Counter-current distribution with a varying partition ratio

In a counter-current distribution in a Craig machine with a moving upper phase of constant solvent composition, and a stationary lower phase the composition of which is a function of the tube number r only (the first tube being No. 1), the fraction R_r of solute in tube number r that is transferred to tube number $(r + 1)$ at any stage is given by $\alpha F_r/(\alpha F_r + 1)$, where α is the ratio (volume of moving phase)/(volume of stationary phase), and F_r is the effective partition ratio for the solute in tube number r, i.e. F_r = (total concentration of solute in upper phase)/(total concentration of solute in lower phase), where "total concentration" refers to the sum of the concentrations (weight/volume) of all the species that will later be isolated as "solute". Consideration of repeated transfers leads to the result that the fraction of the solute in tube number r after n transfers, $P_{n,r}$, is given by the equation

$$P_{n,r} = Q_{n,r} \cdot \prod_{j=0}^{r=1} R_j \tag{1}$$

where

$$Q_{n,r} = Q_{n-1,r-1} + (1 - R_r)Q_{n-1,r};$$

with the boundary conditions: $Q_{n,0} = 0$; $Q_{0,1} = 1$, otherwise $Q_{0,r} = 0$ (equivalent to the condition that all the solute is put into tube No. 1 at the beginning of the run);

$R_0 = 1$, R_j ($j = 1,2 \ldots$) being defined above.

Eqn. (1) is a general one. Replacing R_j therein ($j \geqslant 1$) by a constant gives the binomial distribution described by CRAIG AND CRAIG[1]; and if the moving phase is the one of varying composition, Eq. (1) can be used with the tubes numbered in reverse order, with the tube containing the furthest-moved solvent as No. 1.

The distribution described above can be evaluated only if R is a known function of r. This is the case, in principle, if the solute is a base and the aqueous (lower) phase has a different pH in each tube. Let the free base have a partition coefficient f (f is independent of pH), and acidic dissociation constant K; then, if in the rth tube the hydrogen ion concentration is H_r, $F_r = fK/(K + H_r)$. If there is a constant pH decrease, δ, between each tube, $H_r = H_1 \cdot 10^{r\delta}$. Table I shows the calculated distributions after 5, 10 and 15 transfers with values $\alpha = 1$, $f = 9$, $H_1 = 10^{-8}$, $K = 10^{-6}$, $\delta = 0.5$, and Table II, column 1, the positions of the centre of gravity of the band—defined as $\Sigma(r \cdot P_{n,r})$— after each transfer.

The distribution after many transfers is tedious to calculate unless a computor program is available, but the approximate position of the centre of gravity of the distribution can be calculated by treating R as a continuous function of r. Then, for the solute to move a small distance dr, the solvent must move a distance $dr/R(r)$; and for the solute to move a distance r the solvent must move a distance $\int dr/R(r) = T(r)$. After n transfers the solvent front has moved past n tubes, and if the solute has been moved past j tubes, then

$$\int_{r=0}^{r=j} dr/R(r) = n \tag{2}$$

TABLE I

CALCULATED DISTRIBUTION OF A MODEL BASE

r	$P_{5,r}$	$P_{10,r}$	$P_{15,r}$
1	—*	—	—
2	—	—	—
3	0.009	—	—
4	0.087	—	—
5	0.390	0.001	—
6	0.513	0.017	—
7	zero	0.222	0.014
8	zero	0.521	0.238
9	zero	0.226	0.570
10	zero	0.013	0.169
11	zero	—	0.009
12	zero	zero	—
13	zero	zero	—
14	zero	zero	—
15	zero	zero	—
16	zero	zero	—

* Less than 0.001.

TABLE II

POSITION OF THE CENTRE OF GRAVITY OF THE DISTRIBUTION CALCULATED FROM EQNS. (1) AND (2)

n	Eqn. (1)	Eqn. (2)
1	1.9	1.9
2	2.8	2.8
3	3.7	3.7
4	4.6	4.6
5	5.4	5.4
6	6.2	6.1
7	6.8	6.7
8	7.3	7.2
9	7.7	7.5
10	8.0	7.8
11	8.3	8.1
12	8.5	8.2
13	8.6	8.3
14	8.8	8.5
15	8.9	8.6

and the solute distribution will have a maximum in tube $(j + 1)$ (if the first tube is No. 1).

For a base such as the one above

$$R(r) = \alpha f K / K(\alpha f + 1) + H_1 \cdot 10^{r\delta},$$

whence

$$T(r) = r(1 + 1/\alpha f) + 10^{r\delta}(0.4343\, H_1/\alpha f K\delta).$$

Inserting the values quoted above for these constants,

$$T(r) = 1.111\, r + 0.653 \cdot 10^{0.5\, r-4}$$

and values of $(j + 1)$ for $n = 1$–15 are given in column 2 of Table II, for comparison with the figures derived from Eqn. (1).

Counter-current distribution of alkaloids in a solvent system of this type has been described[2], with benzene as the non-aqueous phase, and, of the experiments whose results are summarised in Fig. 1–4 in this paper, three can be used as a check on Eqn. (2) above. In this paper the tubes are numbered from zero, not from one; therefore, in Table III, H_1 is replaced by H_0, and the tube containing the most

TABLE III

CALCULATED AND OBSERVED VALUES OF j FOR SOME ALKALOIDS

Alkaloids	$S_b{}^a$	$S_w{}^a$	f	K^b	Fig. No.	H_0	α	δ	n	j^c Obs.	j^c Calc.
Brucine	1.86	0.088[d,e]	18.6	$1.09 \cdot 10^{-8}$	1	10^{-10f}	1	0.33	25	13	13
Hydrastine	9.75[g]	0.033	296	$5.88 \cdot 10^{-7}$	1	10^{-10}	1	0.33	25	22	20
Caffeine	0.98[h]	1.34[d,h]	0.64	1.34	3	10^{-8}	1	0.33	20	17	8
					4	10^{-7}	1	0.20	24	21	9
					4	10^{-7}	1	0.20	35	24	14
					4	10^{-7}	1	0.20	24	7	7
Strychnine	0.77	0.021	32.3	$1.00 \cdot 10^{-8}$	4	10^{-7}	1	0.20	35	9	8

[a] Values refer to 20°.
[b] Seidell quotes K_b; K taken as $10^{-14}/K_b$.
[c] To the nearest integer.
[d] Anhydrous; calculated from the value for the hydrated base.
[e] Suitable mean value.
[f] The text[2] quotes 10^{-9}, but the quoted tube numbers, pH values, and the value for δ fit only for $H_0 = 10^{-10}$.
[g] Calculated from the solubility in g per 100 g of saturated solution.
[h] Interpolated.

solute is j, not $(j + 1)$. For none of the alkaloids used is the value of f available; but the density of benzene at 20° is 0.88 and if S_w, S_b, are the solubilities of the bases in g per 100 g of water, or benzene, respectively, f can be taken as $(S_b \times 0.88)/S_w$, provided that the only solute species present in the two phases are the free base and its protonated form. Values for S_w, S_b, and K are available[3], and are given in Table III.

Eqn. (2) thus has some predictive value for three of the four alkaloids, and for caffeine, for which it fails, the value of f is not that given by the expression above, but is of the order of 6 in these experiments.

I thank Professor M. GORDON for helpful discussion.

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