Separation of lanthanides and some associated elements by liquid-liquid extraction and reverse phase thin layer chromatography using high molecular weight amine-citrate system

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Primene JM-T has been used to study the extraction of Ce(III), Gd(III) and Yb(III) and other associated elements such as Y(III), Ti(IV), V(IV), Zr(IV), Th(IV) and U(VI) from citric acid medium. Based on distribution data it has been possible to achieve separation of lanthanides from titanium, zirconium, thorium and uranium with high separation factors. The amine-citrate system has also been used to study the reverse-phase TLC behaviour of Ce(III), Gd(III) and Yb(III) and Y, Ti, V, Zr, Th and U. Binary separations involving lanthanides have also been achieved on amine impregnated layers.

The use of citrate buffers in ion exchange chromatography of lanthanides is well known. However, scanty information is available on the extraction of these metal ions from aqueous citrate medium. The present communication reports the extraction behaviour of three representative lanthanides, namely Ce(III), Gd(III) and Yb(III) along with that of Y(III), Ti(IV), V(IV), Zr(IV), Th(IV) and U(VI) at different citric acid concentrations. Based on the distribution data optimum conditions for the separation of lanthanides from Ti(IV), Zr(IV), Th(IV) and U(VI) have been worked out. The feasibility of the separation procedure is checked by taking binary mixtures. A reverse-phase thin layer chromatographic (TLC) study investigating the effect of concentration of amine and citric acid on $R_f$ values of some lanthanides and other elements has also been carried out to provide some useful correlation between the thin layer and solvent extraction data and to find out optimum conditions for TLC separation.

**Results and discussion**

**Liquid-liquid extraction studies**

The extraction of Ce(III), Gd(III) and Yb(III) was studied using different diluents and it was observed that extent of extraction was much higher with chloroform and benzene but chloroform was preferred as a diluent because of lesser emulsification tendencies. All amines were converted into the citrate form by pretreatment with citric acid. It is found that the extraction of metal ions remains more or less invariable in the pH range of 3-4 and for all studies the equilibrium pH of the aqueous phase was maintained in the above range. The extraction was studied in Primene JM-T, Amberlite LA-2, Alamine-336 and Aliquat-336 and found to be the highest in Primene JM-T. Hence, Primene JM-T was used. The plots of log D versus log [amine] for Ce(III), Gd(III) and Yb(III) give slopes equal to three, suggesting extraction of these metal ions by anion exchange mechanism. A concentration of 0.10 M of Primene JM-T has been chosen for other studies.

The effect of varying [citric acid] (1.0 x 10^{-3} to 5.0 x 10^{-3} M) on the extraction of Ce(III), Gd(III), Yb(III), Y(III), Ti(IV), V(IV), Zr(IV), Th(IV) and U(VI) was studied in chloroform solution of Primene JM-T. The extraction of Ce(III) and Gd(III) increases with increase in [citric acid] up to 5.0 x 10^{-3} M thereafter it remains more or less constant. But in case of Yb(III), the extraction is very poor and remains constant throughout the acid range. In case of Ti(IV), Zr(IV), Th(IV) and U(VI) extraction is very high (90-100\%) in the range of [citric acid]. However, extraction of Y(III) and V(IV) is 60-75\% under the above conditions. Based on these data, separation of lanthanides can be achieved from Ti(IV), Zr(IV), Th(IV) and U(VI).

Experiments for separations were conducted by taking binary mixtures of Ti(VI), Zr(IV), Th(IV), or
U(VI) with Ce(III), Gd(III) or Yb(III) in varying concentration ratios. Titanium, zirconium, thorium and uranium could be recovered quantitatively from organic phase by washing with 6M HCl whereas thorium with 3M H₂SO₄. The results indicated that retention of lanthanides in aqueous phase was above 95% whereas Ti(V), Zr(V), Th(IV) and U(VI) could be recovered from organic phase to an extent of 90%.

**TLC studies**

To study the effect of citric acid on the hR₉ values of the metal ions several plates impregnated with 3% (≈ 0.1 M) Primene JM-T were run with varying [citric acid] (1.0 × 10⁻² - 1.0 M). Results are given in Table 1. It is observed that the hR₉ values increase with increase in [citrate] indicating an inverse relationship between the distribution coefficient and the hR₉ values. Further, Ti(IV), V(IV), Zr(IV), Th(IV) and U(VI) ions are strongly retained and no significant movement is observed even on increasing [citric acid]. These metal ions show consistently high extraction in Primene JM-T at all [citric acid]. Apparently, the tailing seems to disappear at higher [eluant].

On development of chromatographic plates coated with varying concentrations of Primene JM-T it is observed that the hR₉ values of the lanthanide ions decrease with the increase in [Primene JM-T] (Table 2). Here too, there is an inverse correlation between hR₉ values and the %E of the metal ions. Testa reported a similar trend on hR₉ values of rare earths and some other metal ions using trioctylamine coated papers. The trends in hR₉ values of metal ions are more or less similar on layers coated with different high molecular weight amines like Aliquat-336, Alamine-336 and Amberlite LA-2. As expected the hR₉ values in Primene JM-T are the lowest.

Using Primene JM-T-citrate system the optimum conditions for binary separations of Ce(III), Gd(III) or Yb(III), from other associated metal ions [Y(IV), Zr(IV), Th(IV) or U(VI)] are 3% impregnated and 0.1 M eluant. Similar separations have also been achieved using other amines like Aliquat-336, Alamine-336 and Amberlite LA-2.

The above results establish the utility of amine-citrate system for separating lanthanides from some of the commonly associated elements by both liquid-liquid extraction and TLC.

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**References**