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Abstract

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RAPID MICROANALYSIS OF CHEMICAL ELEMENTS BY THE MOVING-BOUNDARY METHOD

In analytical chemistry there are many different directions for the development of quantitative and qualitative methods of analysis. The present work opens up one of the new directions in this field—rapid microanalysis by the moving-boundary method. The moving-boundary method has been known for a long time, since the work of Lodge ([1]), who attempted to use it to determine the absolute velocities of ion motion. Subsequently this method was applied to determining ion transference numbers ([2,3]), to the separation of chemical elements ([4,5]), and to the separation of isotopes ([6,7]). Longsworth ([8]) attempted to use this method for quantitative analysis. The attempt proved unsuccessful because in his experiments he used Tiselius' apparatus ([9]), which is unsuitable for separating mixtures of electrolytes under conditions of hydrodynamic counterflow.

The task of the present work was to investigate the moving-boundary method for its application in analytical chemistry. The conditions for the stability of the boundary between electrolytes in the moving-boundary method were formulated by Uezem and Kolrausch ([10]) and are as follows: 1) the solution of the electrolyte with the more mobile ions is located ahead of the boundary in the direction of motion; 2) the ratio of the concentrations of the electrolytes on the two sides of the boundary is equal to the ratio of the transference numbers of the common ions

$$\frac{C_1}{n_1} = \frac{C_2}{n_2}, \tag{1}$$

where C_1, C_2 are the concentrations of the electrolytes on the two sides of the boundary, in g-equiv/l, and n_1, n_2 are the transference numbers of the common ions of these electrolytes. Relation (1) under conditions of hydrodynamic counterflow is established automatically. It is not necessary to prescribe the concentrations initially. The boundary between solutions, formed under the action of the electric field, is not a geometrical plane because of diffusion. The ions of the electrolytes forming the boundary will be present along the entire length of the separation tube.

The ratio of concentrations along the length of the separation tube for two electrolytes whose common ions are of the same valence may be determined from the relation:

Fig. 1. Change in the relative concentrations of electrolytes at the boundary

Figure 1: Fig. 1. Change in the relative concentrations of electrolytes at the boundary

$$\frac{C_2}{C_1} = be^{-\frac{u_1-u_2}{u_1}\frac{e}{kT}\frac{vx}{u_2}}, \tag{2}$$

where b is a constant, u_1, u_2 are the mobilities of the common ions, k is Boltzmann' s constant, T is the absolute temperature, e is the electron charge, v is the velocity of motion of the boundary, and x is the distance from the origin of coordinates.

Relation (2) is obtained by solving the equations of ion motion.

If as the origin of coordinates one takes the point where $x = 0$ and $\frac{C_2}{C_1} = 1$, then $b = 1$, and the relative concentrations of the electrolytes along the length of the tube will be:

$$\frac{C_2}{C_1 + C_2} = \frac{1}{1 + e^{Ax}}, \tag{3}$$

$$\frac{C_1}{C_1 + C_2} = \frac{e^{Ax}}{1 + e^{Ax}}, \tag{4}$$

where

$$A = \frac{u_1 - u_2}{u_1}\frac{e}{kT}\frac{v}{u_2}.$$

The change in the relative concentrations of the electrolytes is clearly shown in Fig. 1. On the ordinate axis are plotted the relative concentrations of the electrolytes, and on the abscissa axis the dimensionless quantity $y = Ax$. It is seen from the figure that the relative concentrations of the electrolytes change only near $y = 0$ and $x = 0$, over the interval $\Delta y = 4$. Such a change in concentration can occur only at the boundary of the electrolytes. To characterize the structure of the boundary, we introduce the quantity $\Delta x = 4/A$, which is a parameter characterizing the width of the boundary. In the case of compensation of boundary motion by counterflow, the solvent velocity profile also affects the boundary width. It is known that hydrodynamic flow has a parabolic profile, whereas the velocity profile of ions under the action of an electric field is practically flat over the entire cross section of the separating tube. This leads to convective flows that cause mixing of the mixture being separated. Averaged compensation of ion motion by counterflow is equivalent to an increase in the diffusion coefficient and leads to an increase in the boundary width.

Fig. 1. Change in the relative concentrations of electrolytes at the boundary

From consideration of ion motion, the following relation can be obtained for the diffusion coefficient that takes into account hydrodynamic flow for separating tubes of circular cross section:

$$D_{\text{eq}} = D\left(1 + \frac{V^2}{128}\frac{v^2 d^2}{D^2}\right), \tag{5}$$

where D_{eq} is the equivalent diffusion coefficient, D is the ion diffusion coefficient, v is the velocity of ion motion in the electric field, and d is the diameter of the separating tube.

The equivalent diffusion coefficient must be taken into account in designing and selecting the operating mode of the separating tube.

In addition to the factors listed, the boundary width may be affected by the temperature distribution over the cross section of the separating tube. The temperature at the center of the tube will differ from the temperature at the tube walls. A quantitative estimate of the temperature distribution over the transverse cross section of the tube can be made using the formula:

$$\Delta T(r) = \frac{1}{4}\frac{W r_0^2}{\lambda}\left(1 - \frac{r^2}{r_0^2}\right), \tag{6}$$

where W is the power released by the current per unit volume of electrolyte, λ is the thermal-conductivity coefficient, r is the distance from the center of the tube, and r_0 is the internal radius of the tube.

Instead of W, let us introduce the quantity $We = W\pi r_0^2$—the power released per unit length of the tube; then the maximum temperature difference between the periphery and the center can be calculated by the formula:

$$\Delta T = \frac{We}{4\pi\lambda}. \tag{7}$$

Let us consider what the values of the factors affecting the structure of the boundary will be if it is formed under the action of a strong electric field (20–50 V/cm) in a capillary of diameter 0.1 mm with a wall thickness of 0.05 mm under conditions of hydrodynamic counterflow. The equivalent diffusion coefficient under these conditions will differ only slightly from the true diffusion coefficient.

The boundary width, taking into account hydrodynamic flow, will be of the order of

0.2 mm. The temperature difference between the center of the capillary and the periphery will be 1°C. Such a temperature difference will not change the width of the boundary.

Fig. 2

Figure 2: Fig. 2

The formation of a boundary in capillaries in strong electric fields eliminates the requirement of "gravitational stability," imposed by the moving-boundary method prior to the present investigation on tubes not filled with a disperse phase: paper, glass powder, agar-agar,

Fig. 2. Diffraction pattern observed on a screen after complete separation of a solution containing the ions K^+, Na^+, Ca^{2+}, Mg^{2+}, Th^{4+}, Al^{3+}, Fe^{3+}, UO_2^+, Zn^{2+}, In^{3+}; HCl and $CdCl_2$ are indicator electrolytes

silica gel, etc. A sharp boundary is obtained irrespective of the ratio of the densities of the solutions forming it (see Fig. 2).

Separation of a mixture of electrolytes in the above-mentioned regime opens up great possibilities for rapid quantitative and qualitative microanalysis. If one takes a capillary 0.1 mm in diameter, then, at a concentration of the leading indicator electrolyte sufficient for recording the boundaries, only 10^{-5}–10^{-6} g of substance will be required in order to obtain a total length of the columns of the separated electrolytes of not less than 10 cm. This is quite sufficient for quantitative analysis of a multicomponent mixture.

The amount of any element entering into the mixture taken for separation can be calculated from relation (1) and from the lengths of the columns of the separated components. The numerical value of relation (1), needed for calculating the results of the analysis, is determined beforehand for all ions being analyzed, under the conditions of the analysis, using standard mixtures.

The accuracy of the analysis with a uniform cross section of the separating tube will be determined mainly by the accuracy with which the lengths of the columns are measured. The length of a column of pure electrolyte cannot be measured with an accuracy exceeding the width of the boundary. It is natural, therefore, that the accuracy of analysis for a larger percentage content will be higher than for a smaller one. As the amount of mixture taken for separation is increased, the accuracy of the analysis will improve. The sensitivity of the analysis is also determined by the width of the boundary.

The amount of substance contained in a capillary 0.1 mm in diameter, in an electrolyte column equal to the width of the boundary, will be determined by the concentration of the leading indicator electrolyte and by the atomic number of the element in the periodic system, and will vary as these change. For most elements this amount is 10^{-7}–10^{-8} g, and for some elements it can be brought down to 10^{-9} g. The time of analysis is deter-

is determined by the relative difference in the mobilities of the ions, the magnitude of the electric field, and the amount of mixture taken for analysis, and may range from several minutes to several hours.

Fig. 3. Schematic of the apparatus: A —light source, —lens, —diaphragm, —capillary, —screen, —vessels with indicator electrolytes (HCl and $CdCl_2$), —glass filter No. 2, —platinum electrodes

Figure 3: Fig. 3. Schematic of the apparatus: A —light source, —lens, —diaphragm, —capillary, —screen, —vessels with indicator electrolytes (HCl and $CdCl_2$), —glass filter No. 2, —platinum electrodes

The preparation of capillaries presents no particular difficulty and can be carried out with an ordinary gas burner.

Registration of the boundaries between electrolytes in the moving-boundary method may be carried out by various methods based on differences in the refractive indices, specific resistances, and temperatures of the separated electrolytes. The most accurate is the optical method of boundary registration, based on the difference in the refractive indices of the electrolytes. The existing optical arrangements for recording boundaries in the moving-boundary method are unsuitable for capillaries with a diameter of 0.1 mm.

Fig. 3. Schematic of the apparatus: **A** —light source, —lens, —diaphragm, —capillary, —screen, —vessels with indicator electrolytes (HCl and $CdCl_2$), —glass filter No. 2, —platinum electrodes.

For recording the boundaries between electrolytes we used a diffraction pattern obtained on a screen placed behind the capillary, with the capillary illuminated by a narrow parallel beam of light. A photograph of the pattern observed on the screen in the case of separation of a mixture containing ten components is given in Fig. 2. Solutions of HCl and $CdCl_2$ are the indicator electrolytes.

Qualitative analysis of a mixture is possible, when the order of motion of the ions is known, from the pattern observed on the screen.

For analytical purposes the authors designed an apparatus, the schematic of which is given in Fig. 3, studied the order of motion of the cations Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Tl^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, $UO_2{}^{2+}$, Mn^{2+}, Co^{2+}, Ni^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Tl^{3+}, Cr^{3+}, Fe^{3+}, Nd^{3+}, Pr^{3+}, Sm^{3+}, Gd^{3+}, Ho^{3+}, Yb^{3+}, Y^{3+}, Ce^{3+}, La^{3+}, Ti^{4+}, Zr^{4+}, Hf^{4+}, Th^{4+} and the anions F^-, Cl^-, Br^-, I^-, $ClO_3{}^-$, $BrO_3{}^-$, $IO_3{}^-$, $HCOO^-$, CH_3COO^-, CNS^-, $NO_3{}^-$, $NO_2{}^-$, $Cr_2O_7{}^{2-}$, $CrO_4{}^{2-}$, $WO_4{}^{2-}$, $MoO_4{}^{2-}$, $SO_3{}^{2-}$, $SO_4{}^{2-}$, $CO_3{}^{2-}$, $S_2O_3{}^{2-}$, $SeO_3{}^{2-}$, $TeO_3{}^{2-}$, $C_2O_4{}^{2-}$, $Ti[F_6]^{2-}$, $PO_4{}^{3-}$, $C_6H_5O_7{}^{3-}$, $Fe(CN)_6{}^{3-}$, $Fe(CN)_6{}^{4-}$ in electrolyte solutions of high concentrations, and found the optimum conditions for the analysis of various ions.

The proposed method was tested by the authors jointly with the laboratory of the Northwestern Geological Administration in the analysis of the principal components of limestones, silicates, ground waters, and brines, and gave good results.

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Note: Figure translations are in progress. See original paper for figures.