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Tandem Ion-Exchange Fractionation: New Preparative Mode for Separation of Multicomponent Ionic Mixtures

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The paper reports the results on the development of the tandem ion-exchange fractionation (TIEF) concept for separation of n -component ($n > 2$) ionic mixtures on ($n - 1$) ion-exchange columns. TIEF technique is based on a sequential combination of frontal separation (FS) and reverse frontal separation (RFS) of the mixture components. The appropriate sequence of the FS leads to a stepwise elimination of the number of components, and it allows recovery of all ions under separation in a sufficiently pure state. A practical demonstration of this concept has been carried out by applying it to a typical mixture of metal ions present in nonferrous metal alloys, i.e. Cu^{2+} , Al^{3+} , Zn^{2+} , and Mg^{2+} . The values of the equilibrium separation coefficient, α , for quadri-, tri-, and bicomponent mixtures involving the mentioned metal ions on polyacrylic and iminodiacetic resins have been determined. The increase of α values for, e.g., Zn^{2+} – Mg^{2+} exchange from 3.3 to 15.8 on reducing of the number of mixture components from four to two has been observed to illustrate the validity of the TIEF concept. The preparative separation of a Cu^{2+} , Al^{3+} , Zn^{2+} , and Mg^{2+} mixture with an equivalent ratio of $\text{Cu}:\text{Al}:\text{Zn}:\text{Mg} = 1:1:1:1$, carried out by applying the TIEF technique, has been shown to yield Mg^{2+} of around 100% purity and Cu^{2+} , Al^{3+} , and Zn^{2+} of 96.1%, 98.8%, and 95.1% average purity, respectively, at a reasonably high yield. The differential stripping during the RFS stage improves significantly the purity of the products obtained. The results obtained by applying TIEF to separate and recover Cu^{2+} , Al^{3+} , Zn^{2+} , and Mg^{2+} from an acidic mine water sample containing nine metal ions as main components confirm the practical merit of the proposed technique.

The application of ion-exchange resins in scientific research and industry has increased continuously within the past few years. Two main groups of problems can be successfully solved by applying ion-exchange separation techniques. The first comprises separation and purification of nonelectrolytes or weak electrolytes from electrolyte impurities and involves, for example, water demineralization,^{1–3} purification of amino acids from mineral salt

admixtures,^{4–6} manufacture of high-purity silica,⁷ and some others.⁸ The second group involves the purification of electrolytes from electrolyte impurities and the separation of electrolyte mixtures. The last task is far more complex than the first one. This is particularly true for separation of multicomponent ionic mixtures such as, for example, seawater,⁹ acidic mine waters,^{10–12} etc., aiming to recover valuable and/or toxic constituents from complex natural and industrial hydromineral and other sources.¹³ An acute problem in the secondary processing of nonferrous metal alloys also includes a separation of alloy components stage, which remains practically unsolved up to now. Separation and recovery of brass and bronze constituents such as copper, zinc, aluminum, magnesium, and some others as secondary metals are of particular importance, saving vast amounts of energy in comparison with their recovery from the respective ores (primary metals). The difference of energy consumption in the production of primary and secondary metals (energy saving) is 362 GJ/ton for magnesium, 340 GJ/ton for aluminum, 97 GJ/ton for copper, and 49 GJ/ton for zinc (see ref 13, p 31-5). In this context, further development of simple and highly effective ion-exchange separation methods is particularly essential.

Several ion-exchange fractionation techniques are known to be applicable for this purpose, such as frontal separation (FS), known also as frontal ion-exchange chromatography,¹⁴ reverse frontal separation¹⁵ (RFS), and displacement chromatography¹⁶ (DC). FS is applicable for the separation of the component of the weakest sorbability from the mixture components, which are

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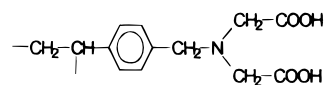
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sorbed more strongly. The RFS allows to separate an ionic species, which is sorbed better than the rest of the mixture ions. The DC technique can be considered, in fact, as a "parallel combination" of FS and RFS, since both of these separation processes proceed simultaneously. Therefore, such a combination within one fractionation method (DC) makes it possible to separate any number of components of either sorbability from each other. One of the first and most impressive applications of DC was the early work of Spedding and co-workers on isolation of transuranium elements^{17,18} and separation of rare earths.^{19–21} Since then, DC remains the only fractionation technique which is widely applied for preparative separation of complex multicomponent mixtures, such as proteins,²² protein hydrolysates,²³ rare earth elements,^{24–26} and others.^{27,28} Although DC represents one of the most powerful tools in ion-exchange separation and still is under intensive development,^{29–33} it is characterized by a number of drawbacks such as, for example, a long time and high resin bed needed for the complete preparative separation of mixture components, low productivity of the separation process, and some others, which limits a wider practical application of this ion-exchange fractionation technique. Furthermore, DC is not applicable when only certain components must be separated from a multicomponent mixture. The above drawbacks can be overcome by applying a new FS–RFS combination, which can be characterized as their "sequential combination". Such a combination will be identified by the term "tandem ion-exchange fractionation" (TIEF), to emphasize that this FS–RFS coupling enhances the separation efficiency of each single fractionation method.

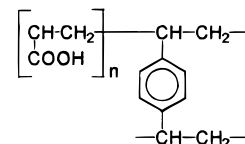
The present study has been undertaken (1) to develop the TIEF concept for the preparative separation of multicomponent ionic mixtures, (2) to obtain information on the ion-exchange equilibrium in the bi-, tri-, and quadricomponent mixtures containing Cu^{2+} , Al^{3+} , Zn^{2+} , and Mg^{2+} on polyacrylic and iminodiacetic resins, and (3) to demonstrate a preparative separation of four components from solutions containing mixtures of four and nine metal ions by applying the TIEF concept. This is the first time that such an approach has been applied successfully to the separation of metal ions from multicomponent mixtures.

EXPERIMENTAL SECTION

Reagents, Ion-Exchangers, and Apparatus. Magnesium, zinc, aluminum, and copper sulfates, sodium chloride, sodium hydroxide, and sulfuric acid (all of p.a. quality) were purchased from Panreac (Barcelona, Spain) and used as received. Iminodiacetic ion-exchanger, Lewatit TP-207, and polyacrylic resin, Lewatit R 250-K, were kindly supplied by Bayer Hispania Industrial, S.A.



Lewatit TP-207



Lewatit R 250-K

Doubly distilled water was used in all experiments. The total concentration of metal ions in the stock solution in all cases was kept constant at 0.04 equiv/dm³. The ratio of metal ion concentrations in the respective model feed solutions always equaled 1. The pH of the initial solution was adjusted to 3.5 using 0.1 M H_2SO_4 . Standard precautions recommended for handling sulfuric acid solutions³⁴ were followed when adjusting pH and preparing the 0.1 M H_2SO_4 solution from concentrated acid. Samples of native acidic mine waters from the Rio Tinto area (Huelva, Spain) were kindly supplied by Rio Tinto Minera, S.A. These mine waters represent the natural generic metal-bearing effluents originating from the pyritic ore deposits typical for the southern provinces of Spain and Portugal. The preliminary treatment of Rio Tinto water (RTW) samples, aiming at the selective oxidative precipitation of Fe(III) hydroxide, was carried out as described elsewhere.¹² The composition of iron-free RTW sample is given below (see Table 4). The concentration of metal ions was determined by atomic emission spectroscopy (ICP-AES technique) using an ARL Model 3410 spectrometer (Fisons, Beverly, MA) provided with a mini-torch. The emission lines used for the spectrochemical analysis were 324.754 nm for Cu^{2+} , 213.856 nm for Zn^{2+} , 279.806 nm for Mg^{2+} , and 394.401 nm for Al^{3+} . The uncertainty of metal ions determination was in all cases <1.5%. pH was controlled using a Crison pH meter 507 (Barcelona, Spain) supplied with a combined glass electrode. Glass columns of 0.5 cm × 5 cm and 1.0 cm × 10 cm from Bio-Rad (Richmond) were used for studying ion-exchange equilibrium and for carrying out the TIEF experiments. Prior to the column experiments, the resins were air-dried and then ground and sieved, so that only a granulometric fraction between 0.100 and 0.250 mm was collected and used for loading the columns.

Procedures. Ion-exchange equilibrium was studied under dynamic conditions by using fixed-bed columns. Experiments were carried out in an air-conditioned room at $22 \pm 0.5^\circ\text{C}$. The initial solution was passed through the columns containing the respective resins (300 and 200 mg of Lewatit TP-207 and Lewatit R 250-K, respectively) in the Na^+ form at a constant flow rate of 0.33 mL/min up to achieving the equilibrium. The eluate was collected in portions of known volume, and the concentrations of metal ions were determined. The achievement of ion-exchange equilibrium in the systems under study was followed by compari-

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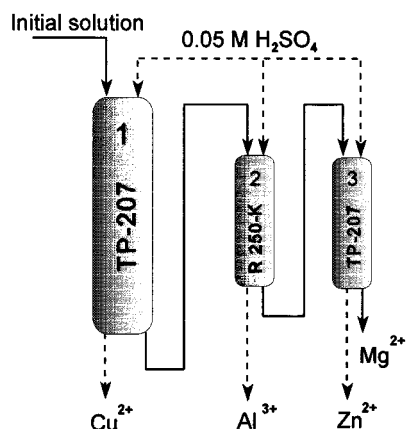


Figure 1. Scheme of three-column setup used in the TIEF experiment. Loading cycle (straight line) and stripping cycle (dotted line), see text.

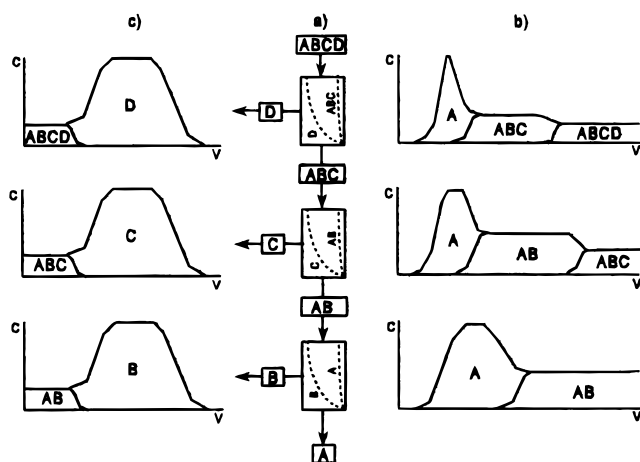


Figure 2. Conceptual scheme of the TIEF technique for separation of a four-component mixture. (a) System of three columns connected in series. (b) Frontal separation of A in loading. (c) Reverse frontal separation of B, C, and D in stripping.

son of the metals concentration in the column outlet with that of the initial feed solution. After the sample with concentrations of metal ions close to the initial values, was collected, the flow of solution was stopped and then resumed after a certain period of time. The coincidence of the initial concentration with that of the sample collected after the break was considered as the criterion indicating the equilibrium in the system. After equilibration, the resin was rinsed with twice-distilled water, and then the stripping was carried out with 0.05 M H_2SO_4 , followed by the analysis of the desorbed metal ions in the resulting eluate. Data of the stripping solution analysis were used to determine both the capacity of the resin toward the mixture components and the equilibrium separation coefficient α , expressed as follows:

$$\alpha_{M_2}^{M_1} = \frac{Y_{M_1} X_{M_2}}{Y_{M_2} X_{M_1}} \quad (1)$$

where Y and X are the equivalent fractions of metal ions (M_1 and M_2) under separation in resin and solution phases, respectively. Indexes 1 and 2 are chosen so that $\alpha > 1$. The relative uncertainty on α determination in all cases did not exceed 7%.

The experiment on TIEF of the Cu^{2+} – Al^{3+} – Zn^{2+} – Mg^{2+} mixture was carried out by passing the initial solution through

the system of three columns connected in the sequential series as shown in Figure 1. The first column (1.0 cm \times 10 cm) was loaded with 2.00 g of Lewatit TP-207 resin. The second and the third columns (0.5 cm \times 5 cm each) were loaded with 200 mg of Lewatit R 250-K and 75 mg of Lewatit TP-207 resins. After the appearance of Al^{3+} in the second column outlet, the third column was disconnected. When Cu^{2+} appeared in the outlet of the first column, the second one was also disconnected, and the solution continued to pass through the first one until equilibrium was achieved. The resins were then rinsed separately with twice-distilled water, and the stripping of each column with 0.05 M H_2SO_4 was carried out, followed by the analysis of metals ions in the eluate obtained. The results of the stripping solution analysis were used to determine (1) the capacity of each resin toward the mixture components, (2) the values of equilibrium separation factors α (see eq 1), (3) the purity of the product in each solution portion collected according to

$$P_{A,i} (\text{mass } \%) = \frac{C_{A,i} \times 100}{C_{A,i} + C_{B,i} + C_{C,i} + C_{D,i}} \quad (2)$$

and (4) an average purity of the products obtained, which can be expressed as follows:

$$P_{A,\text{av}} (\text{mass } \%) = \frac{(\sum_i V_i C_{A,i}) \times 100}{\sum_i V_i (C_{A,i} + C_{B,i} + C_{C,i} + C_{D,i})} \quad (3)$$

In eqs 2 and 3, V_i is the volume of the “ i ” solution sample (dm^3), and C_i is the concentration of the respective ionic species in this sample (g/dm^3).

The final experiment on TIEF of Cu^{2+} , Al^{3+} , Zn^{2+} , and Mg^{2+} from the iron-free nona-component RTW sample was carried out on the same three-column setup (see Figure 1) by following the above-described sequence of operations.

TIEF Concept. A conceptual scheme of the TIEF for the separation of a quadricomponent mixture of A, B, C, and D cations with the equivalent ratio A:B:C:D = 1:1:1:1 is shown in Figure 2. The initial mixture of AX, BX, CX, and DX (X denotes the mutual anion) is passed through three columns, which are sequentially connected with each other. Each column contains a specific cation-exchanger (or -exchangers), which preferentially sorbs one of the mixture components, but *all of them manifest the weakest affinity toward the same cation*, for example, A. The last condition is a necessary requirement in the TIEF technique. We will suppose the sorbability of the mixture components in all columns to follow the sequence $D > C > B > A$.

As can be seen in Figure 2, the loading of each column is accompanied by the FS process (see Figure 2b). The loading of the first column is carried out until the breakthrough of ion D is observed.³⁵ Hence, the number of ionic species entering the

(35) Strictly speaking, the loading of each column should continue until the ion-exchange equilibrium is achieved. This can be done by using a two-column setup at each stage, so that the first column is working in the “up-to-breakthrough” mode of operation, while the second continues being equilibrated with the respective solution. After equilibration, stripping, and preparation of this column for the next run, solution flux leaving the first column can be switched to the inlet of second one, while the first column is now operating in an “equilibration” mode.

Table 1. General Conditions for Separation of Quadricomponent Mixture in Three Columns by Using TIEF Technique

column 1		column 2		column 3	
prod ^a	α	prod ^a	α	prod ^a	α
D	$\alpha_C^D > 1$ $\alpha_B^D > 1$ $\alpha_A^D > 1$	C	$\alpha_B^C > 1$ $\alpha_A^C > 1$	B	$\alpha_A^B > 1$
A	$\alpha_A^B > 1$ $\alpha_A^C > 1$ $\alpha_A^D > 1$	A	$\alpha_A^B > 1$ $\alpha_A^C > 1$	A	$\alpha_A^B > 1$

^a The products to be obtained in a pure state.

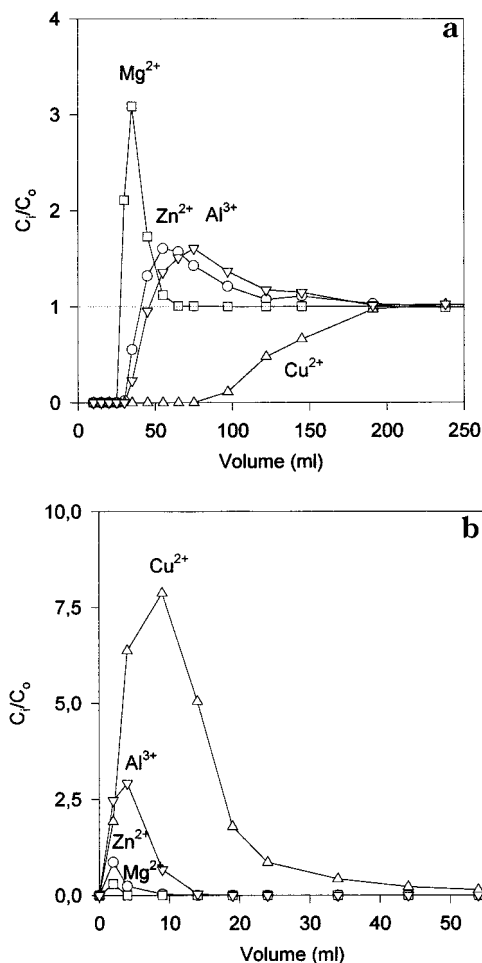


Figure 3. Breakthrough curves for separation of a four-component mixture on Lewatit TP-207 resin, (a) loading and (b) stripping. (○) Zn²⁺, (□) Mg²⁺, (Δ) Cu²⁺, and (▽) Al³⁺.

second column is diminished to three (A, B, and C). Note that, at a determined loading of the resin bed, the equivalent ratio of components in the solution leaving column 1 becomes the same, i.e., 1:1:1. The above condition must be fulfilled in the loading of columns 2 and 3. In this case, the equivalent ratio of ion concentrations in the mixture entering column 3 also equals 1:1. The FS of the A, B, and C mixture in column 2 leads to the additional accumulation of A in the head part of the solution leaving the column, while component C is retarded by the resin phase. The final separation of the residual mixture of A and B is accomplished in column 3. The distribution of components in the solution leaving each column is shown in Figure 2b. As is

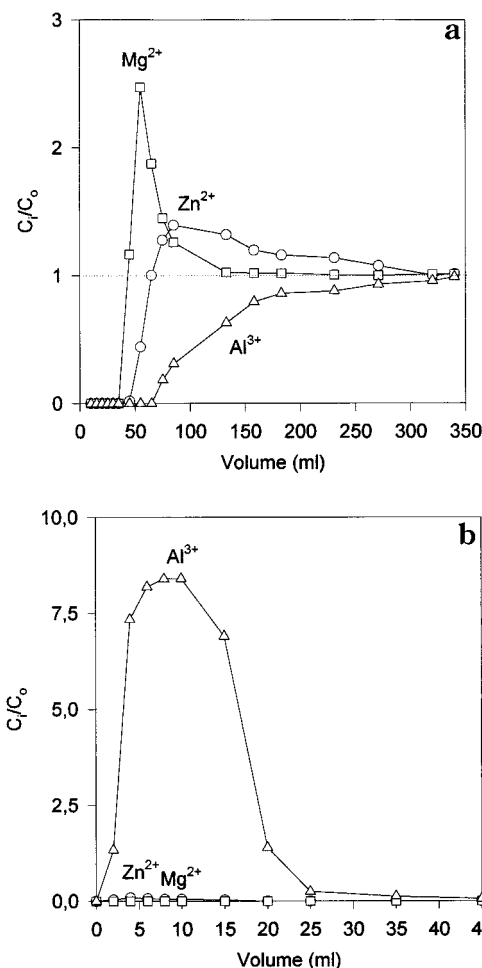


Figure 4. Breakthrough curves for separation of a three-component mixture on Lewatit R 250-K resin, (a) loading and (b) stripping. (○) Zn²⁺, (□) Mg²⁺, and (▽) Al³⁺.

seen in Figure 2b, A is the only component which can be recovered in a pure state from the solution collected after the last column. On the other hand, components D, C, and B accumulated in the resin phases of columns 1, 2, and 3, respectively (as shown in Figure 2a by dotted lines), can be recovered in a pure state during the stripping stage by using the RFS technique. The distribution of components in the stripping solution is shown in Figure 2c.

We will consider now the ion-exchange equilibria in each column to characterize them in terms of the respective α values. As follows from eq 1, for a mixture of ions of equal concentration, for example, A and B, (α_A^B) can be expressed as follows:

$$\text{column 1: } \alpha_A^B[4] = \frac{Y_B}{Y_A} = \frac{1 - Y_A - Y_C - Y_D}{Y_A} \quad (4)$$

$$\text{column 2: } \alpha_A^B[3] = \frac{Y_B}{Y_A} = \frac{1 - Y_A - Y_C}{Y_A} \quad (5)$$

$$\text{column 3: } \alpha_A^B[2] = \frac{Y_B}{Y_A} = \frac{1 - Y_A}{Y_A} \quad (6)$$

The number in brackets denotes the number of components in the respective feed solution.

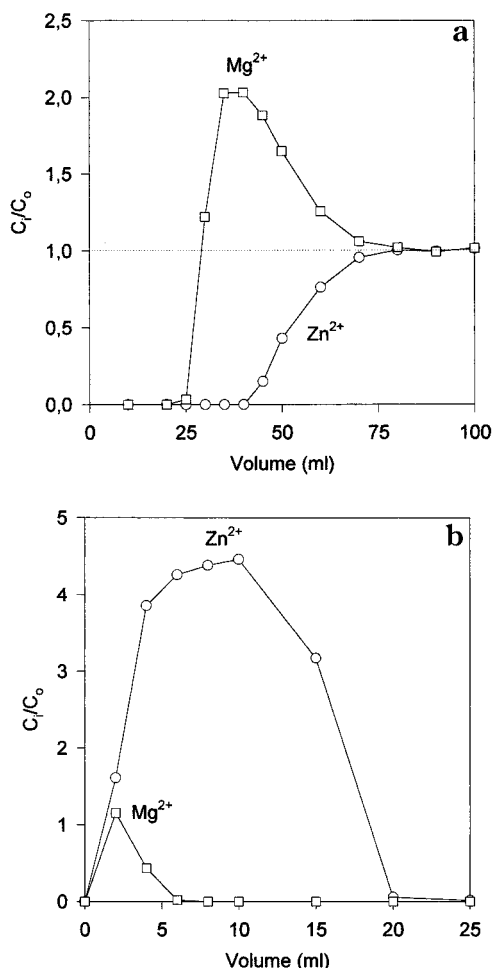


Figure 5. Breakthrough curves for separation of a two-component mixture on Lewatit TP-207 resin, (a) loading and (b) stripping. (○) Zn^{2+} and (□) Mg^{2+} .

Equations 4–6 can be rewritten in the form

$$\alpha_A^B[4] = \frac{1 - Y_A}{Y_A} - (\alpha_A^C + \alpha_A^D) \quad (7)$$

$$\alpha_A^B[3] = \frac{1 - Y_A}{Y_A} - \alpha_A^C \quad (8)$$

$$\alpha_A^B[2] = \frac{1 - Y_A}{Y_A} \quad (9)$$

By assuming $(1 - Y_A)/Y_A$ in eqs 7–9 to be of the same order of magnitude (this approximation is rather rough, but for the discussion given below, better accuracy is not important) and taking into account that $\alpha_A^D > \alpha_A^C$, it follows $\alpha_A^B[2] > \alpha_A^B[3] > \alpha_A^B[4]$, i.e., the separation conditions for the B–A ion couple are far better in column 3 than in column 1. This conclusion can be formulated in a more general way as follows: *Sequential elimination of the number of mixture components results in improving the separation conditions for the rest of ions.* The general conditions for the separation of the A, B, C, and D mixture are summarized in Table 1, where the products to be obtained from each column in a pure state are also indicated. The conclusion made and the separation conditions given in Table 1 are valid for any multicomponent system of either composition where the constant separation

coefficient condition (conventionally accepted in the majority of publications on ion-exchange) is fulfilled,^{36,37} i.e., where the presence of other components (within the mixture of a given composition) does not affect the equilibrium relationships between any two of the components significantly.

In the case when a multicomponent mixture contains one macrocomponent to be purified, e.g., ion A, and B, C, and D are the microcomponents (impurities), the separation procedure can be simplified in the following two cases:

(1) If the major component is sorbed better than the impurities, then the pure substance A is obtained during the RFS (stripping) stage, while all impurities are concentrated in the eluate obtained during the FS stage.

(2) When the impurity ions are preferentially sorbed, component A can be readily obtained in the pure state from the eluate obtained after the first FS cycle, while impurities can be concentrated within the RFS stage. Note that, in both cases, only one column setup is required for separation of A from B, C, and D. Further separation of impurity ions (B, C, and D) from respective concentrates can be carried out (if necessary) on a two-column setup by repeating the TIEF procedure.

The efficiency of the TIEF technique (as for that of any other chromatographic methods) depends both on the equilibrium parameters of the system under separation (respective α values) and on the separation efficiency of the columns used. The last parameter can be characterized by the number of theoretical plates, N . In the simplest case, the separation degree q of any ion couple is connected with α and N through the square cascade eq³⁸ (also known as Fenske equation) as follows:

$$q \approx \alpha^N \quad (10)$$

As can be seen from eq 10, a sufficiently high separation degree (e.g., $q = 1000$) at high α values (e.g., $\alpha = 10$) can be obtained on a column of low efficiency (e.g., with $N \geq 3$), while at low α (e.g., $\alpha = 1.1$), to achieve the same separation degree, the efficiency of the column must be much higher²⁴ ($N \geq 73$).

RESULTS

Figure 3 shows a typical concentration–volume history obtained with column 1 when loading with a quadricomponent mixture of Mg^{2+} , Zn^{2+} , Al^{3+} , and Cu^{2+} (Figure 3a) and stripping of metal ions with 0.05 M H_2SO_4 (Figure 3b). FS and RFS fractionations of Al–Zn–Mg and Zn–Mg mixtures are shown in Figures 4 and 5, respectively.

The results on α determination for binary exchange of metal ion couples from the bi-, tri-, and quadricomponent mixtures on Lewatit TP-207 and Lewatit R 250-K resins are collected in Table 2, where α values for the same ion couples determined from RTW on Lewatit TP-207 resin³⁹ are also shown.

Figure 6 presents the concentration–volume history obtained in the TIEF experiment (see Experimental Section). As can be seen in Figure 6a, the head part of the breakthrough curve contains a practically pure Mg^{2+} . The width of the pure product

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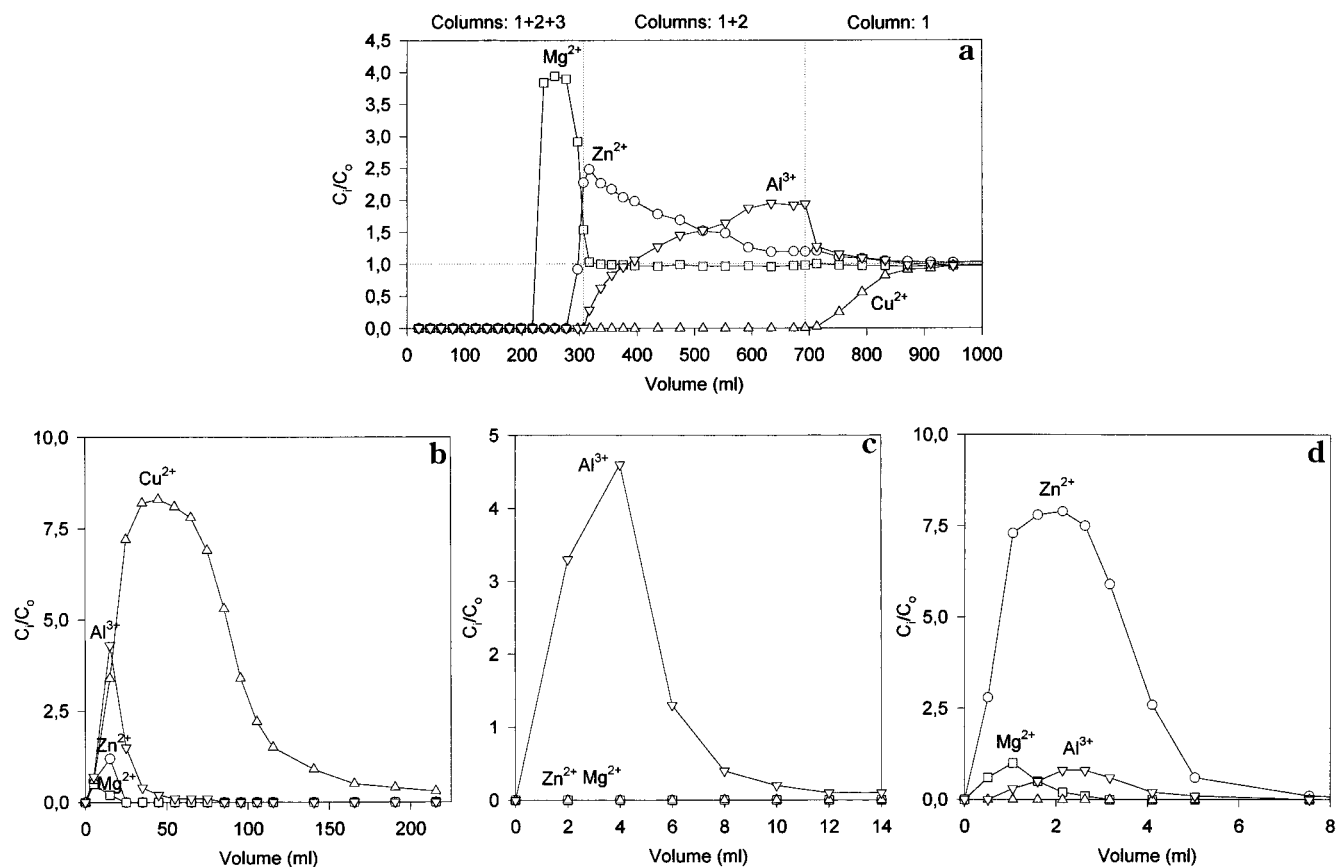


Figure 6. Concentration–volume histories of (a) frontal separation of (○) Zn^{2+} , (□) Mg^{2+} , (△) Cu^{2+} , and (▽) Al^{3+} in three-column setup, and reverse frontal separation of (b) Cu^{2+} , (c) Al^{3+} , and (d) Zn^{2+} .

Table 2. Separation Equilibrium Coefficients of Metal Ions on Lewatit TP-207 and Lewatit R 250-K

no. of components	resin	α_{Mg}^{Cu}	α_{Zn}^{Cu}	α_{Al}^{Cu}	α_{Mg}^{Al}	α_{Zn}^{Al}	α_{Mg}^{Zn}
9 (RTW) ^a	TP-207	254 ^b	116 ^b	39 ^b	6.6 ^b	3.0 ^b	2.2 ^b
4	TP-207	96	30	6.9	15.6	4.6	3.3
3	R 250-K				1230	157	6.6
2	TP-207						15.8

^a For RTW composition, see Table 4. ^b Adapted from ref 40.

zone is far wider than that obtained in a single FS procedure (see Figures 3a, 4a, and 5a). As follows from the results on the stripping of metal ions, shown in Figure 6b–d, Cu^{2+} and Al^{3+} of sufficiently high purity are obtained as a result of the RFS process. Although Zn^{2+} is yielded in a less pure state due to contamination with Al^{3+} and Mg^{2+} , the eventual zinc purity appears to be quite high (see below, Table 3).

The results obtained by separation of Cu^{2+} , Zn^{2+} , Al^{2+} , and Mg^{2+} by the TIEF technique on the three-column setup shown in Figure 1 from the native RTW sample are collected in Table 4, where the initial composition of acidic mine water and initial and final (both average and maximal) purities of metal sulfates obtained are shown.

DISCUSSION

A comparison of the results presented in Figures 3 and 4 with those shown in Figure 6 will provide the main conclusion of the present work. As follows from Figure 3a and b, a combination of the FS and RFS within one separation step (loading–stripping

procedure) allows only two ionic species of the weakest (Mg^{2+}) and strongest (Cu^{2+}) sorbabilities in a pure state to be recovered. The intermediate tricomponent mixture of Zn^{2+} , Al^{3+} , and Mg^{2+} remains nonseparated and is usually wasted. The same conclusion follows from the results shown in Figure 4. Here, Mg^{2+} and Al^{3+} can be yielded as pure products, while the component of intermediate sorbability, Zn^{2+} , remains contaminated with both of these metal ions. This limitation of a single FS–RFS procedure can be overcome by applying the TIEF technique. This is illustrated by the results presented in Figure 6. Indeed, a sequential one-by-one elimination of the mixture components proceeding in columns 1 (Cu^{2+}), 2 (Al^{3+}), and 3 (Zn^{2+}) leads (1) to the concentration of Mg^{2+} in the solution phase up to the maximum level, which corresponds to the total concentration of the initial mixture (cf., $C_i/C_0 = 4$ in Figure 6a with $C_i/C_0 \approx 3$ in Figure 3a) and (2) to the widening of the pure product (magnesium) zone (cf., Figures 4a and 6a). As a result, the purity of the recovered magnesium from the first eluate portions appears to be >99.9%, as can be seen in Figure 7a.

The purity of Cu^{2+} , Al^{3+} , and Zn^{2+} vs volume of the eluate plots shown in Figures 7b–d, respectively, testifies to the high effectiveness of the TIEF technique. Indeed, the purity of Cu^{2+} and Al^{3+} in the last portions of the stripping solution exceeds 99.9%. Values of the initial, maximum, and average purity of the components under separation are collected in Table 3, where the yields of the products obtained by RFS with purity $\geq 95\%$ are also shown. As can be seen in Table 3, although the initial purity of all mixture components is quite low, an average purity of metals obtained with good yields appears to be sufficiently high and can

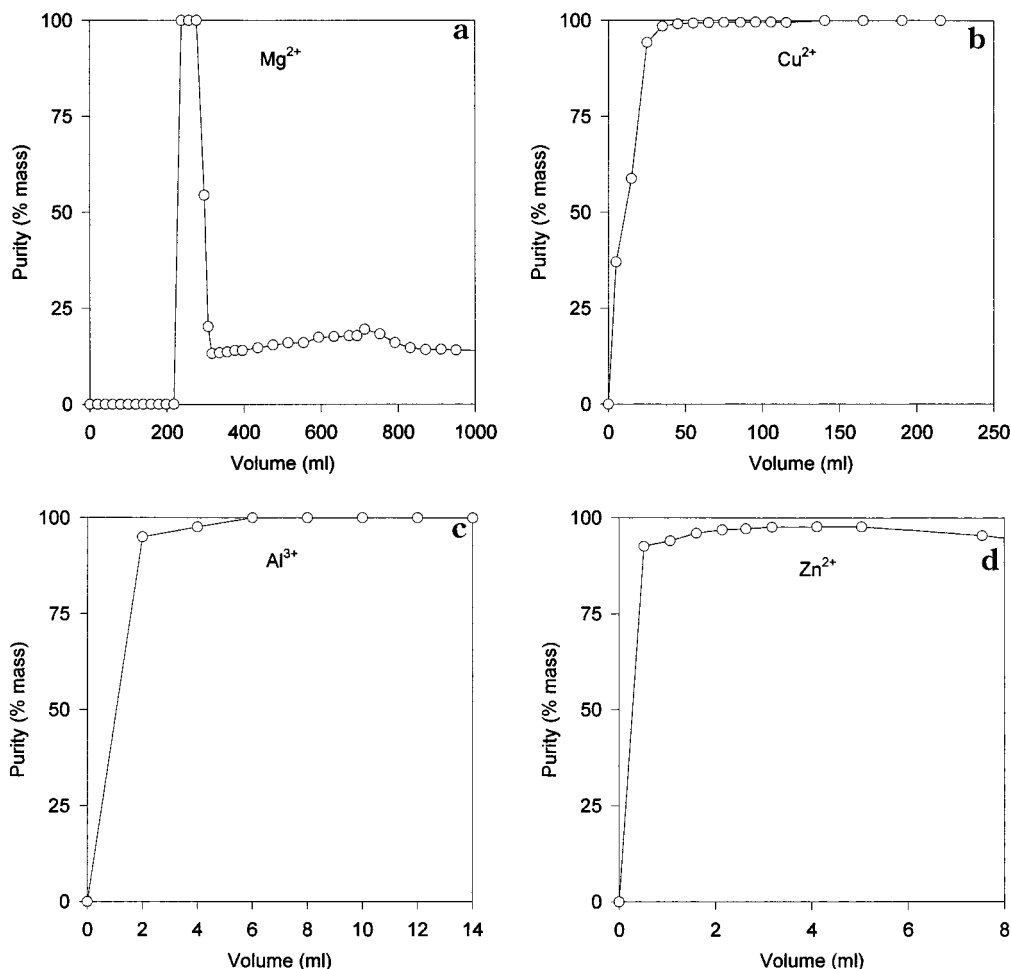


Figure 7. Purity–volume histories for (a) Mg^{2+} , (b) Cu^{2+} , (c) Al^{3+} , and (d) Zn^{2+} (see text).

Table 3. Purity and Yield of Products Obtained in Separation of Mg–Zn–Al–Cu Mixture by Using TIEF Technique

metal	purity (%)			yield of >95% purity product (%)
	initial	average	maximum	
Cu	37.5	96.1	>99.9	83.9
Al	9.8	98.8	>99.9	97.6
Zn	38.3	95.1	97.7	77.3
Mg	14.4		100	

be increased up to $\sim 100\%$ (for Cu^{2+} and Al^{3+}) by using differential stripping. A lower purity of Zn^{2+} is attributed to the breakthrough of Al^{3+} from column 2 into column 3 during the loading stage, which results in to the contamination of the product with this ionic species. This situation can be easily improved by applying a two-column setup³⁵ or by carrying out FS and RFS processes in countercurrent columns.³³

The results on α determination shown in Table 2 confirm the above-mentioned conclusion about improving the separation conditions of metal ions after eliminating the number of mixture components. This is clearly seen from α values for Zn^{2+} – Mg^{2+} exchange determined in bi-, tri-, and quadricomponent systems. Note that α values under consideration refer to a Lewatit TP-207 (quadr- and bicomponent systems) and a Lewatit R 250-K resin (tricomponent system). The comparison of α values determined for macrocomponents of RTW on Lewatit TP-207 resin with those measured in the model quadricomponent system confirms the

Table 4. Initial Composition and Purity of Products Obtained in Separation of Mg–Zn–Al–Cu from Rio Tinto Waters, RTW, by Using TIEF Technique

metal	C (ppm)	purity (%)		
		initial	average	maximum
Cu	217	1.5	87	93
Al	552	3.7	71	79
Zn	1619	10.9	82	94
Mg	903	6.1	99	100 ^a
Fe	1.2	0.01		
Mn	95	0.65		
Ca	364	2.5		
Na	6.6	0.04		
K ^b	11 085	74.7		

^a After precipitation from the binary Mg^{2+} – K^{+} mixture. ^b Introduced into initial RTW (as KOH) during the iron removal stage.

above conclusion. Indeed, α values of Al^{3+} – Mg^{2+} , Al^{3+} – Zn^{2+} , and Zn^{2+} – Mg^{2+} exchanges from a nonacomponent mixture³⁹ appear to be lower than those determined from the mixture under study. Note that equivalent fractions of Al^{3+} , Zn^{2+} , and Mg^{2+} in the RTW sample equal 0.26, 0.18, and 0.40, respectively. On the other hand, the equivalent fraction of Cu^{2+} in RTW equals 0.046; i.e., it appears to be far lower than those of the rest of the RTW components. As the result, the affinity of iminodiacetic resin toward this ionic species in RTW (α values for Cu^{2+} – Al^{3+} , Cu^{2+} – Mg^{2+} , and Cu^{2+} – Zn^{2+} exchanges) appears to be much higher in comparison with that manifested in the quadricomponent mixture with higher

copper content due to the conventionally observed increase of resin selectivities toward mixture microcomponents.⁴⁰

The results on separation of Cu^{2+} , Al^{3+} , Zn^{2+} , and Mg^{2+} from the noncomponent mixture (RTW sample), shown in Table 4, testify to the high efficiency of the TIEF technique when applied for selective recovery of the desired components from the native hydromineral sources of complex composition. Indeed, although the composition of RTW differs dramatically from that of the model system studied, the maximal purity of all metal ions recovered appears to be sufficiently high. For example, the purity of Cu^{2+} and Zn^{2+} obtained within one FS–RFS cycle exceeds 90%, and that of Mg^{2+} reaches >99%. On the other hand, the maximal purity of Al^{3+} recovered, which appears to be <80%, can be significantly improved by carrying out the aluminum separation stage at elevated temperature. This conclusion follows from the results previously reported³⁹ which were obtained by studying the ion-exchange equilibrium of RTW metal ions on Lewatit R 250-K resin at different temperatures. Thus, the increase of the temperature from 293 to 333 K results in the increase of the $\alpha_{\text{Zn}}^{\text{Al}}$ value from 10.7 to 42. Hence, TIEF of Al^{3+} from the rest RTW metal ions (mainly from Zn^{2+}) at 333 K on polyacrylic resin will result not only to the increase of the purity of aluminum obtained (the content of Zn^{2+} in Al^{3+} recovered at 293 K achieves 23%), but also to improve the purity of Zn^{2+} which is yielded within the next TIEF stage (Al^{3+} content in Zn^{2+} obtained at 293 K is around 10%).

(40) Soldatov, V. S. In *Ion Exchangers*; Dorfner, K., Ed.; Walter de Gruyter: Berlin, 1991; p 1243.

In conclusion, this study shows the first successful application of the tandem ion-exchange fractionation technique for the preparative separation of four metal ions from multicomponent mixtures.

DEFINED SYMBOLS

$\alpha_{M_2}^{M_1}$	equilibrium separation coefficient of metal ions (M_1 and M_2) (see eq 1)
Y_M and X_M	equivalent fractions of metal ions (M_1 and M_2) under separation in resin (Y) and solution (X) phases, respectively
$P_{A,i}$ (mass %)	purity of the product A in each solution portion i collected
V_i	volume of the i solution sample, dm^3
C_i	concentration of the respective ionic species in sample i , g/dm^3
N	number of theoretical plates
q	separation degree (see eq 10)

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