum analytical efficiency, viz., $I_{d\ \text{total reflux}}$.

The ratio of the number of theoretical distillation plates N_d to chromatographic plates N_c needed to effect a separation with the same efficiency I is given by

$$\frac{N_d}{N_c} = \frac{2(\alpha - 1)}{2.303 I\pi} \left(\frac{k_1}{1 + k_1}\right)^2 \tag{31}$$

for $N_d = 2n$ $(n = m, n \gg 1)$.

It is apparent from Eq. (31) that the ratio N_d/N_c depends on I, α, and k_1. An important difference from Rony's results is noted in the marked dependence of N_d/N_c on k_1. This causes the ratio to vary by a factor 4 as k_1 varies from $k_1 = 1$ to $k_1 \gg 1$, and shows that large errors can be incurred in the calculation of the number of theoretical chromatographic plates equivalent to a given number of distillation plates, and vice versa, if this dependence is not taken into account.

SYMBOLS

α	relative volatility
C_i	concentration of ith component
η_i	impurity ratio for ith component
H_c	height equivalent to a theoretical plate in chromatography
I	purity index
k_i	mass distribution coefficient of component i
l	column height in chromatography
m	number of stages in extraction section
m_i	area of chromatographic peak of component i
n	number of stages in washing section
n_{ij}	number of moles of species i in region
N_d	plate number in distillation
N_c	plate number in chromatography
r_e	reflux ratio for extraction section
r_w	reflux ratio for washing section
σ_i	standard deviation of ith peak

σ_{t_i}	standard deviation of component i in time units
t_i	retention time of component i
z	axial distance coordinate
z_c	position of cutpoint
z_i	position of distribution mean of ith component

Acknowledgments

One of us (C.E.C.) gratefully acknowledges financial assistance in the form of a bursary by the Industrial Development Corporation of South Africa.

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Received by editor December 6, 1971