923. *The Analysis of Inorganic Compounds by Paper Chromatography. Part V.* The Separation and Detection of Certain Lanthanons.*

By F. H. Pollard, J. F. W. McOmie, and H. M. Stevens.

A preliminary account is given of the application of complex-forming mobile phases to the separation on paper and cellulose columns of mixtures of (i) lanthanum, cerium, praseodymium or neodymium, and ytterbium; (ii) yttrium and lanthanum; (iii) yttrium, lanthanum, and cerium; (iv) yttrium, lanthanum, and ytterbium; (v) yttrium and erbium from cerium; and (vi) yttrium and erbium from lanthanum. Their detection on paper is also described.

The well-known separation of the rare earths on ion-exchange resins has brought about a remarkable change in the availability of these elements in a pure state, but hitherto there have been no records of separations of lanthanons on paper or cellulose, although several authors have hinted that they have attempted them. Burstall, Davies, Linstead, and Wells (*J.*, 1950, 516) reported that it was possible to separate thorium and scandium from rare earths by the use of tetrahydrosylvan containing 5% v/v of water and 10% v/v of nitric acid (*d* 1·42) as the mobile phase. In this process, the relative humidity of the atmosphere within the chromatographic tank had to be controlled by placing a saturated solution of ammonium chloride at the bottom of the tank. Scandium has also been separated from the rare earths by methyl acetate containing 10% v/v of water and 5% v/v of nitric acid (*d* 1·42). Kember (*Analyst*, 1952, **77**, 78), from the same laboratory, has recently described the quantitative separation of thorium from other metals in monazite sand, by allowing a nitrate solution of the latter to pass through a column of cellulose previously prepared in ether containing 12·5% v/v of nitric acid (*d* 1·42). During this work, it was noted that Ce^{4+} moved with thorium but that Ce^{3+} moved far less quickly; hence, it was found necessary to reduce all the Ce^{4+} to the tervalent state before attempting a separation. On using cellulose untreated with nitric acid, yttrium nitrate was found to be partly extracted, but with nitric acid-treated cellulose, yttrium moved more rapidly than the "true" rare earths, but not as rapidly as thorium. Scandium nitrate moved with thorium nitrate unless tartaric acid was added to the original nitrate solution in order to inhibit the movement of scandium. With these precautions, Kember has devised a quantitative separation of thorium.

Following the principles of our previous work in adding complex-forming agents to the mobile phase, we have achieved successful separations of certain lanthanons from one another by the use of 8-hydroxyquinoline ("oxine") in butanol, both on filter-paper and on cellulose columns. This also provides a simple method for identification as well as the possibility of separating larger quantities or purifying impure specimens of lanthanons.

We now describe: (i) the separation of lanthanum, "didymium" (*i.e.*, praseodymium and neodymium, symbolised "Di"), and ytterbium from one another, and from small quantities of cerium; (ii) the separation of yttrium from lanthanum, and from lanthanum and cerium; (iii) the separation of yttrium, lanthanum, and ytterbium from one another; (iv) an apparent partial separation of yttrium and erbium from one another and their separation from lanthanum and cerium; and (v) a separation of cerium from yttrium and erbium.

Experimental

(a) *Preparation of the Solvent Mixture for the Mobile Phase.*—For the separations of lanthanum, "didymium," and ytterbium from cerium, 400 ml. of *n*-butanol were shaken thoroughly with an equal volume of distilled water and, after a short time, the upper layer was separated. To 400 ml. of the latter, 20 g. of 8-hydroxyquinoline and 40 ml. of glacial acetic acid were added, and the mixture was warmed until homogeneous. Suitable quantities of this

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* Part IV, *J.*, 1951, 1863.

solvent mixture were then used for separations upon cellulose columns, or upon sheets of filter-paper (*e.g.*, during the examination of the eluate fractions from a column).

For separations where yttrium or erbium were present, it was found that these two cations and cerium in their presence tended to " tail " backwards when separations were attempted with the above solvent mixture on acid-washed Whatman No. 1 filter-paper. The most concentrated spots, with elimination of tailing, were obtained if 14% v/v glacial acetic acid was added to the solvent mixture, instead of 10%. For cellulose-column separations of mixtures containing yttrium or erbium, a solvent mixture consisting of 400 ml. of water-saturated butanol, 20 g. of 8-hydroxyquinoline, and 56 ml. of glacial acetic acid was therefore employed for the elution. This mixture was found to give a separation of lanthanum and cerium inferior to that obtained by using the less acid mixture.

(b) *Preparation of the Cellulose Column.*—A quantity of I.C.I., acid-washed, powdered cellulose was stirred with sufficient N-hydrochloric acid to produce a thin suspension, filtered off by suction, and washed with cold distilled water until the filtrate was neutral to B.D.H. universal indicator paper. The cellulose was then freed from as much water as possible by suction, and dried at 50—60° in an oven. It was thoroughly stirred into a thin suspension with 150—200 ml. of the prepared solvent mixture (see above). The washing of the cellulose with hydrochloric acid improved the separations and removed small quantities of foreign ions such as Mg^{2+}, whose oxine complexes gives a fluorescent spot similar to that of La^{3+}.

One end of a glass tube 120 cm. long and 1·5 cm. in diameter (internal) was drawn out to a jet, and a small plug of glass-wool inserted into the tube so that it acted as a porous retaining washer behind the jet. The thin cellulose suspension was slowly poured into the tube until the latter was about a quarter full. The compressed air supply was then connected to the top of the tube, thereby forcing the liquid phase through the column under pressure and effecting a tight packing of the cellulose. The latter process was marked by the appearance of a pale cream layer at the base of the column, which gradually extended upwards towards the constantly falling liquid level. When the head of the pale cream band had reached to within a few cm. of the liquid level, the air supply was disconnected, and a further quantity of cellulose suspension poured into the tube. This was packed under air pressure as before, and the process repeated until there was a tightly packed pale cream column of cellulose 90—95 cm. long. Careful packing of the column is essential for successful separations.

(c) *Preparation of the Lanthanon Mixtures.*—(i) The mixture used for the lanthanum, " didymium," and ytterbium separations from cerium was prepared from lanthanum nitrate (B.D.H.), " didymium " nitrate (B.D.H. technical), and ytterbium acetate (tetrahydrate). A spectroscopic examination of these materials showed that small amounts of lanthanum were present in the ytterbium and " didymium " salts, and that the latter also contained some cerium, as shown also by the fact that a bright orange precipitate was produced on addition of hydrogen peroxide and ammonia solution to a solution of the " didymium " salt.

(ii) For the other separations, synthetic mixtures were made from cerous nitrate (technically pure), an yttrium–erbium basic nitrate, yttrium nitrate (B.D.H. quality), which yielded an orange-coloured oxide on calcination, lanthanum nitrate (B.D.H.), and ytterbium acetate tetrahydrate.

The mixed salts were warmed with a little 2N-nitric acid and evaporated gently to dryness. This ensured that basic compounds, free ceria, etc., were converted into soluble salts. To the solid residue were added dropwise a few ml. of the organic solvent mixture to be used as the mobile phase, and the whole was gently warmed until all the solid was dissolved. If the temperature was allowed to rise above about 45°, blackening occurred, owing possibly to the oxidation of some organic constituent by Ce^{4+}, and such a mixture produced inferior separations on the cellulose column.

(d) *Elution from the Column.*—The prepared lanthanon mixture was poured on the top of the cellulose column, and when it had soaked into the latter, a reservoir containing about 200 ml. of solvent mixture was inserted into the top of the tube. The reservoir had a simple constant-level device so that a continuous supply of the mobile phase trickled on to the cellulose. The column was supported over an automatic fraction-collector of the type described by Hough, Jones, and Wadman (*J.*, 1949, 2511) and the eluate was collected in about 2-ml. quantities at intervals.

The rate of flow of the mobile phase through the column was an important factor in the separations, since the slower the rate of flow, the better the separations obtained. This seemed to be largely controlled by the closeness of the packing of the powdered cellulose, and hence the care with which this was done. Experiments with different columns ranging from 61 to

95 cm. suggested that usually the length of column did not have any great effect upon the separations, though no very exact measurements were made to establish this point.

(e) *Analysis of the Eluate Fractions.*—For the analysis, it was desired to convert the lanthanon fractions into oxides. This was done by transferring the selected fraction to a clean porcelain crucible, heating it until the solution began to boil, and then igniting the vapour. When all the butanol had burnt off, the tarry residue was more strongly heated to burn off the 8-hydroxyquinoline and carbon, leaving the lanthanons as oxides.

A portion of the residue was then analysed by paper-strip chromatography, Whatman No. 1 filter-paper being used, which had previously been washed once in N-hydrochloric acid, and then in distilled water until free from acid. The oxide residue from the eluate was dissolved in 2—3 drops of 2N-nitric acid with gentle warming, and then evaporated almost to dryness to remove excess of nitric acid. The latter was found to affect the movement of the cations on the filter-paper chromatogram. The residue was now dissolved in 1—2 drops of distilled water, and one drop of this solution was used to obtain a paper-strip chromatogram in the usual way, the same solvent mixture being used as that employed for the column elution.

After drying, the chromatogram was examined in ultra-violet light after exposure to ammonia. Under such conditions, some of the lanthanon oxine complexes fluoresced, and others remained as dark spots. Finally, the paper was sprayed with a mixture of ammonia solution and hydrogen peroxide, and the colours and persistence of the spots were observed in daylight.

The R_F values of the individual lanthanons, and their behaviour in the tests described, were determined in preliminary experiments with such pure materials as were available.

The following factors were used to assist in the identification of the lanthanons present in the fractions under examination: (i) The colour of the oxide residue, and its solution in nitric acid. (ii) The R_F values and colours of the oxine complex spots in daylight, and their behaviour on the paper chromatogram with (*a*) ultra-violet light in the presence of ammonia, and (*b*) the hydrogen peroxide–ammonia reagent. (iii) Spectroscopic examination. These properties are summarised in Table 1.

TABLE 1.

Ion	Oxide	Nitric acid soln.	Oxine complex spot	Fluor. in U.-V. light	NH_3–H_2O_2 treatment of oxine complex	R_F
Lanthanum ...	White	Colourless	Pale yellow-brown	+ (Green)	Turns brown	$<0{\cdot}5$
Cerium $^{4+}$	Cream	Orange	Reddish-purple	Nil	Turns orange (to purple on standing)	$<0{\cdot}5$
" Didymium "	Brown	Greenish	Yellow	Nil	Yellow	$<0{\cdot}5$
Erbium	Pink	Pink	Yellow	Nil	Yellow	$\simeq 0{\cdot}5$
Yttrium	White *	Colourless	Yellow	+ (Golden-brown)	Yellow	$\simeq 0{\cdot}5$
Ytterbium ...	White	Colourless	Yellow	Nil	Yellow	$>0{\cdot}5$
Nitrate anion	—	—	Yellow	Nil	Faded	$>0{\cdot}5$
Magnesium †	White	Colourless	Pale green	++ (Green)	Pale green	$<0{\cdot}5$

* B.D.H. yttrium nitrate gives orange impure oxide. † Present in unwashed I.C.I. cellulose.

Notes on Sensitivities of Tests.—Some indication of the sensitivities of the tests employed to detect lanthanons on filter-paper can be judged from an investigation into this question for lanthanum and cerium. (1) By the fluorescence of the oxine complex held over ammonia, and viewed under ultra-violet light, $1{\cdot}5 \times 10^{-5}$ g. of La^{3+} could be detected: this corresponded to a drop of a solution containing $1{\cdot}5 \times 10^{-3}$ g. per ml. (2) By the purple colour of the oxine complex of cerium, subjected to the following treatments: (*a*) Exposed to ammonia $7{\cdot}5 \times 10^{-6}$ g. of Ce^{4+}; (*b*) sprayed with ammonia–hydrogen peroxide, 3×10^{-6} g. of Ce^{4+}; (*c*) as (*b*), but set aside for 24 hours, 6×10^{-7} g. of Ce^{4+}.

The success with which separations of lanthanons can be effected is recorded in the following tables, and it is clear that this technique may lead to good separations of some members of this group, and to a means of purifying others. The experiments quoted are in the nature of a preliminary report, for there is still a considerable field to be investigated.

Table 2 is in two sections to indicate procedure. Part A records the analysis of the eluate fractions as they are collected from the column. The analysis which was carried out, first on every fifth eluate fraction, and then on intermediate fractions (to determine precisely at which points the particular lanthanons started to emerge), is based on the bulk of oxide residue and on the relative size and intensity of the spots on the paper chromatograms prepared with a spot of the eluate solution. From such analyses it was possible to decide which fractions could be combined to obtain a particular lanthanon in bulk. Part B records the results of the analysis of such combined fractions together with other relevant data such as the weights of the lanthanon (as oxide) put on the column, the length of column, and the rate of flow of the eluate.

TABLE 2. *Lanthanum, " didymium," and ytterbium, and the removal of cerium.*

A. Eluate analysis for the separation shown in Table 2*B* (*c*).

	Eluate fractions																
Lanthanon	35	41	47	53	59	65	71	74	77	83	89	95	101	107	113	119	125
Ytterbium ...	—	+	++	+	×	—	—	—	—	—	—	—	—	—	—	—	—
" Didymium "	—	—	—	—	—	—	×	++	+	+	+	×	×	×	—	—	—
Cerium	—	—	—	—	—	—	—	—	×	++	++	++	++	×	×	—	—
Lanthanum	—	—	—	—	—	—	—	—	—	—	+	++	++	++	++	++	++

Key to symbols. — Nil; × Trace; + Fair amount; ++ Bulk.

B. Analysis of bulk fractions. (All amounts are relative to the initial concentrations, and are not absolute values.)

	Wts. (approx.) (as mg. of oxide) of cations put on column				Column data		Yb_2O_3		
	Ce (CeO_2)	Yb	" Di "	La	Length (cm.)	Flow rate (ml./hr.)	Combined fractions and wt. (mg.)	Chrom. analysis	Spect. analysis
(*a*)	150	90	100	260	85	12	31—35 (n. w.) *	Pure	—
							36—37 (n. w.)	Trace Ce	
(*b*)		60	135	190	95	9	46—53 (20)	Pure	no La; Ce not detected
							54—59 (10)	Trace Ce	
(*c*)		60	220	190	95	5	40—54 (30)	Pure	—
(*d*)		25	180	150	61	9	33—40 (10)	Pure	no La; Ce not detected
							42—43 (10)	Trace Ce, Di	

	" Di_2O_3 "			La_2O_3		
	Combined fractions and wt. (mg.)	Chrom. analysis	Spect. analysis	Combined fractions and wt. (mg.)	Chrom. analysis	Spect. analysis
(*a*)	No sepn. of Di from Ce	—	—	68—70 (n. w.)	Mg present + trace Ce	
(*b*)	65—69 (10)	Trace Ce	no La; Ce not detected	91—94 (35)	Trace Ce, Di	—
	71—73 (10)	Little Ce	—	101—103 (15)	Pure	—
(*c*)	67—73 (10)	Pure	no La; Ce not detected	120—125 (15)	Pure	no " Di;" Ce not detected
(*d*)	49—53 (25)	Trace Ce	*ca.* 1% La; Ce not detected	78—80 (20)	Trace Ce, Di	—
				81—86 (25)	Pure	no " Di;" Ce not detected

* n. w. = Not weighed.

Note : Numbers shown in parentheses denote weight of recovered oxide samples.

Notes on Table 2. On the whole, the results obtained with conditions of run (*c*) are best, where the rate of flow is the slowest and the column is 95 cm. long. Comparing runs (*b*) and (*d*), where the rates of flow are the same but the column-lengths are different, it is seen that the longer column, *i.e.*, run (*b*), yields the best results. In run (*a*), where the rate of flow is double that in (*c*), the separation is inferior.

TABLE 3. *Separations of yttrium, lanthanum, cerium, and ytterbium.*

Column length = 90 cm. Flow rate = 5 ml./hour.

The cations were eluted in the order : Yb, Y, Ce, La.

	Wt. of lanthanon (oxide) in mixture (mg.)		Wt. of oxide recovered in purest fractions (mg.)	Purity
(*a*)	Y	35	25	Free from La
	La	38	20	Free from Y
(*b*)	Y	70	15	Free from Ce, La
	Ce (as CeO_2)	39	nil	—
	La	150	15	Trace Y, Ce
(*c*)	Yb	23	15	Free from La, trace Y
	Y	35	15	Trace La, Yb
	La	100	75	Trace Y, Yb

Notes on Table 3. The initial yttrium fractions yielded a white or very pale brown oxide on calcination, whereas the oxides of the later yttrium fractions were somewhat darker. The sample of B.D.H. yttrium nitrate used to make the synthetic mixture gave a brownish-orange oxide on calcination, so it probably contained small amounts of other lanthanons, *e.g.*, terbium; hence, as the oxides from the initial fractions from the column were whiter than those from the later ones, the former were considered to be purer. Spectroscopic analysis of the two fractions supported this view, as a number of lines present in the emission spectrum of the later yttrium oxide fractions were missing in the spectrum of the earlier fractions. The combined lanthanum oxide fractions recorded in Table 3 (*a*) were free from yttrium by chromatographic, spectroscopic (emission), and spectrophotometric analyses, but by the last method, holmium (3%) and erbium (2·7%) were found. These two lanthanons were possibly present in the original B.D.H. yttrium nitrate.

TABLE 4. *Separations of yttrium, erbium, and cerium or lanthanum.*

Column length = 90 cm. Flow rate = 5 ml./hour.

The cations were eluted in the order : Y ⟶ Er *, Ce or La.

Wt. of lanthanon in mixture (mg.)		Wt. of oxide recovered in purest fractions (mg.)		Purity
Y–Er (as basic nitrate)	200	(*a*) White oxide	5	Free from Ce
		(*b*) Pale pink oxide	10	Free from Ce
		(*c*) Pink oxide	10	Free from Ce
Ce (as CeO_2)	78		20	Trace Y, Er
Y–Er (as basic nitrate)	200	(*a*) White oxide	5	Free from La
		(*b*) Pale pink oxide	10	Free from La
		(*c*) Pink oxide	40	Free from La
La (as La_2O_3)	95		30	Little Y, Er present

* See Notes on Table 4.

Notes on Table 4. The Y_2O_3–Er_2O_3 fractions marked (*a*) yielded colourless solutions in nitric acid, those marked (*b*) gave pale pink solutions, and those labelled (*c*) gave bright pink solutions. Hence, although there was not a good separation, the evidence seems to point to an enrichment in erbium from fractions (*a*) to (*c*).

One can conclude from this preliminary survey that separations of a number of lanthanons are possible both on filter-paper strips and on columns of powdered cellulose, though the conditions required are, as would be expected, much more difficult to establish than for the common cations. From this work, it is clear that reasonably good bulk separations can be obtained with mixtures containing not more than one element from each of the groups (i) lanthanum, (ii) cerium, neodymium, and praseodymium, (iii) yttrium and erbium, and (iv) ytterbium. Only apparent partial separations have as yet been obtained between Y and Er, and no separation occurs at all between Nd and Pr. The investigation is being continued.

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THE UNIVERSITY, BRISTOL.

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