Investigation of the separation efficiency in static and dynamic preconcentration extractions by a numerical method*

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Two models of the liquid—liquid extraction at equilibrium have been studied mathematically. Using the iterative numerical method the maximum difference between separation efficiencies in dynamic and static extractions, as well as the absolute values of the respective separation efficiencies at this maximum was calculated. These values somewhat differ from those reported earlier.

One of the most important criteria in the choice of an effective preconcentration technique in analytical chemistry is the yield of the concentrated analyte(s) [1, 2]. Liquid—liquid extraction belongs to the very frequently used methods for preconcentration of trace elements based on the separation between two phases. It is known that the separation efficiency of a liquid—liquid extraction in the dynamic (flow) multistage operation is higher than in the static (batch) one-stage operation. Several works were dealing with the separation efficiency under these conditions but only few of them treated this problem thoroughly [3—9].

In this paper the static and dynamic models of the liquid—liquid extraction have been studied mathematically. The differences found in efficiencies of the separation in these two models have been calculated within the entire range of the separation efficiency. The study has resulted in finding a maximum difference of the separation efficiencies in the two models by the iterative numerical method [10, 11], and revealed some unexpected facts concerning the position of this maximum on the separation efficiency scale.

Method

From the theory of the liquid—liquid extraction process it follows [3—6] that

$$E_s = \frac{K_D}{K_D + \dfrac{V_{aq}}{V_{org}}} \qquad (1)$$

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and

$$E_{\mathrm{d}} = \frac{K_{\mathrm{D}} V_{\mathrm{org}}}{V_{\mathrm{aq}}} \left[1 - \exp\left(-\frac{V_{\mathrm{aq}}}{K_{\mathrm{D}} V_{\mathrm{org}}} \right) \right] \tag{2}$$

where E is the separation efficiency, s — static (batch) extraction, d — dynamic (flow) extraction with a stationary extracting and a moving extracted phase. K_{D} is the distribution ratio of the analyte between the extracting and extracted phases at equilibrium, V_{aq} and V_{org} are the volumes of the extracted (usually aqueous) and of the extracting (usually organic) phase, respectively.

Since E_{d} can be expressed in dependence on E_{s} the difference between E_{d} and E_{s} can be written as

$$E_{\mathrm{d}} - E_{\mathrm{s}} = \frac{E_{\mathrm{s}}}{1 - E_{\mathrm{s}}} \left[1 - \exp\left(\frac{E_{\mathrm{s}} - 1}{E_{\mathrm{s}}} \right) \right] - E_{\mathrm{s}} \tag{3}$$

Substituting $y = E_{\mathrm{d}} - E_{\mathrm{s}}$ and $x = E_{\mathrm{s}}$ in eqn (3) and rearranging it, the following function is obtained

$$y = \frac{x \left[x - \exp\left(\dfrac{x - 1}{x} \right) \right]}{1 - x} \tag{4}$$

By investigating the function expressed by eqn (4) in the interval $\langle 0, 1 \rangle$ it was found that this function is defined and continuous in the interval $(0, 1)$. The points $x = 0$ and $x = 1$ are points of discontinuity, in which $\lim\limits_{x \to 0^+} y(x) = 0$ and $\lim\limits_{x \to 1^-} y(x) = 0$. In searching for local extremes of this function the necessary condition is that $y'(x) = 0$. By deriving eqn (4) and from the necessary condition for a local extreme we obtain

$$\frac{2x - x^2 - \dfrac{\exp\left(\dfrac{x - 1}{x} \right)}{x}}{(1 - x)^2} = 0 \tag{5}$$

The sufficient condition for an extreme is that $y''(x) \neq 0$. By the derivation of the left-hand side of eqn (5) and rearranging it we get

$$y''(x) = \frac{(1 - x) \left[2 - \dfrac{\exp\left(\dfrac{x - 1}{x} \right)}{x} \left(3 - \dfrac{2}{x} + \dfrac{1}{x^2} \right) \right]}{(1 - x)^4} \tag{6}$$

Let us solve eqn (5) in the interval (0, 1). After rearranging it the following relation holds

$$x = \frac{1}{1 - \ln\left[x^2(2 - x)\right]} \qquad (7)$$

Eqn (7) is a transcendental equation and for its solution we have chosen an iterative method. In this method the $k + 1$ iteration is calculated according to the relation

$$x_{k+1} = f(x_k) \qquad (8)$$

where $k = 0, 1, 2,$ and x_0 is a suitably chosen initial value [10, 11].

For calculation a PTA-4000 + 16 microcompüter (Hiradástechnikai szövetkezet, Budapest) was used. The used iterative procedure is presented in Fig. 1.
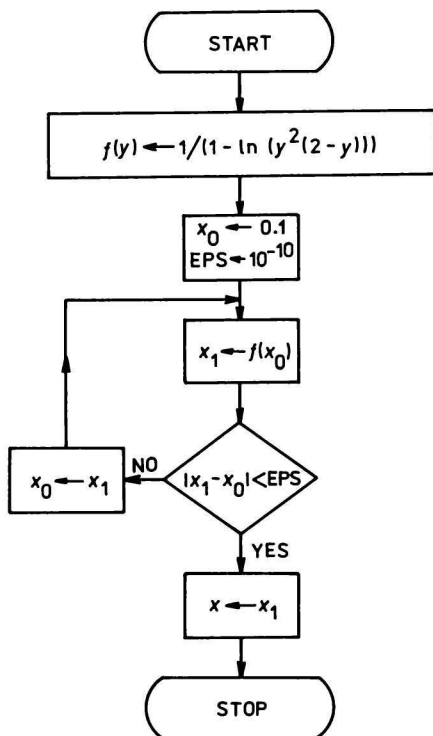

Fig. 1. Iterative procedure for the calculation of maximum difference between E_d and E_s.

Results and discussion

The graphical representation of eqns (*1*) and (*2*) shows that both models are effective for the values of

$$\frac{K_D V_{org}}{V_{aq}} = k_D \qquad (9)$$

greater than 10. The greatest differences in the value of the separation efficiencies are in the central part of the curves, *i.e.* near the value of k_D around 1, when $E_s = 50\%$ as can be seen in Fig. 2. This is confirmed in Fig. 3 where the difference in the separation efficiencies between the two models is expressed as a function of E_s.
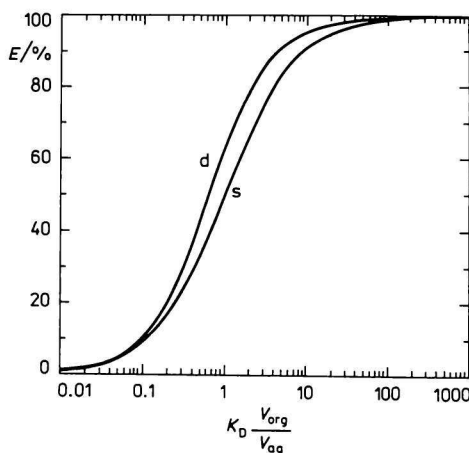

Fig. Dependence of E_d and E_s on $K_D V_{org}/V_{aq}$ according to eqns (*1*) and (*2*).

Solving eqn (*7*) by the iterative numerical method, we can easily calculate the value of x, which is approximately 0.535084638 with the required precision of 10^{-10} Substituting this value into eqn (*6*) we obtain $y''(x) = -1.587$, which means that the function of y (eqn (*4*)) has a local maximum at this point. By substituting the calculated value of x into eqn (*4*) we can obtain the maximum value of $y = 0.133125081$. Thus, the maximum difference between E_d and E_s, 13.31 %, is found at the values of $E_s = 53.51\%$ and $E_d = 66.82\%$, respectively (the values are rounded up to hundredths of %).

From the obtained results it follows that the maximum difference in the separation efficiencies occurs for the value of k_D of about 1.151. This value and the respective values of E_s and E_d at this value of k_D differ from those reported in one of our earlier papers [9]. In the cited paper due to the imperfect investigation of our previous data [3. 4]. as well as the data of other authors [12, 13] a

certain misinterpretation has occurred which resulted in incorrect values as for k_D, E_s, and E_d. These were 1 %, 50 %, and 63.21 %, respectively.

In our previous paper [3], two models of dynamic separation in heterogeneous liquid—liquid system were also investigated. One of them with a stationary extracted and a moving extracting phase, is the opposite to the other one, which is treated here. It was found that the separation efficiencies in both models
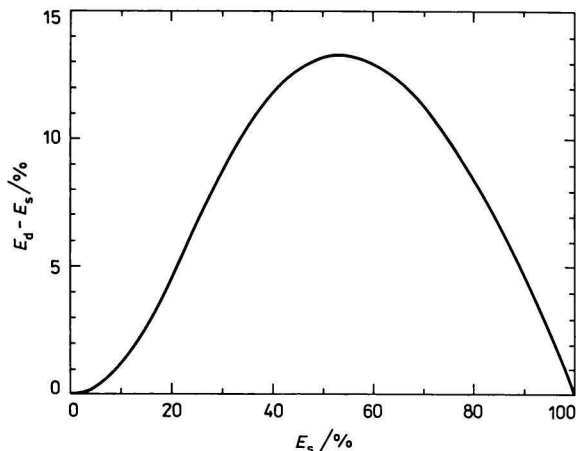

Fig. 3. Value of $E_d - E_s$ as a function of E_s.

are equal if the value of $k_D = 1$. The point of the intersection of the curves of functions $E_{d1} = f_1(k_D)$ and $E_{d2} = f_2(k_D)$, which is at $k_D = 1$, was then mistakenly considered for a value of k_D at which the difference $E_d - E_s = 13.21$ % had been supposed to be a maximum.

Conclusion

The results and conclusions given here are based on theoretical considerations. The used iterative numerical method has been found useful in thorough investigation and exact determination of the maximum difference between respective separation efficiencies. But, on the other hand, the obtained correct values of E_d and E_s at their maximum difference do not affect the previous qualitative conclusions [9]. From the viewpoint of the separation efficiency, dynamic and static extractions in the described system are almost equivalent especially in the analytically interesting range of $E > 90$ % [1, 2].

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