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# SOLUTION THERMOCHEMICAL ASSAY OF LANTHANIDES

## The thermometric titration of binary mixtures of some lanthanide salts in non-aqueous media

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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

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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 silicaceous 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 $Ln(NO_3)_3$ and an methanolic solution of potassium hydroxide can be represented:

$$\underset{(soln)}{Ln(NO_3)_3} + \underset{(soln)}{3KOH} = \underset{(ppt)}{Ln(OH)_3} + \underset{(soln)}{3KNO_3}$$

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

Wheatstone Bridge and moved forward with a speed of 120 mm/min. The delivery system was arranged to operate such that a chart length of 300 mm corresponded to a delivery of 1.0 ml of the titrant. This enabled a precision of 0.003 ml (i.e. 1 mm of chart distance) to be attained.

### *Reagents*

The lanthanide oxides used throughout this work were 99.8% pure (except for neodymium oxide which was 99.5%)

The lanthanide nitrates were prepared by dissolving the appropriate amounts of oxides in concentrated nitric acid with gentle heating. The solutions obtained were evaporated to incipient dryness and each of the residues obtained was dissolved in a 1:1 methanol:acetone solution. The methanol and the acetone were purified as follows:

1. Methanol. Fractional distillation: the fraction distilling at 64.5°C was collected and kept over anhydrous calcium sulphate.
2. Acetone. To eliminate easily oxidizable impurities, sufficient solid potassium permanganate was added to produce a pink solution. After 3–4 days the solution was dried by shaking with fused calcium chloride and then distilled.
3. 0.5 $M$ methanolic potassium hydroxide was prepared by dissolving KOH (ca 2.8 g of Analar grade reagent) in the dried methanol (100 ml). The solution was standardised, by thermometric titration, against recrystallised benzoic acid.

### *Determination of individual lanthanide nitrates*

#### Procedure

Transfer 15 ml of the test solution into a 30 ml capacity polypropylene bottle with a wall thickness of 1–2 mm. Place the bottle in the middle of a 20 cm cube of expanded polystyrene. Immerse the tip of the thermistor and the tip of a delivery tube into the solution. Stir the solution until thermal equilibrium is obtained (ca 2–3 min). Add the titrant at a constant speed using a peristaltic pump via a silicone rubber delivery tube. A typical enthalpogram obtained is shown in Fig. 1; the results are shown in Table 1.

### *Determination of binary mixtures of some lanthanide nitrates*

Mixtures were prepared using known amounts of the assayed individual lanthanide nitrate solutions. The procedure is the same as used above and a typical enthalpogram is shown in Fig. 2. Analytically acceptable results for individual elements were obtained when the atomic numbers differed by at least 7. The results are given in Table 2.

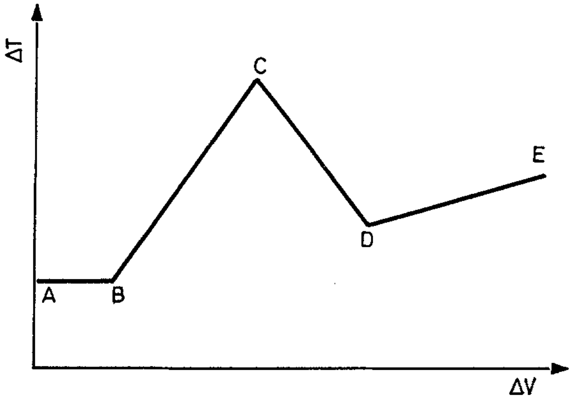

**Fig. 1** Enthalpogram obtained from the titration of a single lanthanide nitrate with methanolic KOH in a 1:1 v/v methanol:acetone medium. AB = base line; BC = exothermic reaction between the mineral acid ($HNO_3$) remaining in solution and the methanolic KOH; CD = endothermic reaction between the lanthanide nitrate and the methanolic KOH; D = end point; DE = "overshoot" i.e. addition of excess of titrant without further analyte reaction. The exothermic dimerisation of acetone catalysed by the first excess of hydroxide ion causes the sharpening of the end point

**Table 1** Assay of some individual lanthanide nitrates in an acetone medium

| Element | Amount (as $Ln_2O_3$) / mg | | Recovery / |
|---|---|---|---|
| | Taken | Found | % |
| La | 1.50 | 1.47 | 98.0 |
| | 53.7 | 53.6 | 99.8 |
| Nd | 1.20 | 1.24 | 103.3 |
| | 7.19 | 7.28 | 101.2 |
| Sm | 1.30 | 1.32 | 101.5 |
| | 4.14 | 4.10 | 99.0 |
| Ho | 1.10 | 1.12 | 101.8 |
| | 4.90 | 4.83 | 98.5 |
| Er | 1.60 | 1.61 | 100.6 |
| | 8.16 | 8.10 | 99.2 |
| Lu | 1.80 | 1.78 | 98.8 |
| | 9.27 | 9.36 | 100.9 |

Results are obtained from the average of quadruplicate assays

**Table 2** Assay of some mixtures of lanthanide nitrates in an acetone medium

| Element (Z) | Amount /mg (as $Ln_2O_3$) | | Recovery / |
|---|---|---|---|
| | Taken | Found | % |
| La (57) | 11.89 | 11.80 | 99.2 |
| Tb (65) | 8.90 | 8.85 | 99.4 |
| La (57) | 12.54 | 12.43 | 99.1 |
| Dy (66) | 14.36 | 14.61 | 101.7 |
| La (57) | 10.89 | 10.85 | 99.6 |
| Ho (67) | 12.48 | 12.43 | 99.6 |
| La (57) | 17.42 | 17.56 | 100.8 |
| Er (68) | 10.30 | 10.31 | 100.1 |
| La (57) | 10.98 | 10.96 | 100.6 |
| Yb (70) | 12.35 | 12.38 | 100.2 |
| La (57) | 9.10 | 9.07 | 99.6 |
| Lu (71) | 15.00 | 14.88 | 99.2 |
| Ce (58) | 10.56 | 10.55 | 99.9 |
| Dy (66) | 9.95 | 9.89 | 99.4 |
| Ce (58) | 10.56 | 10.55 | 99.9 |
| Er (68) | 10.30 | 10.25 | 99.5 |
| Ce (58) | 10.56 | 10.55 | 99.9 |
| Lu (71) | 15.00 | 14.89 | 99.3 |
| Pr (59) | 10.30 | 10.27 | 99.7 |
| Ho (67) | 11.67 | 11.50 | 98.5 |
| Ce (58) | 10.50 | 10.70 | 98.1 |
| Tb (65) | 9.80 | 9.97 | 101.7 |

Results are obtained from the average of quadruplicate assays.

With Ce/Sm; Ce/Gd; Pr/Tb; Gd/Lu mixtures the intermediate equivalence points were indistinct and extrapolation gave results which were not within 3% of the mean.

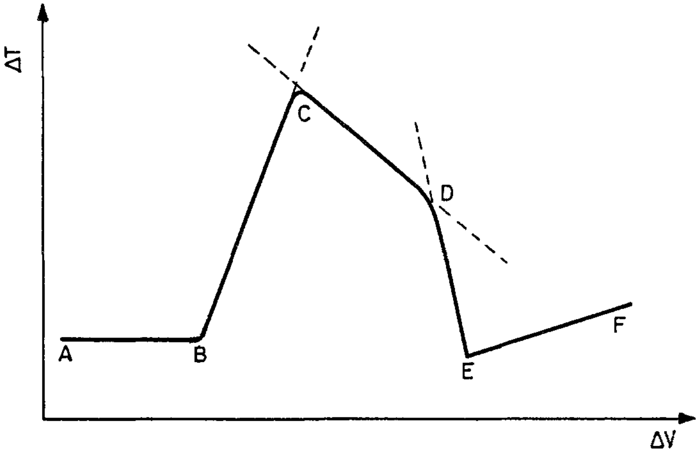

**Fig. 2** Enthalpogram obtained from the titration of a binary mixture of selected lanthanides (La+Ln with atomic number at least 7 greater than La i.e. La-Lu) in 1:1 v/v methanol:acetone medium with methanolic KOH. AB = base line; BC = exothermic reaction between traces of mineral acid ($HNO_3$) and methanolic KOH; CD = endothermic reaction between nitrate of heavier lanthanide and methanolic KOH; DE = endothermic reaction between lanthanum nitrate and methanolic KOH; E = final end point; EF = "overshoot" i.e. addition of an excess of titrant without any reaction with analytes. Exothermic heat change is caused by the catalysed dimerisation of the acetone used

### *Determination of a mixture of nitric acid and lanthanum and lutetium nitrates*

The procedure is as above. The results are given in Table 3.

### *Statistical parameters for the method*

The reproducibility of the method, the standard deviation and associated parameters were assessed by analysing various series of mixtures of two different nitrates. The results of the analyses and the calculated statistics are given in Table 4.

## Results and discussion

In a mixture of acidic compounds of different acidic strengths, it is normal to have the highly ionisable species titrated first. These will, generally, suppress the ionisation of the weaker acids, which will not be sufficiently ionised to be titrated

**Table 3** Assay of some mixtures of nitric acid, lanthanum and lutetium nitrates in a 1:1v/v acetone /methanol medium

| Element | Amount /mg (as $Ln_2O_3$ and $HNO_3$) | | Recovery / |
|---|---|---|---|
| | Taken | Found | % |
| La | 14.63 | 14.78 | 101.0 |
| Nitric acid | 54.50 | 54.57 | 100.1 |
| Lu | 25.00 | 24.83 | 99.3 |
| Nitric acid | 54.50 | 54.57 | 100.1 |
| La | 14.63 | 14.78 | 101.0 |
| Lu | 12.50 | 12.52 | 100.1 |
| Nitric acid | 54.50 | 54.57 | 100.1 |
| La | 9.10 | 9.07 | 99.6 |
| Lu | 15.00 | 14.88 | 99.2 |
| Nitric acid | 31.14 | 31.18 | 100.1 |

Results are obtained from the average of quadruplicate assays.

The amounts of nitric acid are calculated from the volumes of standardised acid used. The acid was standardised thermometrically against purified sodium carbonate

**Table 4** Determination of a series of mixtures of lanthanum and lutetium nitrates

| Assay | Lanthanum | Lutetium |
|---|---|---|
| 1. | 15.31 | 12.20 |
| 2. | 15.50 | 12.36 |
| 3. | 15.26 | 12.15 |
| 4. | 15.35 | 12.36 |
| 5. | 15.42 | 12.20 |
| 6. | 15.31 | 12.30 |
| 7. | 15.35 | 12.15 |
| 8. | 15.31 | 12.36 |
| 9. | 15.42 | 12.30 |
| 10. | 15.26 | 12.20 |
| 11. | 15.23 | 12.30 |

Amounts taken in each aliquot are nominally 15.35 mg of lanthanum nitrate and 12.25 mg of lutetium nitrate.

Standard deviation: La: –0.08 mg; Lu: –0.08 mg until the hydrogen ion concentration resulting from the partially neutralised strong acid, is low enough to allow the weaker acids to ionise.

As expected, the titration sequence for the mixture of nitric acid and the lanthanide nitrates is similar to the sequence found by Miller and Thomason [7] when titrating mixtures of nitric acid and thorium nitrate.

The slight but significant decrease in the electropositive character of the lanthanides with increase in the atomic number is a consequence of the lanthanide contraction and is manifested in several of their reactions. It is, thus, expected that the lighter lanthanide nitrates will be more hydrolysed than are the heavier lanthanide nitrates, i.e. the amount of dissociation of the lanthanide aquo-complex (probably hexa-aquo-) to give aquo-hydroxy complexes will depend upon the size of the lanthanide ion. There will, therefore, be a gradual change in the pKa values of the lanthanide aquo-complexes and whilst thermometric methods are more sensitive than potentiometric methods for the titration of acids of different pKa's, it is necessary to have lanthanides which are at or near to opposite ends of the lanthanide series before a sufficient decrease in pKa is obtained to give clear intermediate equivalence points.

Whilst the acidic strength of the aquo-complexes is greater than that of the keto-enol tautomerism of the acetone, (since the base catalysed dimerisation of the acetone does not occur until the lanthanide complexes have been titrated and this is used to indicate the endpoint of the lanthanide titration) attempts to enhance the difference in the acidic strengths of the lanthanide aquo-complexes by the use of alcohols other than methanol were unsuccessful because the heat of mixing of the titrant and titrand solutions causes the curve at either the onset of titration or the endpoint to be so rounded that extrapolation is required and the necessary analytical precision is lost.

Using the proposed method the standard deviations obtained for the determination of a mixture of lanthanum and lutetium nitrates are below 1% for each of the metal ions and indicate the feasibility of the method.

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**Zusammenfassung** — Es wird ein Verfahren unterbreitet, wie unter Anwendung nichtwäßriger thermometrischer Systeme die Zusammensetzung von binären Lanthanidengemischen in Salpetersäure ermittelt werden kann. Genauigkeit und Reproduzierbarkeit des Verfahrens sind analytisch annehmbar, wenn sich die Ordnungszahl der Lanthaniden um 7 oder mehr unterscheidet.