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Theoretical Models for Electrodialytic Sample Treatment in Trace Analysis by Liquid Chromatography

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Key Words

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Electrodialytic sample treatment
Computer models
Analyte enrichment

Summary

Basic considerations for analyte enrichment and recovery obtainable by electrodialysis as a sample treatment method are given. Equations are derived which describe the dependence of the concentration profiles of ionic compounds on the electric field strength in a set-up with stagnant donor and acceptor solutions. It is shown that analyte recovery increases when less ion-selective membranes are used in the electrodialysis cell. Computer models are used to estimate the analyte enrichment for a flowing donor (sample) and a stagnant acceptor phase. About 10-fold enrichment can be obtained in an electrodialytic sample treatment system within 20 min under maximum current conditions. A compromise has to be found between analyte recovery and the donor (sample) flow rate.

Introduction

In electrodialysis an external electric field is applied to achieve the selective transport of sample components across a semipermeable membrane from a donor to an acceptor compartment. Electrodialysis has been known since the early part of this century [1, 2]. Commercial applications started in the forties, after the development of stable and selective membranes with low electric resistance. Nowadays important industrial applications are in the desalination of brackish water, brine production and in the food industry. Electrodialysis has only rarely been used for analytical-scale work [3-6].

For the determination of trace levels of analytes in complex samples by means of column liquid chromatography (LC), a pre-purification and/or concentration step is often required before the sample can be injected onto the analytical column. Sample treatment is necessary to remove components which are harmful to the column and to decrease the number of interfering compounds. Several separation principles have been utilised in on-line sample treatment techniques, such as solid-phase extraction [7], zone electrophoresis [8-11] and dialysis [12-17]. First studies on electrodialysis as an extraction technique showed adequate separation of drugs from cellulose mixtures and solubilised milk powder [3-5]. Apart from sample clean-up, electrodialysis can also provide enrichment of ions from a flowing (sample) donor solution into a stagnant acceptor solution. Trace metal ions have been enriched from aqueous solution by electrodialysis prior to their spectrophotometric determination [6]. Recently the application of electrodialysis for clean-up of strongly alkaline samples in ion chromatography was described [18].

In previously published studies [19, 20] we have shown that electrodialysis can be used in practice as an on-line sample treatment method for LC. With electrodialytic sample treatment (EDIST), traces of analytes could be enriched from the sample solution. In the present paper the potential and limitations of EDIST will be discussed from a theoretical point of view. Although the theoretical aspects of electrodialysis have already been discussed in the early years of its development, the practical implications under the conditions used in EDIST, still have to be established. Simplified theoretical models will be used to describe concentration profiles in the EDIST unit and analyte recoveries for stagnant sample (donor) and acceptor solutions. Computer simulation models will be applied to estimate analyte enrichment from a flowing sample solution. Also, the influence of the sample matrix and the ion-transport characteristics of the membranes on the performance of EDIST, will be studied. The models will be compared with previously published experimental results.

Experimental

Computer programs to simulate the transport processes in EDIST were written in Turbo C++ version 1.00 (Borland, Scotts Valley, CA, USA). Science and Engineering Tools version 6.1 software packages (Quinn-Curtis, Newton, MA, USA) were incorporated and high-precision floating point variables were used.

The simulation programs were run on an IBM-compatible computer with a 80386 processor and a vb 80287 mathematical coprocessor. Typical run times with this hardware configuration were 30–60 s. Results of the simulation were plotted on a HP 7475A plotter (Hewlett-Packard, Waldbronn, Germany) or imported into Lotus 123 version 2.01 (Borland).

Results and Discussion

Concentration Polarisation of an Electrolyte Solution

In order to study the transport of ions in EDIST, in this section the ion transport is described in an aqueous electrolyte solution in a compartment enclosed by membranes to which an electric field is applied. Figure 1 shows, schematically, the cell used in EDIST. It is confined between two identical selective ion-exchange membranes, while a non ion-selective (cut-off) membrane divides it into two compartments, a donor and an acceptor compartment. For simplicity it is assumed that the cell as well as the electrode compartments contain a 1 : 1 electrolyte.

In order to obtain an ion-transport model it is assumed that the Nernst-Planck equation satisfactorily describes the transport of ions. Due to the different permeability of the (outer) ion-exchange membranes for the positive and the negative ions, a concentration gradient of the electrolyte is built up in the cell. In this situation the transport of an ion depends on its diffusion coefficient, D ($\text{cm}^2 \text{s}^{-1}$), and its electrophoretic mobility, μ ($\text{cm}^2 \text{s}^{-1} \text{V}^{-1}$). These two parameters are related by:

$$\mu = \pm \frac{zF}{RT} D \quad (1)$$

where z is the valency of the ions, F the Faraday constant, R the gas constant and T (K) the absolute temperature.

In the absence of convective flow in the direction of the electric field, the mass fluxes J ($\text{mol s}^{-1} \text{cm}^{-2}$) of the positive and the negative ions, respectively, are given by the Nernst-Planck equation:

$$J_+ = -D_+ \left(\frac{dc}{dx} + \frac{zF}{RT} Ec \right) \quad (2a)$$

$$J_- = -D_- \left(\frac{dc}{dx} - \frac{zF}{RT} Ec \right) \quad (2b)$$

Figure 1
Electrodialysis cell.

where c is the electrolyte concentration (mol cm^{-3}), D_+ and D_- the diffusion coefficients for positive and negative ions, x the coordinate perpendicular to the membranes (cm) and E the local electric field strength (V cm^{-1}).

After a certain time a steady state will have been reached in which transport due to migration and molecular diffusion cancel each other out. Since concentrations now no longer change, the fluxes of positive and negative ions must be independent of the coordinate, x , in the EDIST cell. Also, the fluxes anywhere in the cell must be equal to the fluxes through the ion-exchange membranes. If one assumes that the selectivity of the membrane does not depend on the current density or the electrolyte concentration, the mass fluxes through the membranes can be calculated from the transport numbers for the positive and negative ions – t_m^+ and t_m^- , respectively – of the membrane in use:

$$J_+ = t_m^+ \frac{i}{zF} \quad (3a)$$

$$J_- = -t_m^- \frac{i}{zF} = -(1 - t_m^+) \frac{i}{zF} \quad (3b)$$

where i is the current density (A cm^{-2}).

Selective cation- and anion-exchange membranes obey analogous equations, provided the basic assumptions for both types of membrane are the same. In the following we therefore restrict the discussion to ion transport through an anion-exchange membrane. Hence, t_m^+ and t_m^- (transport number of the positive ion in solution) only will be used.

The combination of Eqs. (2a) with (3a) and (2b) with (3b) gives:

$$\frac{dc}{dx} + \frac{zF}{RT} Ec = - \frac{t_m^+}{D_+} \frac{i}{zF} \quad (4a)$$

$$\frac{dc}{dx} - \frac{zF}{RT} Ec = \frac{(1 - t_m^+)}{D_-} \frac{i}{zF} \quad (4b)$$

By addition of Eqs. (4a) and (4b) the electric field strength term is cancelled:

$$2 \frac{dc}{dx} = \left(- \frac{t_m^+}{D_+} + \frac{(1 - t_m^+)}{D_-} \right) \frac{i}{zF} \quad (5)$$

Eq. (5) can be simplified by introducing the mean ionic diffusion coefficient, D :

$$D = \frac{2 D_+ D_-}{D_+ + D_-} \quad (6)$$

Recognizing that

$$\frac{D_+}{D_-} = \frac{t_s^+}{t_s^-} = \frac{t_s^+}{(1 - t_s^+)} \quad (7)$$

The concentration gradient can be written as:

$$\frac{dc}{dx} = \frac{i}{zF} \frac{(t_s^+ - t_m^+)}{D} \quad (8)$$

Eq. (8) shows that a linear concentration gradient of the electrolyte has been formed, which is proportional to the current through the cell. There will be no gradient if the membrane transport number of the positive ions is equal to the free-solution transport number, i.e. $t_m^+ = t_s^+$.

Since there is no net transport of the electrolyte into or out of the cell, the concentration of the electrolyte as a function of x is given by:

$$c(x) = c^* + \left(x - \frac{b}{2} \right) \frac{i}{zF} \frac{(t_s^+ - t_m^+)}{D} \quad (9)$$

where c^* (mol cm⁻³) is the initial concentration of the electrolyte in the cell, i.e. before the electric field was applied, and b (cm) the distance between the two ion-exchange membranes (cf. Figure 1). When increasing the applied voltage, the current will reach a maximum value when the electrolyte concentration becomes zero at one of the membranes. From Eq. (9) it follows that the maximum current density, $i_{\max}$, is given by:

$$i_{\max} = \frac{2 z F D}{(t_s^+ - t_m^+) b} c^* \quad (10)$$

The current is said to be limited by concentration polarization. When the transport numbers in the membranes equal those in solution, a current maximum will not be reached; theoretically the current will

increase infinitely with increasing voltage. In actual practice, however, the current will be limited by the heat developed in the set-up, particularly in the ion-exchange membranes, as a result of their relatively high electric resistance. When the heat production is too high, decomposition of the membranes may occur and gas-bubble formation, due to electrolysis, will disturb the electrodialytic process which has also been observed experimentally [20].

Recovery of Charged Analytes from a Stagnant Donor Solution

In conventional dialysis, a high molecular mass cut-off membrane is used to separate the donor from the acceptor compartment (cf. Figure 1; central part), and analyte transfer occurs by molecular diffusion only. Low molecular mass analytes, whether charged or neutral, can pass the membrane while high molecular mass material is rejected. For equal volumes of (stagnant) donor and acceptor phase, the analyte recovery will at best be 50 %. If, now, an electric field is applied – that is, if EDIST instead of dialysis is used – molecular diffusion as well as migration of charged analytes will take place (cf. Eqs. (2a) and (2b) above). As a result, the recovery of charged analytes in the acceptor phase will increase and, under proper conditions (cf. below), analyte enrichment can occur.

In biological and environmental samples, high concentrations of background electrolyte are generally present. The low molecular mass, mainly inorganic electrolyte ions, will also migrate through the cut-off membrane and will determine the recovery of the analyte ions. In order to describe this effect, the following assumptions are made:

- the (outer) ion-exchange membranes are completely impermeable to the analyte, j ;
- the cut-off membrane is completely permeable to the analyte as well as the 1 : 1 background electrolyte;
- the analyte concentration is much lower than that of the background electrolyte, so that the presence of the analyte does not influence the current and/or electric field strength;
- analyte ions do not interact with the sample matrix.

The influence of the concentration gradient of the background electrolyte in the EDIST cell, on the recovery of an anionic analyte will first be discussed for stagnant donor and acceptor solutions. As shown in the previous section the electrolyte concentration gradient will depend on the current density. Under maximum-current conditions, the local steady-state concentration of the background electrolyte is given by:

$$c = \frac{2 x}{b} c^* \quad (11)$$

The maximum local electric field strength, $E_{\max}$ (V cm⁻¹), can be derived by substituting Eqs. (10) and

(11) in Eq. (4a). After some rearrangements $E_{\max}$ can be written as:

$$E_{\max} = - \frac{RT}{zF} \frac{1}{x} \frac{t_s^+ (1 - t_m^+) + t_m^+ (1 - t_s^+)}{(t_s^+ - t_m^+)} \quad (12)$$

The steady-state distribution of a charged analyte, j , can also be derived from the Nernst-Planck equation. Since the analyte ion cannot permeate through the ion-exchange membranes, its flux is zero under steady-state conditions, the Nernst-Planck equation can be written as:

$$\frac{dc_j}{dx} + \frac{z_j F}{RT} E c_j = 0 \quad (13)$$

After substitution of Eq. (12) in Eq. (13) the differential equation is easily solved. With the boundary conditions that the total amount of analyte in the cell is constant, the distribution of the analyte over the cell, expressed as c_j (mol cm⁻³), can be calculated:

$$c_j(x) = \left(\frac{t_s^+ (1 - t_m^+) + t_m^+ (1 - t_s^+)}{t_s^+ - t_m^+} \frac{z_j}{z} + 1 \right) \times \frac{t_s^+ (1 - t_m^+) + t_m^+ (1 - t_s^+)}{t_s^+ - t_m^+} \frac{z_j}{z} \times \left(\frac{x}{b} \right) c_j^* \quad (14)$$

where c_j^* is the initial concentration (mol cm⁻³) of analyte in the cell.

The distribution of an ionic analyte in the cell is seen to depend on its charge, and on the transport numbers of the background electrolyte in solution and ion-exchange membranes. In Figure 2 the concentration profiles of an ionic analyte, with $z_j = z = 1$, are given for various values of t_s^+ and t_m^+ . From the figure it is clear that the recovery of the analyte, i.e., the analyte fraction in the acceptor compartment under steady-state conditions, exceeds the value of 0.5 which is reached with conventional dialysis.

For analytes with $z_j = z$ the recovery, RE, is given by:

$$RE = \frac{\int_0^b c_j dx}{\int_0^b c_j^* dx} = 1 - \left(\frac{1}{2} \right) \frac{2 t_s^+ (1 - t_m^+)}{(t_s^+ - t_m^+)} \quad (15)$$

In Table I the recoveries calculated for different values of t_m^+ and t_s^+ are given. It is obvious that the recovery increases when less ion-selective membranes are used, i.e., if t_s^+ and t_m^+ have approximately the same values. This also becomes apparent when comparing Figures 2A and 2B.

Analyte recoveries from a stagnant donor solution in electrodialytic sample treatment coupled to LC were determined experimentally, previously [20]. Although the transport numbers of the solutions and membranes

Figure 2
Calculated concentration profiles for analyte ion j ($z_j = z = 1$) in donor and acceptor compartments, under maximum current conditions. (A) $t_s^+ = 0.4$ and (B) $t_s^+ = 0.6$; (a) $t_m^+ = 0.0$, (b) 0.1 and (c) 0.2. Distance between ion-exchange membranes, b . Initial analyte concentration, c_j^* , dotted line.

Table I. Recovery and enrichment of analyte in acceptor compartment under maximum-current conditions*.

t_m^+	Recovery for:		EF for:	
	$t_s^+ = 0.4$	$t_s^+ = 0.6$	$t_s^+ = 0.4$	$t_s^+ = 0.6$
0.0	0.75	0.75	3.0	3.0
0.1	0.81	0.78	4.3	3.5
0.2	0.89	0.81	8.1	4.3
0.3	0.98	0.86	49.0	6.1

* Analyte, $z_j = 1$.

used are not known exactly the values used in the present paper are very reasonable for the conditions described. Using a home-made electrodialysis system it was observed that recoveries of the basic drug ephedrine of over 90 % could be obtained within 1 min from a stagnant donor solution when potentials > 5 V were applied. When using lower potentials probably maximum-current conditions were not obtained, since decreased recoveries were observed.

Analyte Enrichment from a Flowing Donor Solution

The analyte enrichment described in Eqs. (14) and (15) can be enhanced when a flowing donor solution is used. The depletion of the donor compartment, as observed with a stagnant system, is then counteracted by the supply of fresh analyte-containing solution.

The analyte enrichment can be expressed in terms of the enrichment factor, EF, which is defined as the ratio of the steady-state concentration of analyte in the acceptor compartment and the original donor solution concentration – i.e., the maximum EF value in conventional stagnant donor/stagnant acceptor dialysis is 0.5.

On account of its complexity, a full mathematical description of the flowing donor and stagnant acceptor EDIST set-up will not be presented here. However, a first indication of the enrichment which can be obtained under conditions of maximum-current density, can be derived from the recovery data in Table I. When it is assumed that the final mean analyte concentration in the donor compartment, under stagnant conditions, equals the concentration in a flowing donor solution, EF can be calculated immediately. The pertinent EF values calculated in this way are included in Table I. The data show that under proper conditions –, i.e., when t_s^+ and t_m^+ do not differ too much – analyte enrichment by about one order of magnitude can be expected.

Influence of the Donor Flow Rate

An important factor to be discussed is the time needed to transfer analyte from the donor to the acceptor phase, or, alternatively, the optimum flow rate of the donor solution: when the donor flow rate is too high, the residence time of the analyte ions in the cell will be too short to allow their quantitative transfer to the acceptor compartment. The minimum required residence time can be estimated from the time needed for an analyte to migrate from the ion-exchange membrane of the donor compartment to the cut-off membrane. It is assumed that the ion transport will not be disturbed by the donor flow.

Under maximum-current conditions, the local electric field in the cell is given by Eq. (12). Since the migration time of an analyte ion from the ion-exchange to the cut-off membrane is given by:

$$t = \int_0^{b/2} \frac{dx}{\mu_j E} \quad (16)$$

for the minimum residence time we can write:

$$t_{\text{res}} = \frac{b^2}{8 D_j} \frac{(t_s^+ - t_m^+)}{t_s^+(1 - t_m^+) + t_m^+(1 - t_s^+)} \quad (17)$$

The calculated residence times under maximum current conditions for various values of t_m^+ and t_s^+ are given in Table II. Obviously, for an EDIST cell with equal

Table II. Minimum residence time of analytes in donor compartment required for quantitative recovery*.

t_m^+	Residence time (min) for:	
	$t_s^+ = 0.4$	$t_s^+ = 0.6$
0.0	1.5	1.5
0.1	1.1	1.3
0.2	0.7	1.1
0.3	0.3	0.8

* $b = 0.06$ cm; $D_j = 5 \cdot 10^{-6}$ cm²/s; $z_j = 1$.

donor and acceptor volumes and $b = 0.06$ cm, the required residence time for an analyte is about 0.5–1.5 min.

These findings are supported by experimental results described previously [19, 20]. Using a stagnant acceptor phase and a flowing donor (sample) phase in a home-made electrodialysis cell, the analyte recovery and enrichment were studied. Using the basic drug ephedrine, maximum recovery (and enrichment) was obtained when the residence time of the drug in the donor compartment was 1 min; i.e. with a donor compartment volume of 25 μ l (donor and acceptor compartment volume each 25 μ l; $b = 0.06$) the optimum donor flow rate was 25 μ l min⁻¹ [19]. Decreasing the residence time by increasing the donor flow rate to 50 or even 75 μ l min⁻¹ decreased the analyte recovery. Similar results were obtained for the basic herbicides paraquat and diquat and several sulphonic acids [20]. In this case the optimum donor flow rate in a modified electrodialysis block, with a donor compartment volume of 50 μ l (donor equals acceptor compartment volume; $b = 0.06$) was 50 μ l min⁻¹.

Computer Simulations

The transport processes during transfer of an analyte from a flowing donor to a stagnant acceptor solution are too complicated to allow an exact mathematical description; therefore a computer program has been developed to simulate these processes. Mass transport has been considered in two directions:

- in the axial direction of the donor and acceptor channels, it has been assumed that transport takes place only through laminar flow of the donor or acceptor solutions;
- in the direction perpendicular to the membranes, only mass transport by diffusion and migration has been considered.

A hybrid simulation model has been used, in which the mass distribution in the system is regarded as a continuous function in the axial direction, while in the direction perpendicular to the membranes the model is divided into discrete regions. The donor and acceptor compartments have been divided into slices parallel to the membranes. This simplified model has been chosen since a model with a similar precision which is discrete

Figure 3
Flow chart of computer simulation model for EDIST.

in two dimensions would require much more computer memory and calculation time.

The local flow rate in a slice is calculated from the parabolic flow profile assumed to exist in a channel. The local electric field strength in a slice can be calculated from the equations describing the ion-transport processes, presented in the previous sections, and the selected values of experimental parameters such as current, background electrolyte concentration and transport numbers in solutions and membranes.

It has been assumed that the field strength profile does not change during an EDIST experiment. In practice this would mean that the EDIST procedure should be started, and the steady-state conditions of the background electrolyte should be reached, before the analyte-containing solution is fed into the donor compartment. This has been normal practice in the experimental work.

The analyte concentration profile in each slice is described by a set of orthogonal hermite polynomials. These polynomials are especially suited to describe a peak-type profile. Deviations from a Gaussian peak shape are expressed in the higher polynomials. The

orthogonal coefficients of the polynomials can be calculated from the central moments of the concentration profile in the flow direction, and vice versa.

The mass transport during fixed time increments was calculated in cycles of two consecutive steps: (1) the transport of analyte by solvent flow in a slice was implemented in the simulation program by increasing the first central moment of the concentration profile in that slice with the product of the time increment and the local flow velocity; (2) the transport of analyte between slices by diffusion and migration was implemented by applying a finite difference method to the absolute moments of the concentration profiles in adjacent slices.

In between the two steps absolute and central moments were recalculated from each other. At fixed time intervals a 'detector signal' was calculated, representing the mass eluting from the end of the donor or acceptor compartment. To do this, the central moments for each slice were converted into hermite coefficients and the concentration in the slice at the end of the compartment was calculated from these. The end concentrations were multiplied by the local flow

velocity, and the detector signal was then obtained by integration of the slices over the donor or acceptor compartment. Figure 3 shows the flow chart of the total program. At the start of the simulation a number of parameters were defined:

- the precision of the simulation, which is determined by the time increment for each computation cycle, the number of slices for both channels, the number of hermite polynomials or moments to be included in the calculations and the sampling rate of the detector signal;
- the geometry (lengths and heights) of the channels;
- the flow velocities in the channels;
- the electric field profile across the channels;
- the mass transport resistance of the membrane separating the two channels;
- the diffusion coefficient and the ionic mobility of the analyte;
- the input concentration profile.

The program was tested by simulating the transport during laminar flow in a one-channel system and comparing the results with the Taylor-Aris equation [21] adapted for rectangular channels [22]. From this test the following conclusions were drawn:

1. the transport processes can be adequately described with the first six (0-5) moments or hermite polynomials. When more moments were included in the calculation, irregular results were obtained after a large number of computation cycles, probably due to the imprecision of the floating point variables;
2. with seven slices per channel the accuracy of the simulation is adequate. A higher number of slices did not alter the results significantly;
3. the results of the simulations for the position and variance of a peak matched the Taylor-Aris theory within 1 %.

Figure 4 shows the results of simulations of a flowing donor and a stagnant acceptor solution. The geometry of the cell in the simulation study was equal to that of the cell used in practice before [19, 20], with a channel height of 0.03 cm for both the donor and acceptor compartment. The analyte was assumed to have a diffusion coefficient of $5 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and a ionic mobility of $2 \cdot 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Mean field strengths (the field strength at the cut-off membrane) between 0 and 3 V cm^{-1} were used for the calculations. The dashed line indicates the maximum EF values which can be obtained, i.e. the values obtained when the analyte in the donor solution is transferred completely to the acceptor compartment.

Comparison with the curve obtained with conventional dialysis ($E = 0$) indicates that analyte enrichment is obtained in EDIST. With low mean field strengths of, e.g. 1 V cm^{-1} , a steady state situation, in which migration is balanced by diffusion, is reached. With a donor flow rate of 1 compartment volume per minute, and a field strength of $\geq 2 \text{ V cm}^{-1}$, no steady state was obtained within the defined time interval of 20 min and EF values of 6-10 were then obtained (Figure 4A).

Figure 4
EF vs. electro dialysis time plots by computer simulation, for different electric field strengths and two donor flow rates: (A) 1 and (B) 2 compartment volumes per minute. Electric field (V cm^{-1}) (a) 0, (b) 1.0, (c) 2.0 and (d) 3.0. Maximum EF values, (e).

If the donor flow is increased to 2 compartment volumes per minute (Figure 4B), higher EF values are obtained in the same time: with a mean electric field strength of 3 V cm^{-1} , the EF obtained after 5 min is increased from 3.5 to 5.5. However, although for the 2-fold higher flow also a steady state is not reached for high field strengths, analyte recovery is not complete under such conditions (see dashed line). Obviously, the residence time is too short (0.5 min) to allow complete transfer of the analyte from the donor to the acceptor compartment. These results are in fairly good agreement with the minimum residence times reported in Table II - for realistic values of t_s^* and t_m^* a residence time of about 1 min will generally be sufficient to achieve quantitative transfer of the analyte into the acceptor phase. The results of these computer simulations have been confirmed in practical experiments [19]. Using donor flow rates of $25 \mu\text{L min}^{-1}$ (approx. 1 compartment volume per minute) and high voltages (7.5 V and higher) quantitative recoveries were obtained with ephedrine as analyte, within a time window of 15 min of electro dialysis. Lower applied voltages

Figure 5
EF vs. electrodialysis time plots by computer simulation, for two electric field strengths and various donor flow rates: (A) 1 V cm^{-1} and (B) 2 V cm^{-1} . Flow rates: (a) 0.5, (b) 1 and (c) 1.5 compartment volumes per minute.

showed incomplete recovery, whereas increasing the donor flow rate from 25 to $50 \mu\text{l min}^{-1}$ quantitative recovery was observed for much shorter times only (up to about 5 min). Maximal EF values that were obtained with the used set-up and conditions were 20–23; under the conditions that the recovery should be quantitative EF values up to 10 could be obtained.

In Figure 5 the influence of the donor flow is shown more clearly. At a low (mean) electric field strength (1 V cm^{-1}), an increase of donor flow from 0.5 to 1.5 compartment volumes per minute has only a small influence. At an electric field strength of 2 V cm^{-1} , no steady state situation is reached within 20 min, but now a donor flow of 1 and 1.5 compartment volumes per minute certainly gives better results than a flow of 0.5 compartment volumes per minute.

Design Objectives and System Geometry

The use of EDIST as a sample treatment method for LC imposes certain conditions on the geometry of the electrodialysis (cell) block. The block consists of a set of spacers and membranes, placed between two electrode compartments; they contain the non-corrosive

electrodes. Channels in the spacers form the donor and acceptor compartments. These channels can have different configurations, e.g., straight, coiled or meander shaped. With respect to an on-line coupling of the block in an LC set-up, the latter two types of channel allow smaller block dimensions to be used with long channels.

If an electric field is applied, analytes with the proper charge will migrate from the donor compartment to the acceptor compartment. After EDIST the contents of the acceptor compartment will be transferred to an LC system. For quantitative analyte transfer the use of long channels of small width and height has some major advantages. A small channel width will allow proper support of the membranes so that deformation is prevented during solvent flow through the donor and/or acceptor compartments. A small channel height, i.e. a small b value, will allow the use of a short residence time of the analyte in the donor compartment (cf. Eq. (15)). However, if the channel height is too small, high maximum currents will be obtained (cf. Eq. (8)). Also sagging of the membranes may lead to relatively large and unexpected changes in the volumes of the two compartments and, even more so, in their ratio. In practice satisfactory results were obtained with a channel width of ca. 1 mm and a height of 0.25–0.3 mm.

As the EDIST block consists of a number of spacers and mechanically weak membranes, a pressure-resistant interface is needed for the on-line coupling to a high-pressure LC system. The transfer of the contents of the acceptor compartment to the chromatographic system can be performed via, e.g., a six-port switching valve containing an injection loop. Since the EDIST system is coupled to an LC system, the compounds of interest should be dissolved in a solution suitable for direct injection onto the analytical column. As the acceptor phase is an aqueous solution, transfer of the analyte-containing acceptor solution will actually in many cases lead to peak compression of the analyte on the top of the analytical column. In other words, no practical problems will be encountered, even if the volume of the acceptor solution is somewhat higher than the injection volumes of 20–100 μl normally used with LC on conventional-size (4.6 mm I.D.) columns.

Conclusions

The, mainly theoretical, considerations presented above indicate that sample pretreatment by means of EDIST is a viable approach for the selective separation of low molecular mass, ionogenic analytes from high molecular mass sample constituents. To a certain extent, the selectivity of the procedure can be adjusted by choosing the proper cut-off membrane and by regulating the pH of the donor (sample) solution (ionisable vs. ionic analytes).

Computer simulations using calculations based on the Nernst-Planck equation, show that considerable ana-

lyte enrichment can be obtained in an EDIST system using a flowing (sample) donor solution and a stagnant acceptor solution. About 10-fold enrichment can be obtained within 20 min under maximum-current conditions, the real result being dependent on the transport numbers of the background electrolyte (i.e., sample matrix) across the ion-exchange membranes, which form the outer boundaries of the donor and acceptor compartment. These results have been confirmed in experimental studies.

The speed of the EDIST procedure is in principle limited by the minimum residence time required for the analyte transfer from the donor to the acceptor compartment. Using channels of small height (e.g., 0.03 cm), residence times of about 1 min are required. Or, in other words, donor flow rates of about one donor volume per minute allow essentially quantitative recovery under maximum-current conditions. With typical donor and acceptor compartment volumes of 20–50 µl, this means that sample volumes of 0.2–1 ml can be treated in 10–20 min.

Further research will be devoted to the experimental optimisation of the EDIST system and further characterisation and application.

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