The Analysis of Inorganic Compounds by Paper Chromatography. Part VI.* Further Studies on the Separation and Detection of Lanthanons.

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Tests for distinguishing between lanthanon groups and certain individual lanthanons are given.

A number of substances were investigated for use in the preparation of complex-forming mobile phases and, of the latter, those consisting of 8-hydroxyquinoline in a *n*-butanol–water–acetic acid system yielded the best lanthanon separations. These appeared to depend on differences in ionic radii, with Y coming between Gd and Dy.

Factors affecting the percentage yield of " didymium " from a mixture with cerium have been investigated, and successful separations between members of the cerium group and between this group and Y are described.

Brief qualitative investigations suggested some resolution in two " heavy-earth " mixtures.

OUR previous work (Part V *) using 8-hydroxyquinoline (oxine) as a complexing and detecting agent has been extended. Antipyrine, *o*-aminophenol, and a number of substituted quinolines and pyridines have also been investigated as complex-forming reagents in the separation of lanthanons, but none of these compounds is as efficient as oxine. The movement of lanthanons in oxine-containing mobile phases probably depends on the stability of the " oxinates " in addition to their partition coefficients. Paper-strip experiments upon a number of binary mixtures have shown that in general the degree of resolution increases with the difference in the radii of the lanthanon ions. Yttrium is interpolated between Gd and Dy in the separations (see p. 3438).

The resolution of " didymium "–cerium mixtures on cellulose columns is very satisfactory if small loads are employed. These experiments suggest that in Part V (*loc. cit.*) the columns were too heavily loaded to permit of maximum resolution. The degree of separation is also diminished by increasing the Ce content of the mixture. If the loads are small good resolutions are obtained among lanthanons of the cerium group, and between this group and Y. With antipyrine as the complex-forming agent a good separation between La and Y has been obtained on a column, but resolutions among the metals of the cerium group are inferior to those when oxine is used. The resolutions of a La–Y mixture on paper strips using 8-hydroxyquinaldine or 3-hydroxypyridine as the complex-forming agent are as good as those obtained with antipyrine, but expense prohibited the use of these reagents on the column scale. Qualitative column experiments have indicated some resolution in mixtures containing (*a*) Y, Er, Tm, Yb, and Lu; (*b*) Y, Gd, Dy, Ho, and Er.

Individual lanthanons and lanthanon groups can be distinguished by using four spray-reagents [pyrogallol-4-carboxylic acid, ammonium purpurate (murexide), tetrahydroxy-

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* Part V, *J.*, 1952, 4730.

flavonol (morin) and oxine] upon spots of the nitrates, in addition to the behaviour and R_F values of lanthanon spots on paper strips run in oxine-containing solvents.

EXPERIMENTAL

Preparation of Lanthanon Solutions.—Available lanthanon material consisted of: B.D.H. samples of yttrium nitrate, lanthanum nitrate, and cerous nitrate, and "Specpure" oxides of praseodymium (Pr_6O_{11}), neodymium, samarium, gadolinium, terbium, dysprosium, erbium, thulium, and lutecium. Ytterbium oxide was obtained from a sample of the acetate kindly given by Dr. J. K. Marsh.

Aqueous nitrate solutions were prepared by evaporating to dryness 2—3 mg. of the required oxide or nitrate with a few drops of 2N-nitric acid, and dissolving the residue in 0·25—0·5 ml. of water. The following binary mixtures were prepared similarly: La–Ce, La–Pr, La–Sm, La–Gd, La–Y, La–Dy, La–Yb, Ce–Nd, Ce–Sm, Ce–Y, Ce–Dy, Ce–Yb, Pr–Gd, Pr–Y, Pr–Dy, Pr–Yb, Sm–Gd, Sm–Y, Sm–Dy, Sm–Yb, Gd–Dy.

Reagents for Distinguishing between Lanthanons.—Dried lanthanon nitrate spots on strips of Whatman No. 1 paper were treated by spraying them with the following solutions, and examining them as indicated:

(1) 2% (w/v) Pyrogallol-4-carboxylic acid ("Py·CO_2H") in 50% alcohol, followed by a saturated aqueous solution of sodium hydrogen carbonate; the strip was examined after being kept for a few minutes, or gently warmed. (2) Aqueous ammonium purpurate ("murexide") solution; the strip was examined on exposure to ammonia. (3) 1% (approx.) (w/v) 8-Hydroxyquinoline (oxine) in 50% alcohol; the dried strip was examined over ammonia in ultra-violet light. (4) Tetrahydroxyflavonol ("morin") in 50% alcohol; the dried strip was examined in ultra-violet light. The results are recorded in Table 1.

TABLE 1. (ff = brightly fluorescent, f = fluorescent, d = dark spot in ultra-violet light.)

Cation	(1) "Py·CO_2H"	(2) "Murexide"	(3) "Oxine"	(4) "Morin"
Y	Brown	Pinkish orange	* ff (yellow-green)	ff (green)
La	Bright purple	Bright violet	ff (green)	ff (green)
Ce^{3+}	Purple, turning brown	,,	d	d
Pr	Bright purple	,,	d	d
Nd	,,	,,	d	d
Sm	Dirty purple	Purplish pink	d	d
Gd	Purple brown	,,	* f (deep brown)	f (green)
Tb	Brown	Pink	d	d
Dy	,,	Orange-yellow	d	d
Er	,,	,,	d	d
Tm	,,	,,	d	d
Yb	,,	,,	d	d
Lu	,,	,,	* ff (yellow-green)	ff (green)

* Different colours are obtained if the cations are run on paper strips in an oxine-containing solvent (see Table 2).

With "Py·CO_2H" and "murexide" colours are readily produced with the lighter earths, but the response of the heavier earths is much poorer. The latter, being weaker bases, are presumably more easily precipitated under the alkaline conditions and so do not respond to the tests.

It is noteworthy that the lanthanons which fluoresce with "oxine" and "morin" are those which contain the most stable electronic groupings in their orbitals.

All four reagents have been found useful in detecting and distinguishing between lanthanons of the "light" and "heavy" groups on paper strips which have been run in eluants containing no powerful complex-forming substances (*e.g.*, oxine).

Preparation of Eluants.—Mixtures of the constituents for eluants (A)—(D) were warmed until a homogeneous solution was obtained; (E) and (F) were prepared as described.

(A) Water-saturated *n*-butanol (100 ml.), oxine (5 g.), acetic acid (10 ml.)
(B) ,, ,, (100 ml.), ,, (5 g.), ,, (14 ml.)
(C) ,, ,, (100 ml.), ,, (5 g.), ,, (20 ml.)
(D) ,, ,, (100 ml.), antipyrine (11 g.), ,, (10 ml.)
(E) *n*-Butanol (100 ml.), acetic acid (13 ml.), and water (30 ml.) were mixed; to 110 ml. of the mixture 5 g. of oxine were added (with warming to render the solution homogeneous).

(F) To a mixture of *n*-butanol (100 ml.) and water (30 ml.) ethanol was added until a homogeneous solution was obtained upon vigorous shaking. To 100 ml. of this mixture antipyrine (11 g.) and acetic acid (10 ml.) were added (with warming until homogeneous).

n-Butanol could be replaced by other alcohols, and mixtures of alcohols, which could contain 15% of water and which had similar (or slower) drip-rates compared with *n*-butanol from a capillary tube at constant head of liquid. Of such alcohols, *sec.*-butyl, *tert.*-butyl, or mixtures of (i) *n*-amyl (60 ml.) and *iso*propyl (40 ml.) or (ii) *n*-hexyl (70 ml.) and ethyl (30 ml.) were used to replace *n*-butyl alcohol in paper-strip experiments on La–Pr and La–Y mixtures. To prepare the eluant, 15 ml. of water, 5 g. of oxine (or 11 g. of antipyrine), and 10 (or 14) ml. of acetic acid were added to 85 ml. of the alcohol or alcohol mixture.

The following complex-forming agents gave inferior results to oxine when used in the *n*-butanol–acetic acid system for paper-strip experiments: (i) 8-Hydroxy-2-methylquinoline, (ii) 2-hydroxyquinoline, (iii) 2-hydroxypyridine, (iv) 3-hydroxypyridine, (v) 8-hydroxy-7-iodoquinoline-5-sulphonic acid, (vi) *o*-aminophenol. Partial resolution of a La–Y mixture occurred with (i) and (iv); (ii), (v), and (vi) would not dissolve sufficiently to give a 5% w/v solution.

Section A. Paper-strip Experiments.

Spots of the nitrate solutions were run individually upon acid-washed Whatman No. 1 paper strips in eluant (C). After drying, the strips were examined in daylight and ultra-violet light. The R_F values of the oxinate spots were calculated, and the behaviour of the spots in ultra-violet light noted (Table 2). To prevent backward tailing of the metals Sm to Lu a considerable concentration of acetic acid was necessary.

TABLE 2.

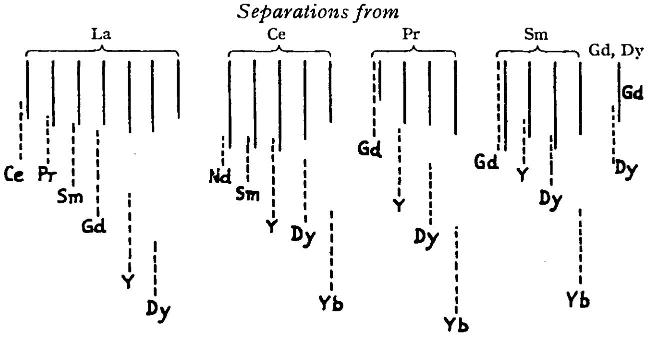
Lanthanon	Colour of oxide	R_F value of oxinate spot or most concentrated zone	Behaviour in U.V. light
Y	White *	0·47	f (golden)
La	,,	0·34	f (green)
Ce	Cream	0·40	d
Pr	Dark brown	0·40	d
Nd	Blue	0·43	d
Sm	Pale yellow	0·44	d
Gd	White	0·44	d
Tb	Dark brown	0·47	d
Dy	Yellowish	0·50	d
Er	Pink	$\simeq$0·50	d
Tm	White	0·66	d
Yb	,,	0·70	d
Lu	,,	0·59 to 0·76	f (golden-brown)

* B.D.H. yttrium nitrate yields a pale orange-brown oxide.

Notes on Table 2.—The R_F values follow, in general, the order of the increasing ionic radii and of decreasing basicity of the lanthanons. The oxinates of the more electrovalent lanthanons of the "light" group would be expected to be less stable than those of the "heavy" group. Consequently, the latter would tend to move to higher R_F values in the organic phase, while the former may tend to be adsorbed on to the paper as ions, giving low R_F values. The movement and separation of lanthanons is cut down by reducing the oxine content of butanol–acetic acid solvent systens, and the total exclusion of the complex-forming reagent causes practically no movement as the lanthanons are presumably adsorbed on to the paper in an ionic state. A similar phenomenon was noted when studying the movement of certain cations in solvent systems containing benzoylacetone (Elbeih, McOmie, and Pollard, *Discuss. Faraday Soc.*, 1949, **7**, 183). The stability of lanthanon "oxinates" may therefore be an important factor which operates in conjunction with a partition mechanism in these separations.

From the results of paper-strip runs upon the binary mixtures in eluant (E) it was observed that backward tailing was prevented by the presence of La. When this metal was not present such tailing could be eliminated by: (i) increasing the acetic acid content of the eluant (this was detrimental to separations between light earths), (ii) using dilute lanthanon solutions, (iii) dissolving the nitrates in the eluant instead of in water—this probably caused the formation of oxinates in solution before the strip run begins: hydrolysis, and the adsorption of cations by the cellulose were thereby prevented.

The Figure shows, diagrammatically, resolutions which were obtained by running aqueous nitrate spots of the binary lanthanon mixtures upon acid-washed Whatman No. 1 paper strips in eluant (E) for approximately 14 hr.



The lines represent to scale the lengths and positions of the "oxinate" spots after elution under the conditions described on p. 3436.

Notes on the Figure—(i) Where one spot is formed (*e.g.*, with Pr, Gd) the colour of the oxide obtained by ashing various portions was used to indicate the distribution of cations within the spot. Thus Pr (dark brown ash) was found to concentrate at the rear, and Gd (white ash) at the front of the zone.

(ii) The greater the difference in the basicities, the more completely will a pair of lanthanons be resolved. Thus from the Figure it is seen that the degree of separation in the four series can be arranged as shown below. Differences in ionic radii are given in parentheses :

(*a*) La, Yb > La, Dy > La, Y > La, Gd > La, Sm > La, Pr > La, Ce
(0·22) (0·15) (0·16) * (0·11) (0·09) (0·06) (0·04)
(*b*) Ce, Yb > Ce, Dy > Ce, Y > Ce, Sm > Ce, Nd
(0·18) (0·11) (0·12) * (0·05) (0·03)
(*c*) Pr, Yb > Pr, Dy > Pr, Y > Pr, Gd
(0·16) (0·09) (0·10) * (0·05)
(*d*) Sm, Yb > Sm, Dy > Sm, Y > Sm, Gd
(0·13) (0·06) (0·07) * (0·02)

From the results marked * it is noted that the degree of separation of La, Pr, and Sm from Y is intermediate between that of the same metals from Gd and Dy. Y is also interpolated between Gd and Dy in Table 2, which suggests that its basicity lies between that of these two lanthanons.

According to Moeller and Kremers (*Chem. Reviews*, 1945, **37**, 97), Y should theoretically follow Dy in order of decreasing basicity, but examples in which Y occupies a place above Dy are quoted by these authors and by Marsh (*J.*, 1947, 118).

Section B. Column Separations.

Preparation of Lanthanon Mixtures.—The Y, La, Ce, Pr, and Nd material used was as described above. In addition the following samples were available : Technical didymium nitrate (containing 12·5% of CeO_2 and a little La) ; mixtures of the compositions (*a*) La_2O_3 18, CeO_2 50, Pr_2O_3 8, Nd_2O_3 24% ; (*b*) mixed lanthanon sodium sulphates containing Y_2O_3 10, Er_2O_3 17, Tm_2O_3 6·8, Yb_2O_3 57, and Lu_2O_3 10% ; (*c*) Y_2O_3 34, Gd_2O_3 40, Dy_2O_3 23, Ho_2O_3 1·9, Er_2O_3 1%.

The lanthanon oxides were converted into nitrates which were dissolved in the eluant before being placed on the column as described in Part V (*loc. cit.*). With (*a*), fuming to dryness with concentrated hydrochloric acid and then with nitric acid was necessary to get the constituents into solution owing to the high Ce content. In (*b*) lanthanon hydroxides were precipitated by alkali, the mixed bases being then centrifuged, washed with water, and dissolved in nitric acid.

Preparation of Cellulose Columns.—The procedure described in Part V was modified. For this work all columns were packed under compressed air or nitrogen with a thin suspension of cellulose in the eluant mixture containing no complex-forming agent. This method was more efficient in eliminating air bubbles from the column, besides being more economical. The complex-containing eluant was run for a few cm. on the column before the mixture of cations was put on.

Analysis of Eluate Fractions.—This was carried out as described in Part V. In separations of lanthanons from Ce, paper-strip analysis was not essential as the first (or last) trace of Ce to be eluted imparted a pale yellow colour to an otherwise colourless lanthanon solution in nitric acid, and a pale green colour to an otherwise bluish-purple didymium solution. The purity of samples was tested by paper-strip chromatography, and selected lanthanon material, which appeared to be pure, was analysed by arc-spectroscopy as a check.

TABLE 3. *Separations of* Y, La, Ce, *and* " Di " (= Pr + Nd) *on narrow columns.*

Column : 100 cm. × 1·5 cm. (int. diam.). Flow rate = 2·5—3·0 ml./hr. on I.C.I. cellulose, 8—9 ml./hr. on " ashless " cellulose.
The cations were eluted in the order : Y, " Di " (Pr or Nd), Ce, La.

Mg. of lanthanon oxide in mixture		Cellulose	Eluant	Mg. of lanthanon oxide recovered in purest fractions		Purity
Pr_6O_{11}	20	I.C.I.	(A)	Pr_6O_{11}	15	Free from La
La_2O_3	20			La_2O_3	9	,, Pr
Nd_2O_3	50	I.C.I.	(A)	Nd_2O_3	30	,, La
La_2O_3	50			La_2O_3	30	,, Nd
Nd_2O_3	50	I.C.I.	(D)	Nd_2O_3	31	,, La
La_2O_3	50			La_2O_3	nil	—
" Di_2O_3 "	35	I.C.I.	(A)	" Di_2O_3 "	20	,, Ce
CeO_2	5			CeO_2	nil	—
" Di_2O_3 "	35	Ashless	(A)	" Di_2O_3 "	22	,, Ce
CeO_2	5			CeO_2	nil	—
" Di_2O_3 "	17·5	I.C.I.	(A)	" Di_2O_3 "	10	,, Ce, La
CeO_2	2·5			CeO_2	nil	—
La_2O_3	200			La_2O_3	100	,, Ce, Di
Y_2O_3	35	I.C.I.	(A)	Y_2O_3	14	,, Ce, La
CeO_2	20			CeO_2	nil	—
La_2O_3	150			La_2O_3	not collected	—
Y_2O_3	35	Ashless	(A)	Y_2O_3	19	,, Ce, La
CeO_2	20			CeO_2	nil	—
La_2O_3	150			La_2O_3	not collected	—
Y_2O_3	35	I.C.I.	(F)	Y_2O_3	25	0·01% La
La_2O_3	37·5			La_2O_3	12	Trace of Y

TABLE 4. *Separations of* Y, La, Ce, " Di " (= Pr + Nd) *on a wider column of ashless cellulose.*

Column : 100 cm. × 5·2 cm. (int. diam.). Flow rate : 100 ml./hr. (20—22 ml. fractions collected). The cations were eluted in the order : Y, " Di," Ce, La.

Mg. of lanthanon oxide in mixture		Eluant	Mg. of lanthanon oxide recovered in purest fractions		Purity
" Di_2O_3 "	210	(A)	" Di_2O_3 "	128	Free from Ce
CeO_2	30		CeO_2	not collected	—
Y_2O_3	420	(B)	Y_2O_3	317	,, Ce, La
CeO_2	240		CeO_2	not collected	—
La_2O_3	225		La_2O_3	not collected	—

Notes on Tables 3 *and* 4.—Technical didymium nitrate constituted the didymium–cerium used; 100 mg. of the nitrate contained 35 mg. of " Di_2O_3 " and 5 mg. of CeO_2.

The yields of didymium diminished if an increase was made in the column load or the cerium content of the mixture (by adding cerous nitrate). Table 5 illustrates this.

Note on Table 5.—From section (*a*) it is noted that ashless cellulose is more efficient than the I.C.I. variety. Owing to the greater flow-rate with the former, the break-through time is considerably reduced.

Resolutions of Mixtures (b) *and* (c).—40 mg. of the oxides of each mixture were converted into nitrates which were run on narrow columns in the usual manner.

Mixture (b). Column (I.C.I. cellulose) 124 cm. Flow rate 2·5 ml./hr. Eluant (C). The cations appeared to be eluted in the order Lu, Yb, (Tm), Y, Er. Early fractions on burning gave white oxides from which colourless nitrate solutions were obtained. Paper-strip chromatography yielded with the first 4—5 fractions a deep golden-brown fluorescent zone at $R_{\mathrm{F}} \simeq 0{\cdot}7$ (Lu) and with the rest of the early fractions a dark zone at $R_{\mathrm{F}} \simeq 0{\cdot}7$ (Yb). Later fractions gave pink oxides and nitrate solutions (Er), which on paper-strip analysis yielded a golden fluorescent spot at $R_{\mathrm{F}} \simeq 0{\cdot}5$ (Y).

TABLE 5.

(a)

Mg. of didymium nitrate run on small column	Yield (%) of " Di_2O_3 " free from Ce obtained		Mg. of didymium nitrate run on small column	Yield (%) of " Di_2O_3 " free from Ce obtained	
Cellulose :	I.C.I.	Ashless	Cellulose :	I.C.I.	Ashless
100	57	63	200	30	43
125	34	46	300	21	not run
150	32	not run	400	14	not run

Mg. of didymium nitrate run on large column	Yield (%) of " Di_2O_3 " free from Ce obtained	Mg. of didymium nitrate run on large column	Yield (%) of " Di_2O_3 " free from Ce obtained
600	61	1500	46
1200	51	3000	33

(*b*)

CeO_2 (%) in didymium nitrate (100 mg. run)	Yield (%) of " Di_2O_3 " free from Ce obtained	CeO_2 (%) in didymium nitrate (100 mg. run)	Yield (%) of " Di_2O_3 " free from Ce obtained
12·5 (tech. nitrate alone)	57	37·5	28
25	47	50 [mixture (a)]	15

Mixture (c). Column (ashless cellulose) 100 cm. Flow rate 9 ml./hr. Eluant (B). The cations appeared to be eluted in the order Dy ⟶ Y. Gd, Ho, and Er were not detected with certainty.

Paper-strip analysis on the oxides of the initial fractions mixed with Pr_6O_{11} gave two substantial separate spots which did not fluoresce in ultra-violet light. These were deemed to be Pr (upper) and Dy, as Gd was not separated totally from Pr. Er is usually eluted with Y (see below), and Ho was thought to be present in too low concentration ($<2\%$) to be solely responsible for the lower spot.

Similar treatment of the oxides from late fractions gave two almost separate spots, an upper one which did not fluoresce in ultra-violet light (Pr) and a lower one which fluoresced golden-yellow (Y).

From the results of the paper-strip and column experiments it is predicted that good separations would be obtained between La or Ce and Pr to Lu (including Y) and between Pr or Sm and Dy to Lu (including Y), provided that the correct conditions of column length, flow rate, and load are observed.

Most of the oxine used could be recovered from the eluates by distillation.

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