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Countercurrent Electrophoresis

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Summary

Historical development, principal operation, different ways of experimental realization, and typical examples of application of countercurrent electrophoresis are reviewed. The separation process is principally capable of being applied to all types of ions, as far as any difference is shown in their ionic behavior. Different types of columns can be adapted to varying amounts of substance from approximately 10^{-6} mole up to several moles (in the laboratory scale). The production of high purity components and the use of the column as an absolute ion filter are further possible applications.

INTRODUCTION

Countercurrent electrophoresis (CCEP) is easily carried out in the laboratory for the separation of ions (mainly in aqueous solution) based on their differences in migration velocity. All ions are in principle separable, as far as—under proper electrolyte conditions—they show any difference in their ionic behavior.

The principle is simple: a countercurrent flow of the solvent is directed against the ionic mixture migrating in the electric field. If the flow rate corresponds to the average velocity of the ions, their center of gravity will remain stationary, while the faster moving ions migrate against the stream and the slower will be gradually flushed back. In this way it is

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possible to let the mixture migrate—if necessary—over a very long distance relative to the solvent, reaching a high degree of separation.

A definite and homogeneous flow pattern over the entire cross section of the column is an important precondition for successful operation; at the same time the joule heat must be disposed of. These are the main experimental problems in realizing the stated principle. In comparison with electrophoretic methods using a limited distance for the electromigration (e.g., paper or column electrophoresis) CCEP presents three advantages which may be of importance for several applications: (1) A much larger amount of substance can be processed (in the laboratory up to about 1 mole for each run); (2) the process can be operated continuously; (3) a much higher degree of separation can be obtained. Furthermore, a CCEP column can be used as an absolute ion filter.

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HISTORICAL DEVELOPMENT OF CCEP

Brewer et al. (*1*) were the first to develop ionic migration as a continuous countercurrent process. They successfully separated isotope mixtures by ionic migration, the isotopes being those of potassium, chlorine, and copper. Figure 1 shows a typical cell as used for the enrichment of potassium isotopes. It is made of glass, and the central part is packed with sand. The lower and right-hand part of the cell is filled with KCl solution, and the cathode compartment is filled to the boundary B–B with HCl solution. The boundary between the HCl and KCl solutions remains stable while the current is flowing, provided that the condition

$$[\mathrm{HCl}]/[\mathrm{KCl}] = t_{\mathrm{H}^+}/t_{\mathrm{K}^+}$$

is satisfied (t = transport number). If the solution were stationary, the passage of 1 F would move the boundary in such a way that it passes over a volume of $t_{\mathrm{K}^+}/[\mathrm{KCl}]$ in the tube. To keep the boundary stationary, the same volume of solution must be introduced into the cathode compartment for every 1 F. The solution must also contain one equivalent of HCl. The condition that no over-all transport of potassium should take place is given by

$$E\bar{u}_+ + v_L = 0 \tag{1}$$

with

$$\bar{u}_+ = \gamma^{39}{}_{\mathrm{K}} u^{39}{}_{\mathrm{K}} + (1 - \gamma^{39}{}_{\mathrm{K}}) u^{41}{}_{\mathrm{K}}$$

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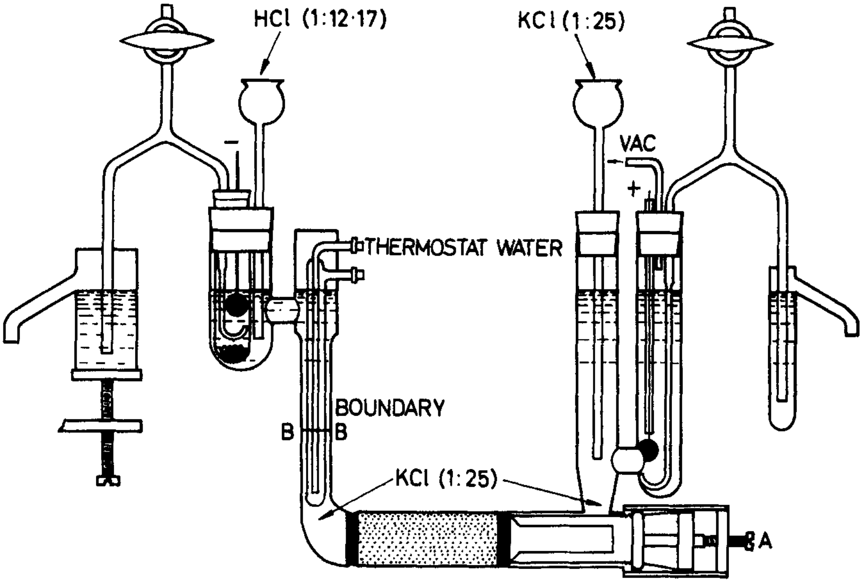

Fig. 1. Cell used for the enrichment of potassium isotopes, after Brewer and Madorsky (*1*). The anode compartment is continuously flushed with natural KCl solution. The feed of HCl solution into the cathode compartment is controlled in such a way that the boundary B–B remains constant.

where E (V cm^{-1}) = electric field strength, $\bar{u}_+$ (cm^2 V^{-1} sec^{-1}) = mean mobility of the potassium ions, v_L (cm sec^{-1}) = flow rate of the liquid in the separating column and $\gamma_{^{39}\mathrm{K}}$ = fraction of total K represented as ^{39}K. This condition would then be satisfied, and the flow rate (averaged over the cross section) would lie between the migration velocities of the two isotopes:

$$v_{(^{39}\mathrm{K})} > |v_L| > v_{(^{41}\mathrm{K})}$$

An attempt was made to control the process in this sense with the aid of remote sensing elements and an automatic control system.

However, the columns used by Brewer proved unreliable in continuous use owing to channel formation in the sand packing and to the ultimate formation of gas bubbles.

An important advance concerning this problem was made by Clusius, Ramirez, and Huber (*2*), who did not use a column packing and deliberately did not suppress convection, but used a large number of diaphragms to confine convection to directions perpendicular to the field direction. This leads to faster equalization of concentration within the electrolyte and good heat dissipation. At the same time channel formation and trouble due to gas bubbles are avoided. They also used a process control similar to that of Brewer et al. Martin et al. (*3*), who developed a countercurrent process independently of the American workers, carried out the electrolysis in packed columns between the anode and cathode compartments, which were in the form of containers at the ends of the column. However, the control of this process is more elaborate than that used by Brewer and Clusius.

Konstantinov et al. (*4*) as well as Preetz (*5*) report on processes similar to that of Brewer, but they need a less elaborate control mechanism. The early work of London (*6*) using capillary tubes should also be mentioned.

The necessary precision of the process control for satisfying condition (1) requires a considerable amount of equipment. This difficulty can be avoided by running CCEP as a self-stabilizing process (*7*).

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SELF-STABILIZING CCEP; PRINCIPAL OPERATION

Self-stabilizing countercurrent electrolysis can be most readily understood if the process is thought of as being divided into two steps. The first step comprises the mechanism that leads to a stationary distribution of the mixture as a whole in the separating column (all the ions in the mixture being assumed for the present time to migrate with the same velocity). The second step comprises the actual separation of the components within the stationary over-all distribution. The essential idea of this method is contained in the first step. This idea is that the required "equilibrium" between the electric transport of ions and entrainment by the solvent is no longer achieved by control of the liquid flow, but follows automatically under the given (but more or less arbitrary) operating conditions.

The principle is based on the fact that at a given current intensity the local field strength in the column, which determines the equilibrium ($Eu + v_L = 0$), depends on the local salt concentration. At the start of electrolysis this involves displacement of the salt concentration in the column, whereas it is necessary in the controlled countercurrent process to prevent any concentration displacements.

A scheme of a plant for the use in this process is shown in Fig. 2. The

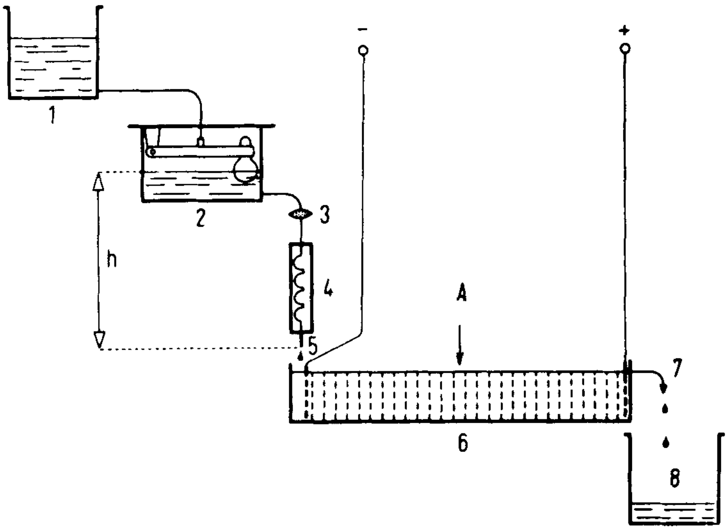

FIG. 2. Construction of an electrolytic separation plant for the self-stabilizing CCEP process (schematic). Explanations are given in the text.

main part of the apparatus, i.e., the separating column 6, is shown here as a trough divided into compartments by diaphragms. The shape and dimensions of the trough may be adapted to suit widely varying requirements and various forms, ranging from capillary tubes to troughs having a capacity of about 10 liter (which may also be connected to an end container). The operating conditions that have to be chosen in advance are the flow rate of the electrolyte solution, the electric field strength (or the electric current), and the temperature of the solution. Items 1 to 5 (storage vessel, constant-level intermediate tank, filter, thermostated tube, capillary) ensure that the electrolyte solution is supplied at a constant feed rate. This solution passes through the separating column in the longitudinal direction and then runs through an overflow 7 into a collector vessel 8, from which it can be returned to the storage vessel.

The electrodes (platinum gauze) produce an electric field whose direction and strength are so chosen that all the ions of the mixture in question (which are introduced into the column as a salt solution at an arbitrarily chosen point A) migrate countercurrent to the liquid toward the "upstream" end of the column, where they accumulate. (An eventual deposition of the ions on the electrode can be avoided by the use

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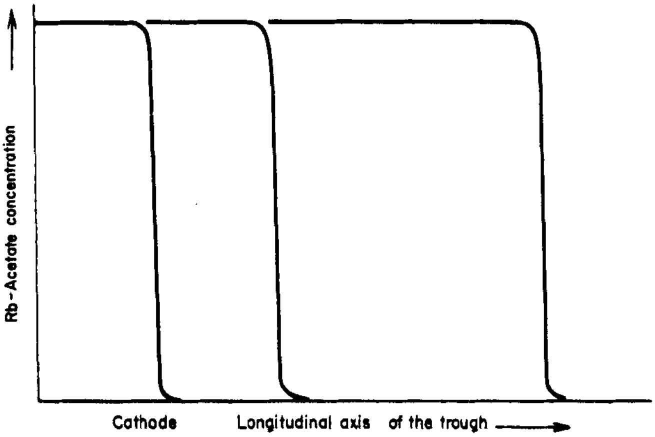

FIG. 3. Concentration distribution of rubidium acetate in the trough of the apparatus shown in Fig. 2 with addition of salt at various stages and at a given current intensity I. [$I = 1$ A at an electrolysis voltage of approximately 1000 V; transport number of Rb^+ in rubidium acetate solution = 0.66; feed rate of countercurrent liquid: $\dot{M} = 0.1$ cm^3 sec^{-1}, from which the stationary salt concentration (Eq. 3) is calculated to be $c_s = 0.07$ N, which is in fact observed.]

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of a protective electrolyte; see below.) During this migration of the mixture of ions, the condition $|E\bar{u}| > |v_L|$ is satisfied. If the introduction of the salt solution into the trough is continued, ions continue to accumulate at the "upstream" electrode, and the conductivity of the solution increases in this part of the column.* According to Ohm's law, the strength of the field at a given current density j depends only on the conductivity κ of the solution. If we assume for simplicity that the conductivity contribution of the electrolyte (acid, base, or a buffer mixture) dissolved in the countercurrent liquid is negligible in the salt sphere, an approximately reciprocal relationship exists between the field strength and the salt concentration c_s (Λ_s = equivalent conductivity of the salt):

$$E = j/\kappa \approx j/\Lambda_s c_s \tag{2}$$

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* In the separation of cations, the upstream electrode is the cathode. The mixture of cations is then at rest in relation to the separating column, while the anions migrate through the column with a velocity $v_- = Eu_- + v_L$. The principle of electric neutrality is always satisfied. To separate anions, one need only reverse the direction of the field; generally a different countercurrent electrolyte is used.

Thus, as further salt ions migrate, the field strength decreases until the salt concentration reaches its maximum value under the experimental conditions:

$$c_s = -It/F\dot{M}\ (\text{mole cm}^{-3}) \qquad (3)$$

where I (A) = current, t = transport number of the mixture of ions in question, F = Faraday constant, and $\dot{M}$ ($\text{cm}^3\ \text{sec}^{-1}$) = feed rate of countercurrent solution.

Further added ions do not increase the concentration, but accumulate in compartments situated farther away from the electrode (a right-angled distribution is obtained for the salt concentration, see Fig. 3). As can be seen from Eq. (3), arbitrary values of c_s can be obtained by an appropriate choice of the ratio $I/\dot{M}$. It can also be seen that the concentration distribution of the salt is stable, provided that the operating conditions are kept constant. Thus, if a small local disturbance (increase or decrease) of the salt concentration occurred, the field strength at this point would immediately change, and ions would mi-

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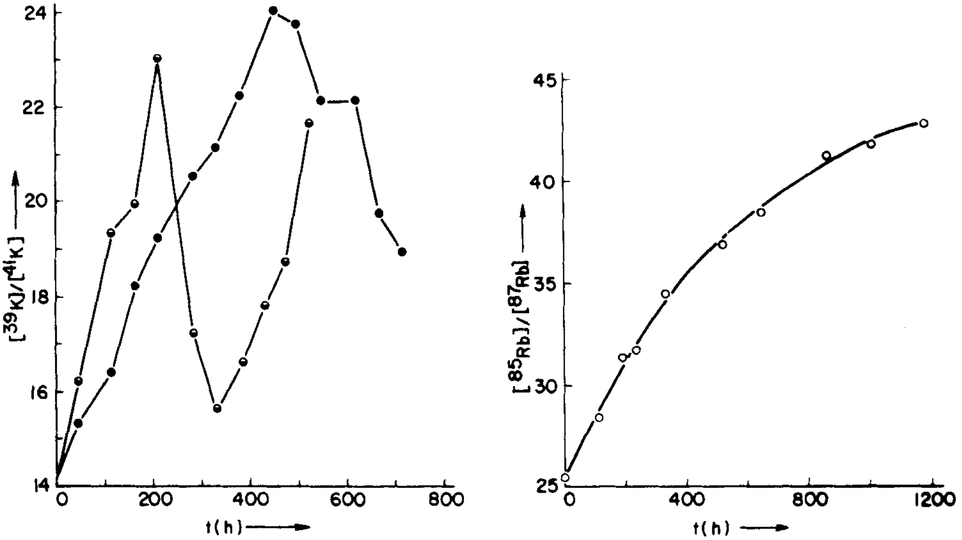

FIG. 4. Isotope ratio at the end of the column (cathode compartment) as a function of time. Left diagram: Example of the separation of potassium by Brewer with the cell shown in Fig. 1. The discontinuity is due to disturbances of the countercurrent equilibrium. Right diagram: Example of the separation of rubidium in the apparatus shown in Fig. 2.

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grate away from or toward this point to compensate for the disturbance. The effectiveness of this self-stabilization mechanism can be very clearly seen from Fig. 4, which shows a comparison of the course of enrichment at the column end with time in the Brewer and in the self-stabilizing methods.

The apparatus required for self-stabilizing countercurrent electrophoresis is very simple, since no control equipment is required, and the plant consequently no longer contains any moving parts. Numerous continuous tests extending over periods of weeks and months have shown that this process is very reliable.

THEORETICAL CONSIDERATIONS

The generally known formalism of separation processes can also be applied to CCEP. Consider a binary mixture of ions (Components 1 and 2) to be separated by ionic migration. The ionic mobilities may be u_1 and u_2, their relative difference assumed to be small. Then the *elementary effect* of this separation process is

$$u_1/u_2 = 1 + \epsilon \tag{4}$$

Since in most cases ϵ will be much smaller than 1,

$$\epsilon = (u_1 - u_2)/u_2 \approx \Delta u/\bar{u}$$

where $\bar{u}$ is the mean mobility of the mixture.

The *separation factor* Q, obtained in the stationary state of the process, is then given as the amplification of the elementary effect by the number of theoretical plates:

$$Q = (1 + \epsilon)^{nx} \tag{5}$$

where n (cm^{-1}) is the *density of theoretical plates* of the column, and x (cm) the length of that part of the column which is occupied by the stationary distribution of the ionic mixture. Quantity n depends on process parameters as well as on the quality of the column:

$$n = v_L/D_{eff} \tag{6}$$

where D_{eff} (cm^2/sec) is the effective diffusion coefficient of the ions in the solution under process conditions. This remixing effect has two major contributions: (a) the parabolic velocity pattern of flowing liquids and (b) thermal convection in the liquid, whereas molecular

TABLE 1

Properties of Different Types of CCEP Columns[a]

Type of column	Cross section q (cm^2)	Specific cooling power N (watt cm^{-3})	$qN^{1/2}$	Number of theoretical plates (approx) (cm^{-1})
Trough	10–1000	1–2	10–1400	10
Capillary tube				
Inner diameter				
0.5 mm	0.20×10^{-2}	730 (glass)	0.05	35
1.0 mm	0.78×10^{-2}	260 (glass)	0.13	25
Slit chamber				
Width				
0.5 mm	0.25	80 (glass)	2.2	30
2.0 mm	1	100 (ceramics)	10	

[a] $qN^{1/2}$ characterizes the separation power (see Eq. 8). Outer diameter of the capillary tubes assumed to be 5 mm, thickness of slit chamber walls 2 mm. The figures for the specific cooling power were obtained by allowing a temperature difference of $\Delta T = 50°$ between electrolyte solution and cooling water.

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processes are negligibly small. In CCEP processes as described here D_{eff} is generally of the order of 10^{-4} cm^2/sec.

A measure for the *separation power* of a column is the attainable electric transport

$$T_{el} = I/F \qquad (\text{moles sec}^{-1}) \tag{7}$$

where I (A) is the electric current passing through the column, and F Faraday's constant. A certain transport can be obtained in different ways: by applying a high electric field strength to dilute solutions or a moderate one in more concentrated solution. The limiting factor is generally the specific cooling power of the column which, inserted into Eq. (7), gives the maximum electric transport

$$T_{\max} = (q/F)(N\kappa)^{1/2} \qquad (\text{moles sec}^{-1}) \tag{8}$$

where q (cm^2) is the cross section of the column, N (W/cm^3) the specific cooling power of the column, and κ [ohm^{-1} cm^{-1}] the specific conductivity of the solution. n, q, and N characterize the different types of CCEP columns (cf. Table 1).

The course of enrichment at the column ends, with time, depends on the process parameters and is well known for separation processes in general (*8*). For a closed process (no withdrawal of product during the process) using a column without compartments at the ends, the characteristic time for approaching the stationary state is

$$t = x^2/4\, D_{eff} \tag{9}$$

For a column working between containers, the initial slope of enrichment for the product with time (binary mixture; mole fraction of components being γ and $1 - \gamma$) is

$$\frac{\partial}{\partial t} \ln\left(\frac{\gamma}{1 - \gamma}\right) = \pm \frac{\dot{M}}{V}\frac{\Delta u}{u} \tag{10}$$

where $\dot{M}$ ($cm^3\ sec^{-1}$) is the feed rate of countercurrent solution, and V (cm^3) the volume of end container. Equation (11) is a good approximation for practical use to calculate the *dependence* of the degree *of enrichment on the withdrawal rate of product* concerning the following procedure (*9*):

The column is working between two compartments. By first running a closed process, the course of enrichment with time (see, e.g., Fig. 4, right diagram) can be observed, which allows the determination of $\partial\gamma/\partial \ln t$ (t = time). Under constant process parameters (flow rate of countercurrent solution, temperature, electric current or applied potential difference, respectively) this value is practically constant over long periods of time (neglecting the very beginning of the process and the final approximation to the stationary state). Then follows

$$P(\gamma') \approx \frac{V(\partial\gamma/\partial \ln t)_{t'}}{[\gamma(t) - \gamma(0)]t'} \qquad (cm^3\ sec^{-1}) \tag{11}$$

where P ($cm^3\ sec^{-1}$) is the withdrawal rate of product solution, giving a mole fraction γ' of the enriched component in the substracted product, and t' the time needed in the closed process to reach this degree of enrichment; $\gamma(t') = \gamma'$.

Finally, it should be mentioned that any difference in the ionic migration of two different species (which is the precondition for any separation by CCEP) can have different origins. Differences in size, mass, or configuration are the primary causes for different kinetic properties (mobilities); but different behaviors in chemical equilibria (such as dissociation or complex formation) can also become very important as a

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basis for separation by CCEP (*10*). A very simple model case would be the dissociation of n, n electrolytes, where, e.g., the cations consist of two different Species 1 and 2. The different dissociation constants are K_1 and K_2, and they result in differences in the time-average charge numbers $\bar{z}_1$ and $\bar{z}_2$ of the two components. It is easily shown that under optimum conditions

$$\Delta\bar{z}/\bar{z} = \tfrac{1}{2}\Delta K/\bar{K} \tag{12}$$

and that this maximum is reached when the degree of dissociation is 0.5. In the general case of n, m electrolytes the relation (12) is more complicated. It has been found in many cases that the relative differences in ionic migration caused by these equilibrium effects exceed the pure kinetic effects in the mobility of the free ions by about a factor of 10. It can therefore be most useful to find the optimum electrolyte conditions for a given separation problem.

A general theoretical treatise on the stationary state of CCEP is given by Gaus (*11*).

TYPES OF COLUMNS

1. Troughs

For diluted solutions (up to about 0.1 N) the most common and adequate type of column is the *trough*. Two types of construction have been approved.

(a) *Filter-press principle.* Diaphragms and U-shaped rubber seals, made from chemically resistant rubber sheets, are pressed together in alternating sequence. Often used dimensions: diaphragms, made from 2 mm acryl sheets, 100 × 100 mm^2 in size and with an opening of about 40 mm diameter. The openings are covered with fine-pore nylon gauze (pore width about 25 μm). Distance between diaphragms (equal to compartment width) 6–7 mm, each compartment containing a U-shaped cooling tube of glass, which surrounds the opening of the diaphragms. 60–80 diaphragms, giving a total length of 50–70 cm. Liquid capacity of approximately 2 liters (depending on the filling level).

The same principle was used for troughs of up to 500 cm^2 cross section (compartment width, 15–20 mm), using diaphragms in the form of a rectangular triangle.

(b) *Slide principle.* Shape of cross section: rectangular triangle. All parts are made from acryl sheets. Grooves are milled into the inner sur-

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TABLE 2

Application of CCEP to Various Separation Problems (Selected Examples)

Separation problem (components of mixture)	Column		Result (Q = separation factor)	Remarks	Ref.
	Type	Dimensions (l = length, q = cross section, d = diameter of tube)			
Isotope separation (^{39}K–^{41}K)	Tube with sand packing	$l = 10$ cm $d = 1.4$ cm	$Q = 1.69$	Cf. Fig. 1 of this paper	Brewer et al., 1947 (*1*)
Isotope separation (^{6}Li–^{7}Li)	Trough	$l = 49$ cm $q = 34$ cm^2	$Q = 3.58$	Batch process 5 g Li-acetate	Thiemann and Wagener, 1963 (*14*)
Isotope separation (^{85}Rb–^{87}Rb)	Trough	$l = 50$ cm $q = 34$ cm^2	(a) $Q = 3.3$ (b) $Q = 1.37$	(a) Batch process 8 g Rb-acetate (b) Continuous process; products: 3 g Rb with 30.8% ^{87}Rb, 3 g Rb with 24.5% ^{87}Rb	Wagener, 1967 (*9*)
Mixed-ligand complexes ($IrCl_6^{2-}$ . . . $IrBr_6^{2-}$)	Capillary tube	$d = 0.8$ mm	Complete separation		Preetz and Pfeifer, 1967 (*5*)
Quantitative extraction (^{7}Be from rain water)	Trough	$l = 22$ cm $q = 500$ cm^2	Quantitative preparation	Turnover = 500 liters per day at 250 W power consumption	Reinert, Thiemann, and Wagener, 1969 (*15*)
Isotope separation (^{12}C–^{14}C)	Trough	$l = 24$ cm $q = 25$ cm^2	$Q = 2.64$	Ionic species: formiate	Thiemann, 1969 (*14*)

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Preparation of high purity calcium (Ca, Na, Sr, Ba, Mn, . . .)	Slit chamber	$l = 15$ cm	Highest purity	Purity control by activation analysis	Bilal, 1969 (*17*)
Rare earths (Sm, Nd, Pr, Ce, La)	Slit chamber with diaphragms	$l = 80$ cm width = 2 cm	Complete separation	Cf. Figs. 7 and 8 of this paper	Bilal and Metscher, 1970 (*19*)
Radiochemical nuclide generator (^{131}Cs–^{131}Ba and other radioactive nuclides)	Slit chamber	$l = 10$ cm	Radiochemically pure ^{131}Cs	Controlled by γ-spectrometry	Bilal, 1970 (*20*)

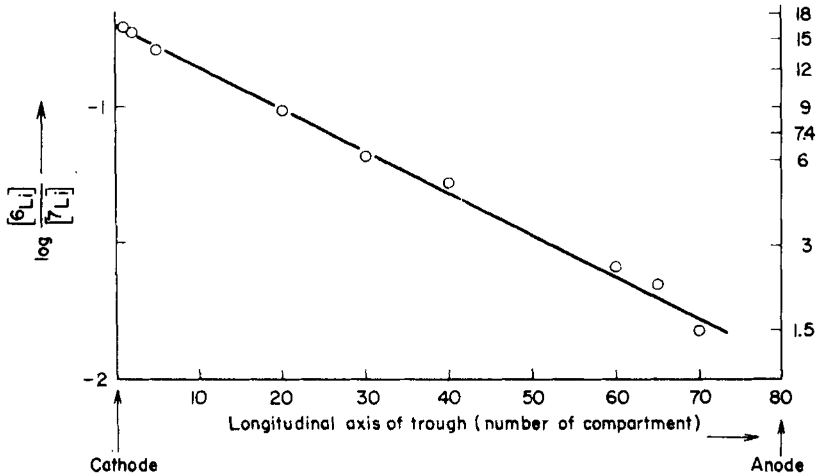

Fig. 5. Distribution of lithium isotopes (natural mixture: 7.4 mole-% of ^{6}Li) along the separation column in the final separation state (apparatus as shown in Fig. 2). The separation is performed over the entire length of the column. (Trough consisting of 80 compartments and constructed by the filter-press principle; total length, 65 cm; volume, 1.2 liter; pore width of nylon gauze, 53 μ.)

face of the side parts, their width equal to the thickness of the diaphragms, and at a distance of the compartment width. The advantage of this type is that there are no chemical problems with rubber seals, but the construction requires more mechanical precision in order to have the diaphragm slides tight in the grooves and to prevent parasitic channelling. For details of construction see Ref. *12*.

The most important parts of the troughs are the diaphragms. Their function is to give as true an approximation as possible to the ideal laminar flow pattern with uniform velocity over the whole cross section. Precise uniform pore size of the gauze is important, but the principally parabolic flow pattern in each hole is the reason that the number of theoretical plates does not depend on the mean flow rate v_L in that way as expected in Eq. (6). If we increase the liquid flow through the column, D_{eff} will also be increased, so that the main result of increasing the flow rate (and the electric current at the same time) is an increase in the enrichment kinetics rather than of the steady state concentration gradients. Nylon gauze of about 25 μm pore size gives about 10–15 theoretical plates per diaphragm, with small dependence on the flow rate. The

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properties of different types of diaphragms have systematically been studied by Freyer (*13*).

Troughs of different sizes and lengths were used for various problems (*14*); see also Table 2. One example of a separation problem is given in Fig. 5. It should be mentioned that a CCEP column is also an excellent ion filter, e.g., the complete extraction and quantitative preparation of very small amounts of ions from very large amounts of water can easily be managed by CCEP. The preparation of ^{7}Be from large amounts of rain water is one example (*15*). A turnover of 1 cbm of water per day requires a column of about 500 cm^2 cross section and about 0.5 kW of electric power.

2. Capillary Tubes

To find favorable separation conditions for very similar components often requires more concentrated electrolyte solutions, e.g., of the order

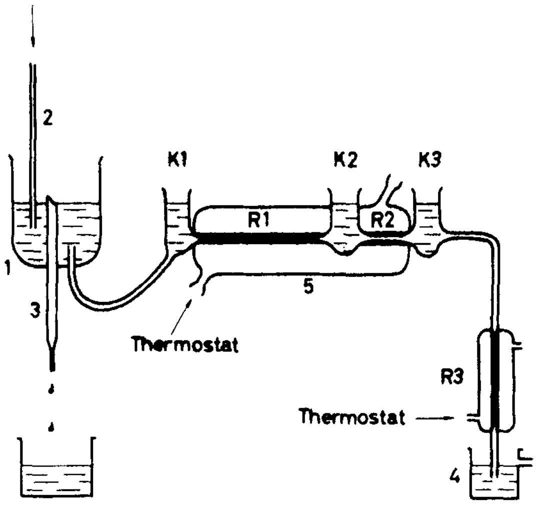

FIG. 6. Cell for self-stabilizing CCEP using a capillary tube as applied to problems of nuclear chemistry (*16*). The tube R1 is working between the chambers K1 and K2. The stationary distribution of the ionic mixture extends from K1 over R1 and K2 and ends anywhere in the capillary tube R2. The electrodes are in K1 and K3. Items 1, 2, 3, 4, and capillary R3 (with the highest flow resistance in the system) give a constant flow rate. (Inner diameter of R1, 0.5 mm, 5 cm long; R2, 1.6 mm diameter, 2 cm long; about 1 ml solution in K1, K2, and K3; flow rate about 1 ml/hr; applied voltage 1000 V, giving 3 to 5 mA.)

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of 1 N or more. The application of high electric field strengths under these conditions is only possible if the column has a very good specific cooling power (W/ml of solution). This can only be achieved in capillary spaces. The simplest realization is the *capillary tube*. Figure 6 gives an example. This type of column is, of course, only suitable for small amounts of substance, e.g., for analytical or radiochemical applications ($<1/100$ mole of product); but capillary tubes have a high number of theoretical plates (e.g., at 0.7 mm diameter about 30–35 theoretical plates per cm), so that high degrees of enrichment can be achieved in one stage.

3. Capillary Chambers

An almost ideal combination of the advantages of the trough and the capillary tube is the vertical *slit chamber* (*17*). At a width of about

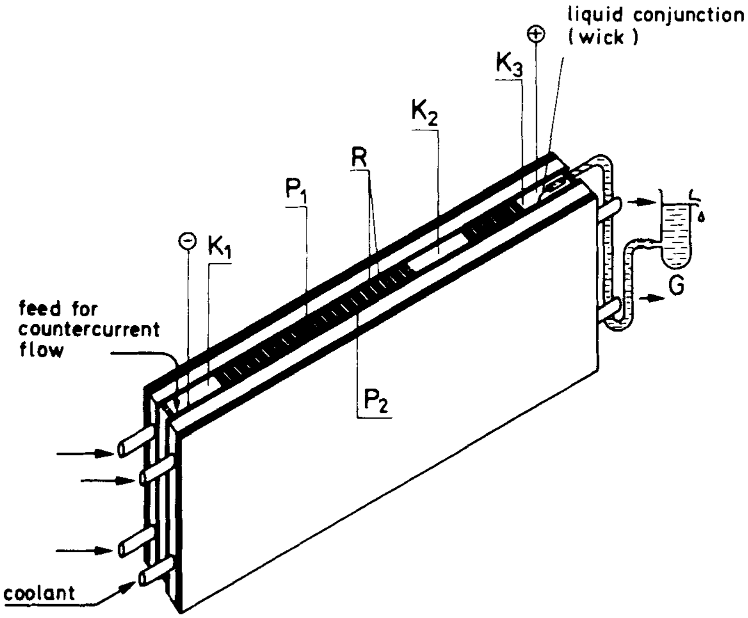

FIG. 7. Vertical slit chamber with diaphragms as used by Bilal (*18*). Two double-walled plates of oxide ceramics (flushed with cooling water) form the vertical chamber. The diaphragms are sitting in the grooves. The electrodes are in the compartments K1 and K3; K2 being an intermediate compartment. (Total length of column is 80 cm with a width of 2 mm; 380 diaphragms, filling height approximately 5 cm; flow rate 6 ml/hr; 200 to 300 mA at 3000 V.)

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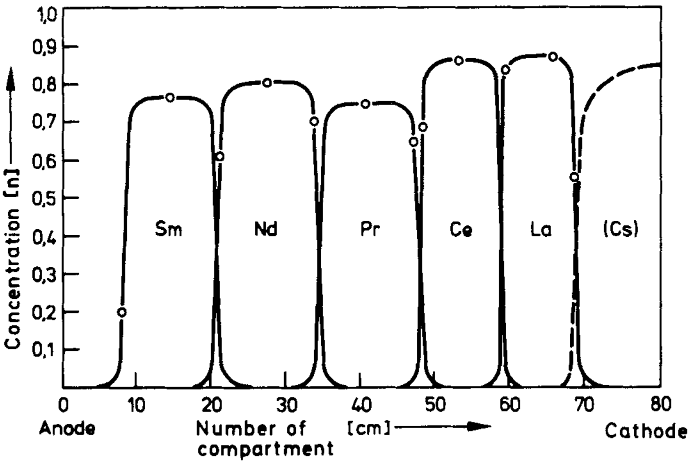

FIG. 8. Separation of lanthanides using the apparatus shown in Fig. 7. Final state of the process. (Approximately 7 g of lanthanides, 0.8 *N* solution of acetate; the salt distribution extends over 65 cm of the column.) After 4 days of operation the purity of all components was tested by activation analysis. No contamination by any other component could be detected (*19*).

(0.3–1) mm and a height between 5 and 10 cm it combines excellent cooling properties and the easy stabilization of the liquid flow by capillarity with a comparatively large cross section. Furthermore (and different than in the capillary tubes), the formation of gas bubbles does not disturb the process. The walls are made of glass or (for better thermal conductivity) of oxide ceramics. The construction, of course, needs some care and mechanical precision. Chambers with a width greater than 1 mm require a lower degree of precision, although in this case again it is advisable to use diaphragms in order to adjust the flow pattern. For construction details see Fig. 7. Figure 8 gives an example of application. In Table 1 the properties of the different types of CCEP columns can be compared.

PRINCIPAL APPLICATIONS AND LIMITATIONS OF CCEP

(1) *Amount of substance* processable by CCEP: lower limit about 10^{-6} mole (using a capillary tube). On the other hand, there is not a definite upper limit because the cross section of the trough can be increased as necessary, or two identical troughs may be used in parallel.

(2) *Types of processes.* For binary mixtures the process can be run *continuously*, feeding fresh solution into the center of the column and, at the same rate, separating the products from the ends. Feeding and separating can be carried out discontinuously (e.g., every 24 hr). If there are more than two components to be separated, the *batch process* must be used (see, e.g., Fig. 8).

Isolation or *enrichment* of the *fastest or slowest* moving *component* from any mixture of ions requires an end container of sufficient capacity for

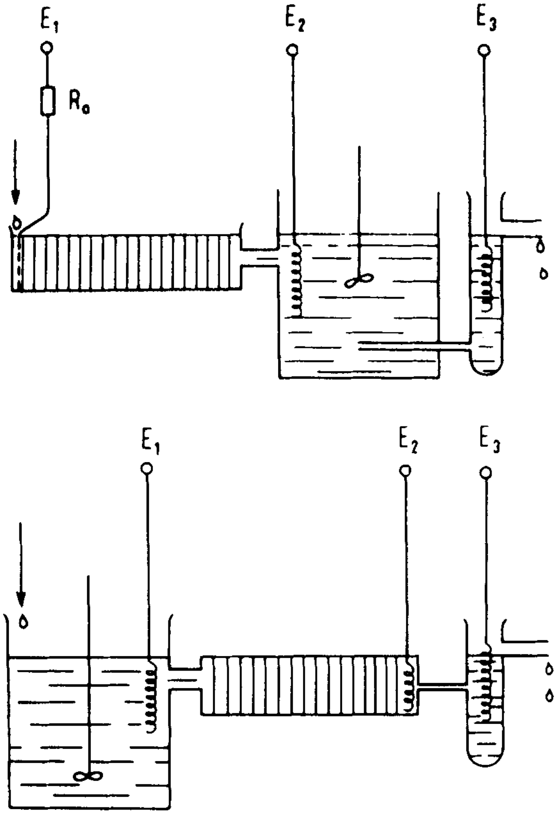

FIG. 9. Top: Apparatus for the enrichment of the fastest-migrating component from a mixture. Reservoir vessel at the overflow end of the column. Ohmic resistance R_a is necessary for self-stabilization of the process [cf. Wagener (7; 1964)]. Bottom: Apparatus for the enrichment of the slowest component. Reservoir vessel at the feed end for the counterflow.

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the mixture. It is placed before or after the column, respectively (referring to the direction of the liquid flow; see Fig. 9). The process can be run continuously. Using the CCEP column as an *absolute ion filter* has already been mentioned. If the liquid flow is going from the cathode to the anode, *all* cations (except H^+) will be kept in the column (provided the electric field strength has been chosen high enough). After changing the flow direction (or the polarity of the electrodes) the same holds for anions (except OH^-). Using two columns in sequence and with different direction of the electric field, all types of ions present in the entering water will be extracted.

A special application of the batch process is the *production of high purity components*. Since in the stationary state of the process all ions present in the column will be arranged in the sequence of their mobilities, it follows that in the range of one special component no other component (with different mobility) can be present. If, therefore, we obtain a component of interest partly from the center of its steady-state distribution in the column, we usually will obtain it of highest purity. The success of this procedure has been examined in several cases by activation analysis (*18, 20*).

(3) *Types of ions* suitable for the CCEP process. For separation processes all elementary and molecular ions are suitable as long as they give (under proper conditions) a sufficient contribution to the total conductivity of the solution. Such a contribution is necessary for obtaining a self-stabilizing process. (For ion filters, of course, this is not necessary.)

Ions which would undergo a chemical reaction at the electrode (e.g., deposition) can be prevented from any contact by using a protective electrolyte. (In this connection only one electrode is of interest, and it is at the end of the column where the counterflow enters.) In the case of electrode-sensitive cations, e.g., potassium can be used as the protective electrolyte. Since K^+ is the fastest moving cation, all other will be arranged behind the potassium distribution. In the case of anions, sulfate or nitrate may be used.

If necessary, buffer solutions can be used for the counterflow (e.g., for organic ions). Continuous flushing of the electrode compartment (or any other compartment in between) may accomplish the same result.

Typical examples of different applications of CCEP are listed in Table 2.

(4) *Other competing methods*. For a critical judgment we have to

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compare the properties and possibilities of CCEP with other competing methods. The different types of electrophoresis [without countercurrent flow; cf. also displacement electrophoresis (*23*)], ion exchange, exchange electrolysis (*21*), and ionic migration in fused salts (which is not reviewed here) (*22*) are the main competing methods based on ionic properties.

Other methods, such as liquid–liquid extraction, have to be taken into account. No method will be the best in general, so selection depends on the special aspects of each case. Ionic migration in fused salts is a method almost exclusively designed for isotope separation. The application of exchange electrolysis is limited to metals soluble in other liquid metals. The separation of components giving a high elementary effect in ionic migration (relative difference larger than 10%) may be carried out easier by conventional zone electrophoresis rather than by CCEP if the amount of substance is small enough.

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