8.7. Solid – liquid extraction

8.7.1. Theoretical background

Solid – liquid extraction (or leaching) is the separation of a solid solute from a mixture of solids by dissolving it in a liquid phase. Basically, there are three components in leaching: solid solute, insoluble solids and solvent. In most cases, the diffusion of intra-particle soluble component(s) controls the extraction rate. Therefore the process is often called as diffusion extraction.

Solid – liquid extraction is widely used in food (e.g. extraction of sugar from sugar cane or sugar beet; isolation of vegetable oils from different seeds) and pharmaceutical industries (e.g. extraction of active components from medicinal plants), and in hydrometallurgy (e.g. leaching of metal ions from ores).

For mathematical modeling of leaching an ideal solid – liquid extraction is defined. The solvent added to the dry raw material is partly taken up by the solid material and the soluble ingredients are instantaneously dissolved. Often all the solute is already dissolved (e.g. sugar in sugar beet). The solution is then split into two parts. The external solution is called extract and the internal one raffinate (in the case of plant materials this is cell liquor).

The simplifying assumptions are defined as follows:

1. For batch extraction the mass ratio of extract (B) and raffinate (A) does not change during extraction (liquid ratio: $f = B/A$ =constant). In a continuous system the mass flow rate ratio of extract and raffinate remains constant throughout the equipment.

2. The densities of solutions remain practically constant during extraction.

3. The solid matrix has no absorptive properties. Hence, after infinite time the concentrations in the extract and raffinate phases are the same.

4. The surface of solid material available for mass transfer does not change with time.

5. The concentration of the raffinate (cell liquor) is initially the same throughout the solid matrix: x_0 (kg solute/ kg raffinate).

6. The solid phase consists of regular particles of the same shape and size: plates (leaves of plants), infinitely long cylinders (e.g. stems), or spheres (e.g. ground plant material). The shape and size of particles does not change during extraction.

7. The interior of the solid matrix is isotropic in all direction of diffusion, thus a constant „apparent or effective" diffusion coefficient (D_{eff}) can be defined for the given material.

8. In a batch system the extract phase is mixed, hence, the concentration gradient is zero in every direction in the system. If the extract is circulated or continuous system is used this gradient is zero in the direction perpendicular to the fluid flow.

For the calculation of any of the operations mentioned we may start from Fick's equation of diffusion.

8.7.1.1. Batch operation mode

If the diffusion coefficient (D_{eff}) of the solutes inside the solid particles can be considered as constant, Fick's second law may be written as

$$D_{eff}\left[\frac{\partial^2 x}{\partial r^2} + \frac{C-1}{r}\frac{\partial x}{\partial r}\right] = \frac{\partial x}{\partial t} \tag{8.7-1}$$

Where x concentration of raffinate (kg/kg),
   r coordinate relative to the axis of symmetry (m),
   t time (s),
   C factor of geometrical symmetry (C =1 for plates/planes, C =2 for cylinders, C =3 for spheres).

The surface to volume ratio of particles can be expressed as:

$$\frac{F_p}{V_p} = \frac{C}{R} \tag{8.7-2}$$

Where F_p surface of particle (m^2),

   V_p volume of particle (m^3),

   R half thickness or half diameter of solid particles (m).

The boundary conditions:

1. At the phase boundary the concentration in the raffinate phase is equal to concentration of the extract phase, since the resistance of mass transfer in the extract phase may be neglected (the mass transfer coefficient in the extract phase is much more higher than that in raffinate phase).

$$x\left(r = R, t\right) = y\left(t\right) \tag{8.7-3}$$

2. The second boundary condition at $r = 0$ arises from the symmetry of particles. The concentration passes through a maximum at symmetric plane, axis or point.

$$\left[\frac{dx}{dr} \right]_{r=0} = 0 \qquad (8.7\text{-}4)$$

8.7.1.2. Solute balance for batch operation

$$Ax_0 + By_0 = A\bar{x} + By \qquad (8.7\text{-}5)$$

Where x_0 initial concentration of cell liquor (kg/kg),

$\quad\quad y_0$ initial concentration of solvent (kg/kg),

$\quad\quad \bar{x}$ mean solute concentration inside the particles (kg/kg).

For infinite time the concentrations in both phases become identical.

$$y_\infty = \bar{x}_\infty = \frac{x + fy_0}{1 + f} \qquad (8.7\text{-}6)$$

The mass transferred at the phase boundary can be given by the Fick's first law

$$B\frac{dy}{dt} = -D_{eff} F\rho_A \left[\frac{dx}{dr} \right]_{r=R} \qquad (8.7\text{-}7)$$

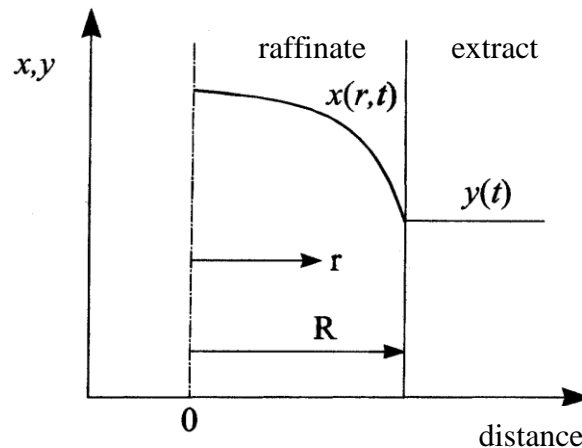where ρ_A density of raffinate (kg/m^3).

Figure 8.7-1.
The concentration profile of solute inside the particle and in extract phase

The surface through which the diffusion occurs

$$F = \varepsilon F_p = \varepsilon \frac{C}{R} V_p \qquad (8.7\text{-}8)$$

where ε liquid hold-up inside the particles (m^3/m^3):

$$\varepsilon = \frac{A}{\rho_A V_p} \qquad (8.7\text{-}9)$$

substituting into equation (8.7-8) gives

$$F = \frac{A C}{\rho_A R} \qquad (8.7\text{-}10)$$

From equations (8.7-3), (8.7-7) and (8.7-10) we obtain

$$-\frac{fR}{C D_{eff}} \left[\frac{\partial x}{\partial t}\right]_{r=R} = \left[\frac{\partial x}{\partial r}\right]_{r=R} \qquad (8.7\text{-}11)$$

The solution of equation (8.7-11) can be given as [2]:

$$\frac{\overline{x}(t) - x_\infty}{x_0 - x_\infty} = \frac{y_\infty - y(t)}{y_\infty - y_0} = P(t) \qquad (8.7\text{-}12)$$

$$P(t) = 2 f (1 + f) C \sum_{j=1}^{\infty} \frac{exp\left(-\xi_j^2 \cdot Fi\right)}{\left(f \xi_j\right)^2 + (1 + f) C^2} \qquad (8.7\text{-}13)$$

where $\quad Fi = D_{eff} t / R^2 = t / t_D^*$ FICK-number,

$t_D^* = R^2 / D_{eff}$ time constant of diffusion (s),

ξ_j j-th root of the characteristic equation relevant to the given geometrical shape

planes : $tg\,\xi_j = -f \xi_j$

cylinders: $\dfrac{J_1(\xi_j)}{J_0(\xi_j)} = -\dfrac{f \xi_j}{2}$

J_0 and J_1 are the Bessel-functions [3].

spheres: $tg\,\xi_j = \dfrac{3 \xi_j}{3 + f \xi_j^2}$

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The values of $\dfrac{y_\infty - y(t)}{y_\infty - y_0}$ term as a function of Fick-number for spherical particles are presented in Figure 8.7-2.
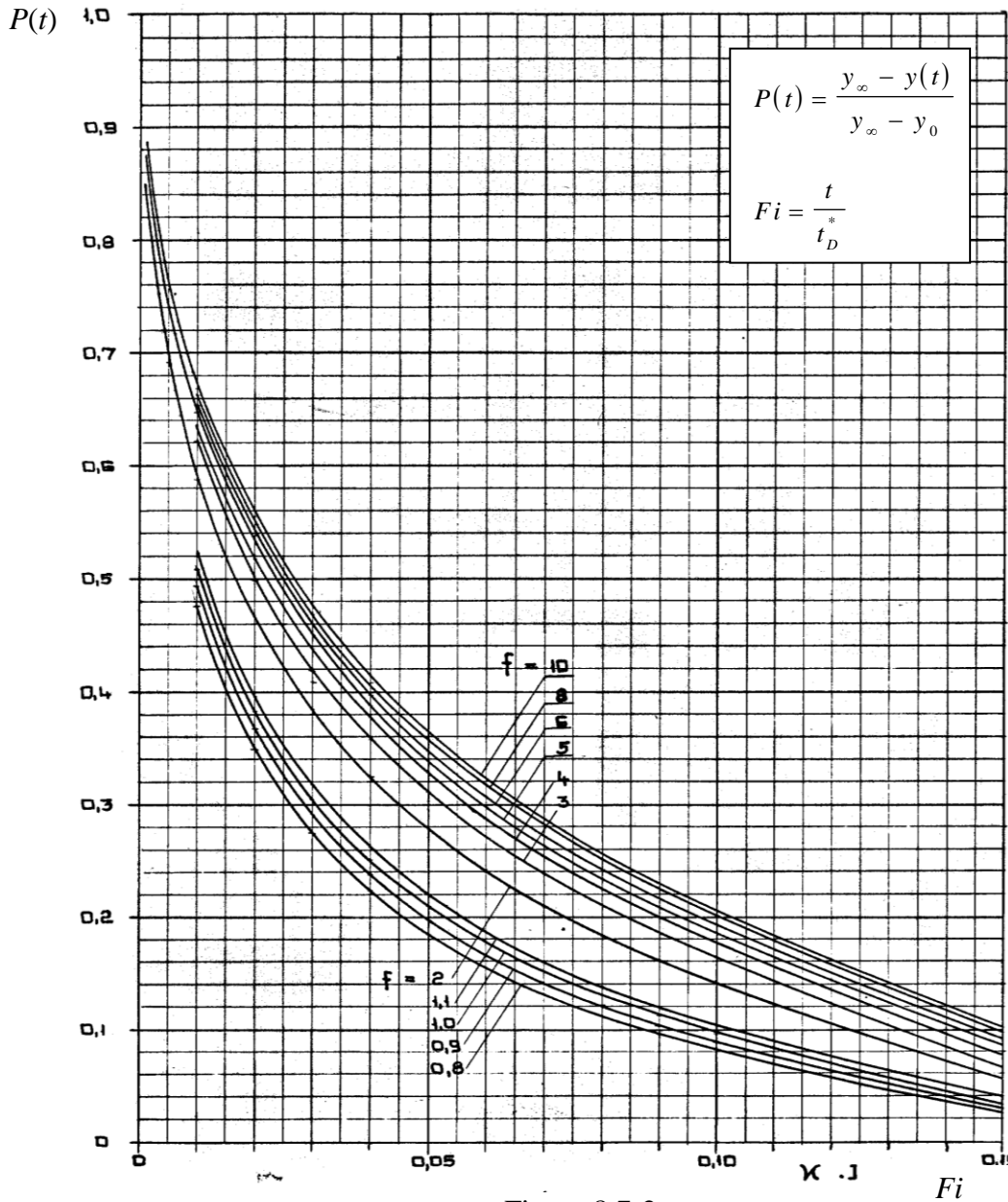

$$P(t) = \frac{y_\infty - y(t)}{y_\infty - y_0}$$

$$Fi = \frac{t}{t_D^*}$$

Figure 8.7-2.
Batch extraction of spherical particles

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The expressions for the concentration in a continuous countercurrent operation are formally very similar to batch extraction. The relative loss of solute $\dfrac{\overline{x}_n}{x_0}$ (where $\overline{x}_n$ is the solute concentration in the solid phase leaving the extractor) is plotted versus the Fick-number in Figure 8.7-3. For continuous system the Fick-number is defined as $Fi = D_{eff}\,\overline{t}\,/\,R^2$, where $\overline{t}$ is the mean residence time of solid material (assuming plug flow). The time constant of diffusion ($t_D^* = R^2\big/D_{eff}$) is the same for both batch and continuous operations. It includes the characteristics of solid – liquid system (material properties, structures). It is independent of time, liquid – solid ratio, and is only slightly affected by the flow characteristics. Hence, t_D^* can be determined from simple batch experiment, and it can be used for design of continuous extraction unit.
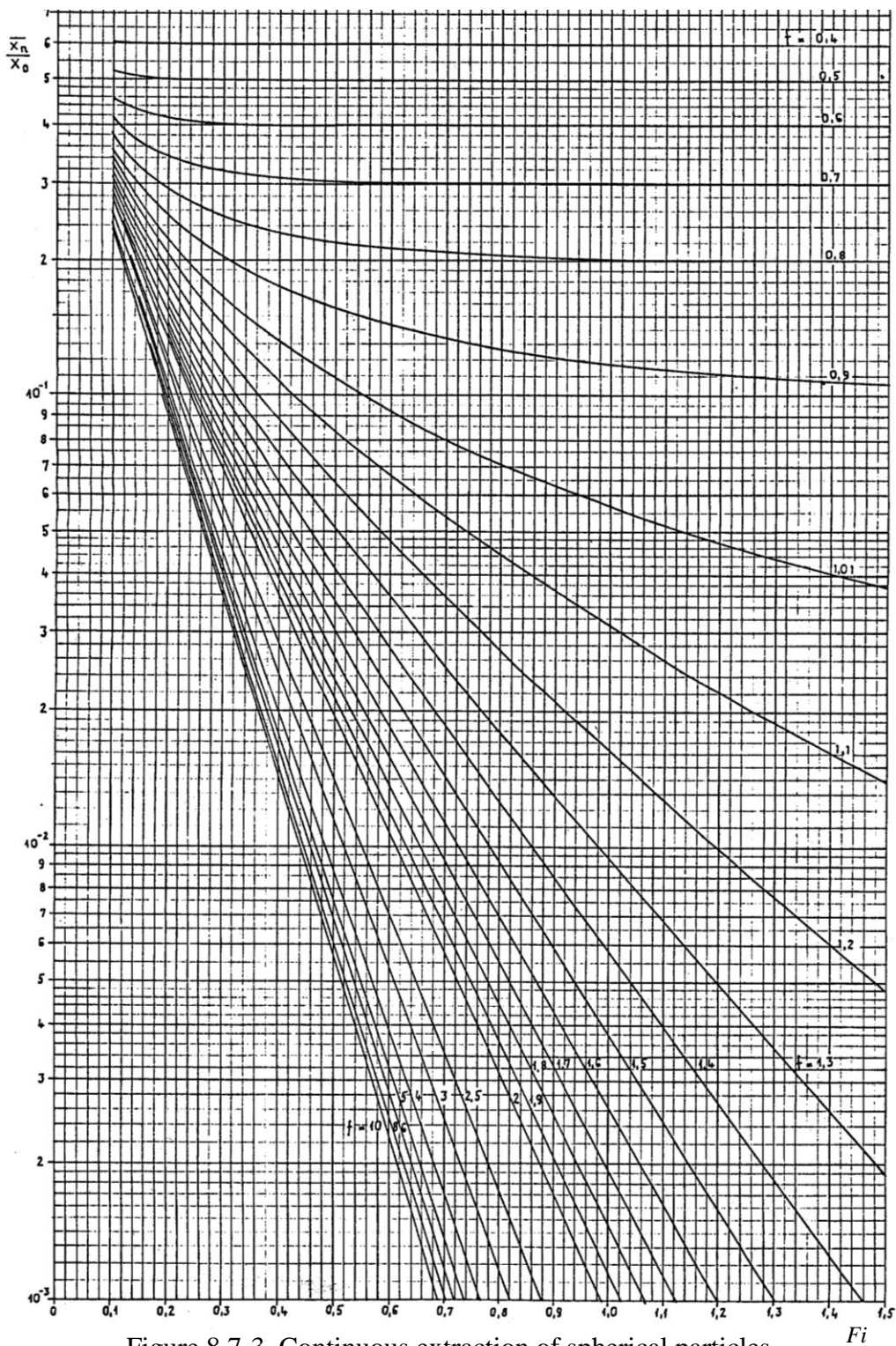
Figure 8.7-3. Continuous extraction of spherical particles

8.7.2. Objectives

Laboratory batch extraction is carried out to determine the time constant of diffusion $\left(t_D^* = R^2 / D_{eff} \right)$. From the experimental t_D^* value the effective diffusion coefficient (D_{eff}) can be calculated, if the geometry and size of the particles are known.

8.7.3. Equipment

The experimental set-up is presented in Figure 8.7-4.

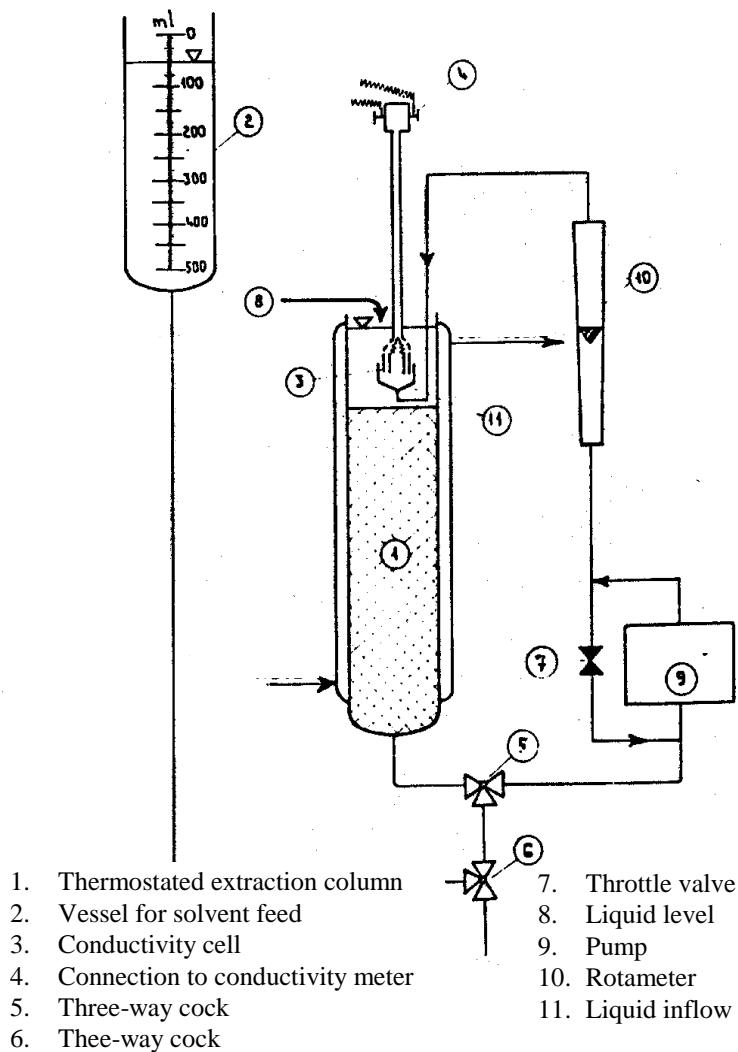|			
1.	Thermostated extraction column	7.	Throttle valve
2.	Vessel for solvent feed	8.	Liquid level
3.	Conductivity cell	9.	Pump
4.	Connection to conductivity meter	10.	Rotameter
5.	Three-way cock	11.	Liquid inflow
6.	Thee-way cock		

Figure 8.7-4.
Flow diagram of a laboratory solid – liquid extractor

The thermostated extraction column (1) is filled with porous Al_2O_3 tablets, which are saturated with NaCl solution. The diameter of the tablets is 8 mm ($R = 4$ mm), and they are approximated as spheres. The inner diameter of the column is 40 mm, The height of the column is 500 mm, and the packed height is 400 mm. The solvent is circulated with a gear pump (9). The liquid flow rate is measured by a rotameter (10), which is calibrated with water (unit is dm^3/h). The flow rate can be controlled by throttle valve (7). The concentration of extract is measured by conductivity meter (4).

8.7.4. Experimental procedure

The previous group filled the extractor tube with NaCl solution, so that the tablets were soaked for one day or more. The mass values of dry and soaked tablets are given at the notice board near to the extraction unit. The NaCl solution is discharged from the extractor column, and the initial concentration is determined by measurement of conductivity. The surface of tablets is wetted with concentrated NaCl solution, which should be rinsed with about 100 ml distilled water.

The conductivity cell is put into the holder. The calibrated solvent vessel is filled with distilled water. The operation of gear pump should be checked by moving the belt by hand. The proper positions of three-way cocks (presented on notice board) should be checked before filling the extractor. Any mistake may result that the measurement can not be carried out the same day.

The extractor is filled with distilled water. The gear pump is started, and the flow rate will be given by the instructor. The extraction starts with the circulation of liquid. The extract concentration is read at certain time intervals (every 2 minutes between 0 – 20 min; every 5 minutes between 20 – 50 min; and every 10 minutes until the end of measurement).

The readings are taken till the concentration becomes stable and steady. The total extraction time is about 90…120 min, depending on liquid flow rate and temperature. After steady concentration is reached, the pump is stopped and the apparatus is emptied. The system is washed with distilled water by circulation in the apparatus for some minutes. Then the washing liquid is discharged and the extraction column is filled with NaCl solution to be prepared for the next experiment. The filling of pump or circulation tube with NaCl solution should be avoided.

8.7.5. Data analysis

The extract concentration (y) can be read directly from the conductivity meter. The density of the sodium chloride solution can be taken as 1 g/cm^3-nek through-out. The measured y_∞ value is the last reading. The measured final extract concentration should be compared with that calculated from the component balance equation (8.7-6).

Plot the extract concentrations against time (y - t diagram). Plot the calculated time constant of diffusion versus time (t_D^* - t diagram), and determine the mean value in the range where it is really constant. Calculate the effective diffusion coefficient from the mean value of t_D^* (please note, that $R = 4$ mm). Compare the effective diffusion coefficient with the molecular diffusion coefficient of NaCl, measured in pure water at 20 °C ($D = 1.39 \cdot 10^{-5}$ cm^2/s).

The following Table should be completed and attached to the report:

Dry mass of tablets: g
Mass of tablets saturated with NaCl: g
Mass of raffinate (A):   g
Mass of extract (B):   g
Phase ratio ($f = B/A$):
Rotameter scale: dm^3/h
Temperature: °C
Initial concentration of raffinate (x_0):   g/kg
Measured final extract concentration y_∞:   g/kg
Calculated final extract concentration (Eq. 8.7-6) y_∞:   g/kg
D_{eff}/D :

Set up a Table with the headings for determination of the time constant (t_D^*)!

Time (min)	y $\left(\dfrac{g}{kg}\right)$	$\dfrac{y_\infty - y}{y_\infty}$	Fi	t_D^* (min)

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8.7.6. Design of continuous extraction

On the basis of batch experiment the mean residence time in a continuous extraction unit can be designed. The steady value of t_D^* is determined from batch laboratory experiment. The relative loss and extract concentration are given by the instructor. If neat solvent ($y_0 = 0$) is used for extraction, the phase rate ratio can be calculated from the material balance of continuous extraction

$$x_0 = x_{out} + f\, y_{out} \qquad\qquad (8.7\text{-}14)$$

where y_{out} and x_{out} are the outlet concentrations in the extract and raffinate, respectively. The Fick-number can be read in Figure 8.7-3.

The results should be summarized in the following Table:

Given	Determined
Relative loss (x_{out}/x_0):	Phase flow rate ratio (*f*):
Relative extract concentration (y_{out}/x_0):	Fick - number (t_{extr}/t_D^*):
Time constant of diffusion (t_D^*)	Mean extraction time ($\bar{t}$):

References

[1] Fourier, J. B. J.: Théorie analytique de la chaleur, 1808.
[2] Akszelrud, G. A.: Zsurnal Fizicseszkoj Himii, *33,* 2316 (1959)
[3] Crank J.: The mathematics of diffusion, Clarendon Press, Oxford, 1956.