A method is proposed for the determination of binary mixtures of lanthanides in nitric acid using a non-aqueous thermometric system. If the atomic numbers of the lanthanides differ by 7 or more then the precision and reproducibility of the method are analytically acceptable.

**Keywords:** lanthanide salts, non-aqueous media, thermometric titration

**Introduction**

Reviews of methods for the assay of lanthanides [1–3] generally recommend procedures for the final assay of these elements to be done with aqueous solutions of the salts using either titrimetric or spectrophotometric methods. In many instances the separation of these elements from one another is necessary prior to the determination of any one element.

The behaviour of lanthanides in non-aqueous solvents, including acetic acid, alcohols, ketones and other solvents has been investigated [4] and it has been reported that in a methanol-acetone mixture, the lanthanide nitrates behave as acids of different strengths and consequently individual elements can be determined by differential potentiometric titration. One of the problems associated
with such procedures and involving solvent extraction is that of ensuring the presence of sufficient polar materials to obtain a relatively high conductivity of the solution. In some cases of extraction of the lanthanides from monazite sand, the siliceous materials must be removed before any assay can be done, since it affects both electrode and visual indicator systems. These factors do not cause problems in thermometric titrimetry since the sensors used do not depend upon the electrical conductivity of the solution and are not affected by the presence of chemically inert materials.

The most serious factor that affects the thermometric method is generally the heats of mixing of the solvent used for the titrand and that used for the titrant. Preliminary investigations of the solvents considered for use (methanol, ethanol, propanol, iso-propanol, butanol (1y:2y:3y)) indicated that most of the solvents gave large endothermic heats of mixing with the acetone solution of the nitrate. It was found that only a small thermal effect is obtained when mixing 1:1 v/v methanol/acetone solution of lanthanum nitrate with ca 0.5 M KOH in methanol as envisaged in the titration system. It was thus considered that the thermometric titration of some lanthanide nitrates in this mixed solvent system could be achieved without interference from the heat of dilution of the titrant. It was also recognized that the onset of the dimerisation of acetone, catalysed by hydroxide ion [5], may also be of use in enhancing the endpoint of these titrations.

The reaction, in an acetone medium, between lanthanide nitrates (of the general formula \(\text{Ln(NO}_3\text{)}_3\)) and an methanolic solution of potassium hydroxide can be represented:

\[
\text{Ln(NO}_3\text{)}_3 + 3\text{KOH} = \text{Ln(OH)}_3 + 3\text{KNO}_3
\]

and a reaction such as this may be considered to be suitable for investigation since many precipitation reactions have considerable entropy changes and hence, considerable molar enthalpy changes and the consequent enhancement of these by the low specific heats of the solvents, results in relatively high temperature changes in the system with concordant high sensitivity.

Experimental

The general apparatus for continuous thermometric titrations (i.e.) the reaction vessel, the titrant delivery system and the temperature sensing and recording system have been previously reported [6]. In all the work reported here, the recorder used had a full scale deflection of 250 mm for 2 mV off-balance of the