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Combined Ion Exchange–Solvent Extraction (CIESE): A Novel Separation Technique for Inorganic Ions

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Summary

In the present paper a novel separation technique for inorganic ions is described. This has been termed combined ion exchange–solvent extraction (CIESE), because it is assumed that both ion exchange and solvent extraction are operative simultaneously to effect the separations. This concept is illustrated with two examples: the separation of iron(III), Co(II), and Ni(II) on the ion-exchange resins Dowex 50 and Dowex 1 using acetone or tetrahydrofuran–hydrochloric acid mixtures, and the separation of uranium from numerous metal ions on Dowex 50, employing as eluent a medium consisting of tetrahydrofuran–nitric acid. Because this separation principle is superior to methods employing the conventional separation techniques of ion exchange in pure aqueous solutions and of common liquid-liquid extraction, it is expected that it will also find application for the solution of other problems encountered in inorganic analytical chemistry.

Up to the present a great number of methods have been developed for the analytical separation of inorganic ions by means of ion exchange (*1*). Most of these techniques are based on the selective uptake of various ions from pure aqueous systems by cation or anion exchangers, thus making possible their mutual separation.

For analytical purposes ion-exchange materials on a resin basis were found to be the most advantageous. These can be regarded as cross-linked, and hence insoluble, polyelectrolyte gels of limited swelling ability. Most frequently used are copolymers prepared from styrene and divinyl benzene, containing as fixed ions sulfonic acid or quaternary amine groupings. The mobile counterions of these exchangers are in the first case either hydrogen ion or other cations, and in the second case chloride, nitrate, etc. Consequently, one differentiates between cation and anion exchangers, which in the cases mentioned above are called strongly acid and strongly basic, respectively, according to the properties of the fixed ions. Among these, Dowex 50 and Dowex 1 of varying degrees of cross-linking have most frequently been used in analytical separation chemistry.

Because the spectrum of analytical applications of these two types of exchangers alone is very broad, so that an exhaustive discussion of the various methods employing these resins would be extremely lengthy, the present discussion will be limited to two inorganic analytical applications of the two exchangers—the separation of iron, cobalt, and nickel, and the separation of uranium from other elements. This selection has been taken with respect to the fact that these separations, especially, clearly demonstrate the advantages of mixed aqueous organic systems over pure aqueous systems as exchange media. A virtually complete survey of the analytical application of ion exchange in mixed and nonaqueous media, but not including the novel separation concept to be outlined on the following pages, has recently been published by the author of the present paper (2).

From a pure aqueous solution with a hydrochloric acid concentration of 0.6 *N*, iron(III), cobalt, and nickel are not at all retained by Dowex 1, although they are relatively strongly taken up by Dowex 50. Under these conditions the distribution coefficients have values of 180 for Fe(III), 45 for Co(II), and 45 for Ni(II). This means that separation of these elements on a column of Dowex 1 is impossible, whereas by the use of the cation exchanger Dowex 50 a separation of the sum of cobalt and nickel from the more strongly retained iron is possible because the separation factor (the ratio of the distribution coefficient of iron to that of cobalt or nickel) is 4. This is in accordance with the fact that the selectivity of cation exchangers toward ions of higher valency is greater than to those of lower valency and that cations of the same valency are as a rule retained by the exchanger with equal affinity. Consequently, metal ions of the same valency can in most cases only be separated by means of chromatographic techniques, as, for example, by elution chromatography. Even if the ions to be separated are of different valency, a serious overlapping of the elution curves may occur, especially if one of the ions to be separated is only present in traces while the accompanying ions are present in great quantities. Thus for a separation of traces of cobalt or nickel from gram amounts of iron(III) on Dowex 50 and 0.6 *N* hydrochloric acid as the sorption solution and eluent, a very long column would have to be employed to ensure the quantitative uptake of iron and the other two elements. Furthermore, large volumes of the eluent would be required to elute cobalt and nickel before the iron. By means of gradient elution, the volume of eluent could be appreciably reduced and tailing avoided to a large extent. But even under these conditions separation of cobalt from nickel is impossible, because their distribution coefficients are equal and because (for capacity reasons) the use of a relatively long column would be unavoidable.

If, however, in place of this pure aqueous 0.6 *N* hydrochloric acid solution a mixture is used consisting of 80% acetone or tetrahydrofuran, 10% 6 *N* hydrochloric acid, and 10% water (v/v) showing the same over-all acidity, the distribution coefficients on Dowex 50 of iron(III), cobalt, and nickel are 1, 332, and 411, respectively. From this it is evident that the exchange behavior in this medium is very different from that observed in the pure aqueous system. If a mixture of this composition containing great quantities (for example, gram amounts of iron and milligram or microgram amounts of the other two elements) is passed through a column of this cation exchanger, iron, because of its low distribution coefficient, is selectively eluted while cobalt and nickel are strongly retained by the resin. After elution of the iron, for which purpose varying volumes of the same aqueous-organic mixture are required (according to the amount of iron originally present in the mixture), cobalt can be separated from nickel by elution of the former with a mixture consisting of 90% acetone or tetrahydrofuran and 10% 6 *N* hydrochloric acid (v/v). Under these experimental conditions the distribution coefficients of cobalt and nickel are 5 and 107, respectively. After the elution of cobalt, the nickel can be desorbed by means of 3 *N* hydrochloric acid.

The elution curves obtained for this separation of Fe(III), Co, and Ni on Dowex 50 are schematically presented in Fig. 1(a). If in place of this cation exchanger the anion exchanger Dowex 1 is used, the elution curves shown in Fig. 1(b) are obtained. In this case iron is also eluted first; thereafter, however, not the cobalt but the nickel follows the iron into the eluate. As mentioned previously, successive separation of all three elements is impossible with pure aqueous 0.6 *N* hydrochloric acid solution because the

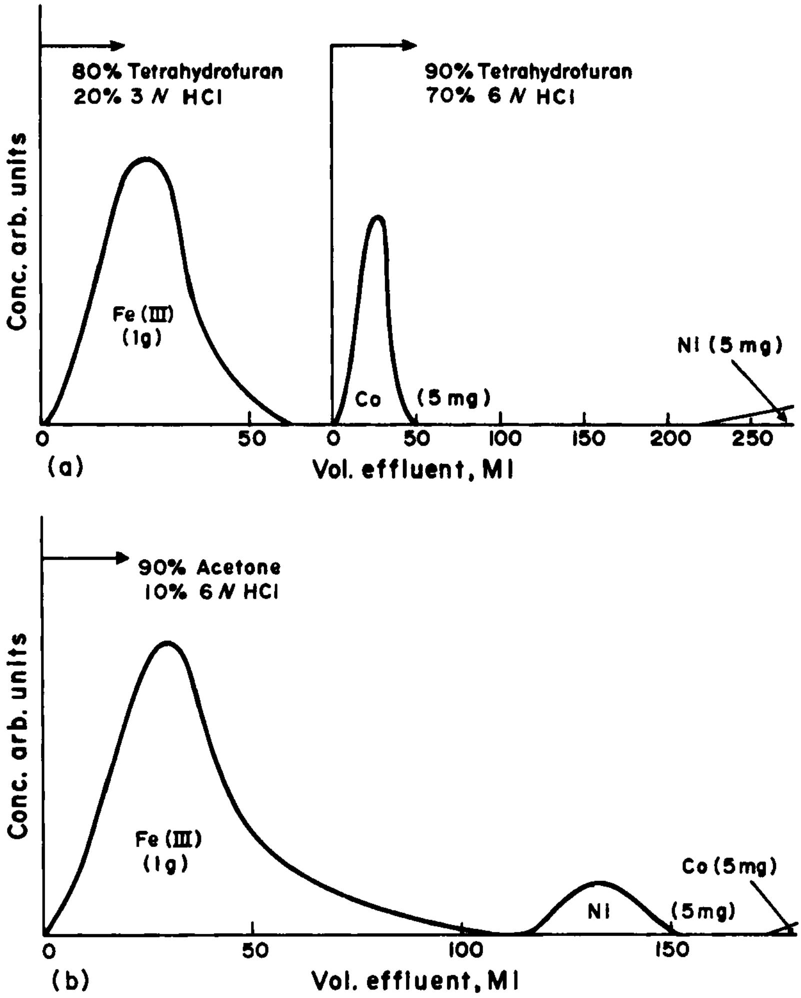


FIG. 1. Separation of iron, cobalt, and nickel. (a) 10 cm × 1.0 cm column of Dowex 50, X8 (100–200 mesh; H^+ form). Flow rate = normal back pressure of the column. (b) 10 cm × 1.0 cm column of Dowex 1, X8 (100–200 mesh; Cl^- form). Flow rate = 0.5 ml/min.

distribution coefficients do not differ sufficiently. This separation can be effected, however, if the concentration of hydrochloric acid is increased considerably and if Dowex 1 is used as the exchange resin. Thus iron(III) and cobalt are retained on this resin from 10 *N* hydrochloric acid, whereas nickel passes into the effluent. After removal of the nickel by washing with 10 *N* hydrochloric acid, cobalt can be desorbed by means of 4 *N* hydrochloric acid, leaving iron(III) further strongly adsorbed on the resin. This separation technique suffers from the same disadvantages as the method mentioned earlier for the separation of these elements on Dowex 50 using pure aqueous hydrochloric acid solution.

Another striking example of the increased selectivity of ion exchangers by the use of mixed aqueous-organic systems is the separation of uranyl ion from many other elements on Dowex 50. As seen in Table 1, uranium in a mixture consisting of 90% tetrahydrofuran and 10% 6 *N* nitric acid (v/v) has by far the lowest distribution coefficient while practically all other investigated di- and higher valent ions, except bismuth, have coefficients of the order of magnitude $>10^3$ to 10^4. Consequently, separation of uranium from these

TABLE 1

Variation of Distribution Coefficients of Uranium and Other Metal Ions with Percentage of Tetrahydrofuran at the Constant Over-all Acidity of 0.6 *N* HNO_3 (5-mg Load per 1 g Dowex 50)

	Percentage of tetrahydrofuran					
Metal ion	0	20	40	60	80	90
UO_2(II)	40	96	134	243	51	40
Mg(II)	18	21	36	72	357	$>10^3$
Ca(II)	38	50	102	145	760	$>10^3$
Sr(II)	68	109	228	676	$>10^3$	$>10^3$
Al(III)	132	137	258	479	878	$>10^3$
In(III)	173	235	630	$>10^3$	$>10^3$	$>10^3$
Pb(II)	105	185	463	934	$>10^3$	$>10^3$
Bi(III)	135	280	630	592	195	47
Zn(II)	46	58	157	704	$>10^3$	$>10^4$
Cd(II)	46	49	178	10^3	10^4	$>10^4$
Y(III)	$>10^3$	$>10^3$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
La → Lu(III)	$>10^3$	$>10^3$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
Ti(IV)	70	127	300	10^3	$>10^3$	$>10^3$
Zr-Hf(IV)	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
Th(IV)	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	1,420
Cr(III)	125	230	600	$>10^3$	$>10^3$	$>10^4$
Mn(II)	40	61	130	405	$>10^3$	$>10^3$
Fe(III)	171	200	287	550	$>10^3$	$>10^3$
Co(II)	32	42	119	306	$>10^3$	$>10^3$
Ni(II)	30	40	115	316	$>10^3$	$>10^3$

elements on a column of this resin can readily be achieved. In the absence of tetrahydrofuran, i.e., at 0% (see Table 1), separation of uranium from most of the metal ions having similar distribution coefficients is in some cases only possible by means of elution chromatography on long columns of this exchanger.

Because this tetrahydrofuran–nitric acid mixture preferentially elutes the uranium, this method is particularly well suited for the separation of large amounts of uranium from smaller or trace quantities of other metal ions. Thus on a microcolumn containing 1 g of Dowex 50 having a diameter of 0.5 cm, 2 mg of cobalt and 2 g of uranyl nitrate hexahydrate dissolved in 5 ml of the mixture can be separated within a short time, whereby 90% of the uranium is found in the first 50 ml of eluate if the tetrahydrofuran–nitric acid mixture is used as the eluent. Even after the passage of 2 liters of this mixture, the zone occupied by the cobalt can clearly be seen on the upper part of the resin column, and a quantitative recovery of cobalt is obtained after its subsequent elution with, e.g., 90% tetrahydrofuran–10% 6 *N* hydrochloric acid (v/v). Consequently, this separation technique can also be employed for the purification of uranyl nitrate and for the enrichment of the strongly adsorbable elements before their quantitative determination. Furthermore, it is suitable for the analysis, purification, and preparation of high-purity uranium samples, offers the possibility of rapidly removing fission products from uranyl nitrate solutions, and allows the subsequent group separation of the retained radionuclides by means of mixed aqueous-organic systems, e.g., by using the hydrochloric acid–tetrahydrofuran or acetone mixtures earlier mentioned.

From results shown in Table 2, it is seen that if in place of tetrahydrofuran other organic solvents are used, the conditions for separating uranium are much less favorable and that for effective separation only the 90% tetrahydrofuran–nitric acid medium can be employed. In all other systems the distribution coefficient of uranium increases steadily, whereas in the tetrahydrofuran and acetone systems adsorption maxima are observed at 60% and in methyl glycol at 80%; thereafter the distribution coefficients decrease with an increase in the percentage of the organic component of the mixtures.

This extraordinary behavior or uranium as well as of iron(III) in the tetrahydrofuran and acetone systems can be explained by assuming that in these mechanisms, ion exchange and solvent extraction operate simultaneously. It is a well-known fact that uranyl

TABLE 2

Distribution Coefficients of Uranium in Various Organic Solvent–Water Mixtures Containing 10% 6 *N* HNO_3
(5-mg Load per 1 g Dowex 50)

Solvent	% Organic solvent					
	0	20	40	60	80	90
Methanol (32)[a]	40	49	85	150	350	750
Ethanol (26)	40	52	119	224	535	750
n-Propanol (23)	40	85	168	207	500	890
Isopropanol (27)	40	67	159	364	890	$>10^3$
Acetone (22)	40	85	127	364	207	141
Tetrahydrofuran (8)	40	96	134	243	51	40
Methyl glycol (18)	40	54	110	207	434	314
Ethyl glycol (14)	40	45	141	330	350	390
Acetic acid (6)	40	76	159	350	480	$>10^3$

[a] *The approximate values of the dielectric constants of the pure solvents at 25°C are given in parentheses.*

nitrate can be extracted from nitric acid solutions by means of ethers, esters, ketones, etc., and is also readily soluble in these solvents. Similarly, ferric chloride can be extracted with the same organic solvents from strong hydrochloric acid solutions. Extraction behavior similar to iron(III) is shown by gallium(III), gold(III), and molybdenum(VI), and on Dowex 50 and Dowex 1 they are eluted together with iron if the same mixed aqueous-organic systems are used as for the separation of iron, cobalt, and nickel (see Fig. 1).

By the use of these media, therefore, two processes are operative: liquid-liquid extraction and ion exchange. Consequently, separations carried out in such mixtures may be termed as performed under conditions of combined ion exchange–solvent extraction (CIESE). Thus the organic solvent is acting as an extractant for one or a group of elements, whereas for other metal ions it causes an increase of selectivities toward the ion exchanger, so that, as shown by the two examples discussed previously, selective separations can be achieved. Compared to most other separation procedures on columns, CIESE can be regarded as being bidimensional, because with the other techniques (e.g., ion exchange in pure aqueous systems, adsorption chromatography, and partition chromatography) either ion exchange or adsorption or partition are the single separation parameters.

An explanation of the reason this CIESE effect is becoming effective, especially at high percentages of organic solvent, and how it can be understood in a qualitative theoretical way will now be presented, using as an example the adsorption of the uranyl ion on Dowex 50.

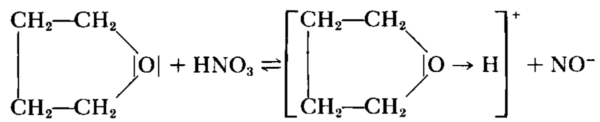
As already mentioned, the distribution coefficient of uranium increases to a maximum at 60% tetrahydrofuran (see Table 2) and then decreases rapidly. This increase is very probably due to enhanced ion-pair formation between the uranyl ion and the fixed ions of the exchanger and is caused by the decrease of the dielectric constant (DC) with increasing percentage of tetrahydrofuran. As seen from Table 2, this increase in adsorption is observed in all organic solvents, except that in most instances no maxima are observed in the whole concentration range of organic solvents from 0 to 90%. In all these cases the distribution coefficient of uranium is inversely proportional to the DCs of the mixed aqueous-organic systems; i.e., with a decrease in DC, which means an increase in the percentage of the organic solvent component (water has a much higher DC value), uranium is more strongly retained by the resin, in other words, the formation of ion pairs is enhanced.

The decrease of the distribution coefficient of uranium from 60 to 90% tetrahydrofuran can be explained by the fact that in this region of organic solvent concentrations the uranyl ion displays an increasing tendency to form with the nitrate ion a neutral weakly dissociated compound—uranyl nitrate—or with nitric acid an anionic nitrate complex. This is promoted by the decrease in the DC of the organic solvent in this region. Because tetrahydrofuran has by far the lowest DC value (see Table 2) it is comprehensible that this effect of DC is much greater in this case than with the other organic solvents. As a consequence, the tetrahydrofuran-water-nitric acid mixture can much more effectively compete with the cation exchanger for the uranyl ion than in the presence of other organic solvents, of higher DC. That even in these solvents this effect is operative, although to a much less extent, is evident from the fact that the distribution coefficient of uranium [e.g., in the 90% organic solvent mixtures (see Table 2)] is in most cases smaller than that of the divalent transition metals [e.g., cobalt and nickel (see Table 1)] for which the selectivity of the resin in pure aqueous nitric acid solution is the same as for uranium.

However, the DC of the solvent is not the only decisive factor regulating adsorption, as is evident from the values shown in Table

2. Judging from these, uranium adsorption from 90% acetic acid should be about the same as from the comparable tetrahydrofuran mixture. Furthermore, in acetone uranium should behave as in *n*-propanol. That this is not the case is most probably due to influences of the constitution and configuration of the organic solvent molecule. It is the opinion of the author that these influences are due to the Lewis basicity of the solvent in question. If one assumes that the basicity is in the case of tetrahydrofuran much higher than that of acetic acid (which is very probably true, because in the tetrahydrofuran molecule no hydrogen ion is present to repel an approaching proton of a donor molecule such as nitric acid), the reaction shown by Eq. (1) is more likely to proceed from left to right, and consequently uranium will be less strongly adsorbed.

To illustrate the competition between ion exchange and the extraction effect of the organic solvent the oxonium mechanism can be used. This mechanism is frequently employed to explain liquid-liquid extraction procedures involving ion association complexes. Thus in the liquid phase, e.g., in 90% tetrahydrofuran-10% 6 *N* nitric acid, the reactions schematically represented by the Eqs. (1) and (2) may be thought to occur:



(1)

Tetrahydrofuran acting as Lewis base

Oxonium salt or liquid anion exchanger in nitrate form $[(THFH)^+NO_3^-]$

$$(THFH)^+NO_3^- + (UO_2(NO_3)_3)^- \rightleftharpoons (THFH)^+(UO_2(NO_3)_3)^- + NO_3^-$$

or

$$(THFH)^+NO_3^- + (UO_2(NO_3)_2)^0 \rightleftharpoons (THFH)^+(UO_2(NO_3)_3)^- \qquad (2)$$

Ion association complex or liquid anion exchanger loaded with uranyl nitrate complex

At high concentrations of tetrahydrofuran the oxonium salt (liquid anion exchanger) is formed to a higher percentage and hence can more effectively compete with the solid cation exchanger Dowex 50 for the uranyl ion, which, as shown by Eq. (2), may be present as anionic nitrate complex or neutral salt, which means that the formation of the weakly ionized ion association complex is enhanced. Consequently, reaction (2), if uranium is present as anionic nitrate complex, can be regarded as an ion-exchange process taking place in the liquid phase, and thus can effectively compete with the ion-exchange reaction of Eq. (3), which occurs on Dowex 50.

$$2R_sSO_3^-H^+ + UO_2^{2+} \rightleftharpoons (R_sSO_3^-)_2UO_2 + 2H^+ \qquad (3)$$

(R_s = resin matrix).

Behavior similar to that of uranium in the 90% tetrahydrofuran–10% 6 *N* nitric acid medium is shown by bismuth and thorium, which are much less strongly adsorbed on Dowex 50 from this medium than from mixtures containing a lower percentage of tetrahydrofuran (see Table 1), so that in these two cases, reactions (1) and (2) occur to a greater (bismuth) or lesser (thorium) extent. Thorium, although it forms a much stronger anionic nitrate complex (*3*), is much more strongly adsorbed on Dowex 50 than uranium and bismuth are, owing to its higher valency.

Under similar conditions [90% tetrahydrofuran–10% 5 *N* nitric acid (v/v)], uranium, thorium, and bismuth are also not strongly retained by the anion exchanger Dowex 1 (*4*), although thorium and bismuth, especially, are known to form stable anionic nitrate complexes (*3*). They are, however, strongly retained on this resin from pure aqueous nitric acid systems (*3*) as well as from organic solvent–nitric acid media containing high concentrations of aliphatic alcohols (*5*) [e.g., isopropanol (*6*) and acetic acid (*7*)]. This is strong evidence that the CIESE system tetrahydrofuran–nitric acid can also effectively compete with this strongly basic anion exchanger for these metal ions. A further indirect proof that the CIESE principle is also effective in the case of thorium in acetone–nitric acid solutions is evident from the fact that the distribution coefficient of thorium increases less strongly than that of lanthanum with an increase in acetone concentration. Thus the distribution coefficient of thorium in 90% acetone–10% 6 *N* nitric acid (v/v) on Dowex 1 has a value of 530, whereas that of lanthanum under identical experimental conditions shows a value of 1740 (*8*). At acetone concentrations below 80% the situation is reversed, i.e., the distribution coefficient of thorium is much higher than that of lanthanum, which is in accordance with results found in pure aqueous nitric acid solutions (3) and other mixed aqueous organic solvent–nitric acid mixtures (5). Thus in a mixture consisting of 60% acetone–30% water and 10% 6 *N* nitric acid (v/v) the distribution coefficients of thorium and lanthanum are 85.2 and 7.2, respectively (8).

An explanation similar to that in the case of uranium can be given with respect to the nonadsorbability of iron(III) on Dowex 50 and Dowex 1 from hydrochloric acid–tetrahydrofuran or acetone solutions. The excessive tailing shown by the elution curve of iron(III) [see Fig. 1(b)] from Dowex 1 can be explained by the fact that two anion exchangers compete for the anionic ferric chloride complex $(FeCl_4)^-$: the liquid exchanger [see Eq. (1)] and Dowex 1. Because of the strongly basic character of the solid exchanger, its influence on the equilibrium represented by Eq. (2) is much greater than that of Dowex 50. Consequently, the equilibrium of the anion exchange (liquid-liquid extraction in the mobile phase) is continually disturbed, so that the iron can only be removed from the resin column after prolonged washing with the mixture.

The reversal of elution sequence of cobalt and nickel, which is evident from a comparison of the elution curves of these two elements (Fig. 1), is due to the fact that the anionic chloride complex of cobalt is much more stable than that of nickel. Consequently, it will react much more readily according to Eq. (2) and hence be less strongly retained by Dowex 50. On the other hand, it will be more strongly adsorbed on Dowex 1, for the reason mentioned above for iron. As in the case of uranium, when using other organic solvents (such as the aliphatic alcohols, ether alcohols, or liquid organic acids such as acetic acid) the CIESE effect is more or less pronounced. From such media the iron is adsorbed by cation or anion exchangers in a manner similar to adsorption from pure aqueous hydrochloric acid solutions, but not as strongly. On this fact is based a selective method for the separation of uranium from large amounts of iron(III) and many other elements, using 90% methyl glycol–10% 6 *N* hydrochloric acid (v/v) as the sorption solution and Dowex 1 as the exchanger. Under these conditions, uranium is very strongly retained, whereas iron(III) and many other elements can be washed out from a column of this resin with a mixture of the same composition. This procedure was employed for the isolation of microgram amounts of uranium from ferrous alloys (9), marine sediments (*10*), sea-water samples (*10*), etc. In pure aqueous hydrochloric acid solutions uranium cannot be separated from iron(III), because of the similar distribution coefficients of the two elements at all acid concentrations. Separation can be effected, however, if iron is reduced to the divalent oxidation state before the separation, e.g., through the addition of ascorbic acid. The separation is more effective in hydrochloric acid–mixed aqueous-organic systems (*11,12*) because the CIESE effect reduces the adsorption of tervalent iron from solutions containing a high percentage of an organic solvent such as methanol (*11*) or ethanol (*12*). (Even after careful reduction of iron a certain amount of ferric iron is found in the sorption solution.) Furthermore, the affinity of the exchanger for uranium is increased, owing to the decrease of the DC of the mixture in the presence of an organic solvent.

Summing up, it can be said that the CIESE principle in the cases cited is superior to methods employing conventional separation principles of liquid-liquid extraction and ion exchange in pure aqueous systems if the following points are taken into consideration:

1. After elution of uranium or iron from the exchanger by means of tetrahydrofuran–nitric acid or tetrahydrofuran– or acetone–hydrochloric acid, respectively, subsequent fractionation of the adsorbed metal ions is possible on the column.
2. Because no salting-out agents or high concentrations of strong acid are required, these separations can easily be carried out free of interferences that might be caused in the presence of these reagents.
3. The bulk constituent of the mixture to be separated [Fe(III) or UO_2(II)] may be present in gram amounts without interfering with the isolation of traces or smaller amounts of the other metal ions, and hence the CIESE principle is especially suited for trace analysis (e.g., for the analysis of ferrous materials, uranyl nitrate, etc.).

It is to be expected that CIESE will find more extensive analytical application in the near future by the use of other organic solvents, mixtures of solvents, various organic or inorganic acids and bases, chelating agents, etc., which have hitherto not been investigated. Because the separations can be performed virtually automatically and recovery of the organic solvents by distillation or partition in the presence of salting-out agents is feasible, its use in radiochemistry and preparative chemistry is advocated.

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