Lanthanon Sulphites and their Separation by Selective Oxidation.

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Evidence is produced suggesting that under certain conditions lanthanon " bisulphite " solutions contain the anion $[\mathrm{Ln(SO_3)}]^{3-}$. The preparation and properties of simple and complex lanthanon sulphites are described.

Oxidation of double sulphites to double sulphates has been employed as a means of separating the light from the heavy lanthanons. By fractional oxidation of the anionic trisulphito-complex to cationic sulphates, which are progressively removed by a cation-exchange resin, good separations are obtained within the light and the heavy lanthanon group.

The success achieved in separating the lanthanons by means of their complexes with polycarboxylic amino-acids has tended to overshadow the use of simpler compounds for this purpose; so it is appropriate to re-examine some of the longer-known, simpler reactions of the lanthanons and to assess their value for separation of lanthanons. The use of lanthanon sulphites as the starting point of a homogeneous double sulphate precipitation appeared attractive although there was little information available on their chemistry.

The simple lanthanon sulphites were first prepared by Berthier (*Ann. Chim. Phys.*, 1843, **7**, 74) and Marignac (*ibid.*, 1853, **38**, 167), and some of the alkali double sulphites were prepared and examined by Cuttica (*Gazzetta*, 1923, **53**, 769), but hitherto their only application to separations has been for the removal of thorium from lanthanon compounds (Chavastelon, *Compt. rend.*, 1900, **130**, 781; Bartek, *Z. anorg. Chem.*, 1905, **44**, 87; Grossman, *ibid*, p. 229). A more detailed study of these compounds was therefore undertaken and two processes have been devised which provide effective means of separating the lanthanons.

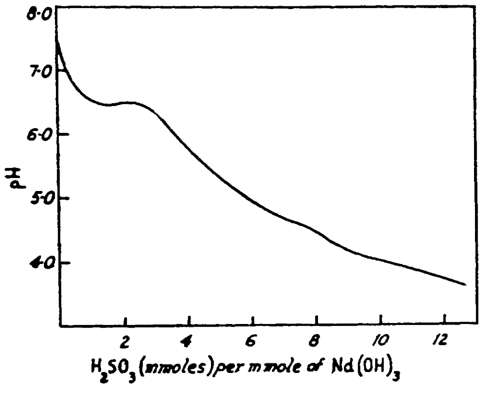
Lanthanon " Bisulphites."—On passage of sulphur dioxide through an aqueous slurry of lanthanon oxide, hydroxide, or carbonate, a solution is obtained in which the lanthanon has been assumed (Cuttica, *loc. cit.*) to be associated with the bisulphite ion as $Ln(HSO_3)_3$. On removal of part of the sulphur dioxide, by strongly heating the solution or reducing the pressure, lanthanon sulphite is precipitated, but can be redissolved by the further passage of sulphur dioxide. The reaction has been represented by Cuttica as the equilibrium :

$$2Ln(HSO_3)_3 \rightleftharpoons Ln_2(SO_3)_3 + 3SO_2 + 3H_2O$$

and this is supported by the titration curve for $Ln(OH)_3$ against H_2SO_3 (Fig. 1), which indicates the formation of a compound with a Ln : SO_3 ratio of 1 : 3. However, this is equally compatible with evidence now presented that under certain conditions the lanthanon is associated with SO_3^{2-} as a complex anion.

A spectrophotometric examination of neodymium " bisulphite " solutions showed effects similar to those previously observed in sequestered lanthanon compounds (Vickery, *J.*, 1952, 421). The 673 mμ absorption band of 0·1M-neodymium chloride was absent from 0·1M-neodymium " bisulphite." Bands at 510 and 475 mμ were unaffected but the 576, 522, and 463 mμ bands were displaced 12, 10, and 6 mμ respectively to longer wavelengths, with the 576 mμ band displaying six discrete peaks. The other bands showed similar evidence of dissection. These changes were most marked between the pH values 5·5 and 6·1. Over the pH range 5·5—3·5, neodymium sulphite was gradually precipitated, but it redissolved at pH 3·5, and the absorption spectrum assumed the form characteristic of ionic neodymium compounds; above pH 6·1, until the hydroxide was precipitated quantitatively at *ca.* pH 7·3, it was characteristic of the ionic form. Thus the spectroscopic evidence is consistent with the formation of a complex which is stable within pH range 5·5—6·1.

FIG. 1. *Titration of* $Nd(OH)_3$ *against* H_2SO_3.



In Fig. 2 a comparison is made of acid–base titrations of lanthanon chloride and lanthanon " bisulphite " solutions. The curve for the latter, unlike that for the chloride, shows points of inflexion corresponding to 3, 5, and possibly 7 equiv. of alkali. At pH 3·8, corresponding to 3 equiv. of alkali, a sodium salt was precipitated of composition $Na_3[Ln(SO_3)_3]$ in which the lanthanon has its usual covalency of six. This formula being assumed correct, subsequent steps in the titration could be considered as signifying progressive replacement of sulphite to form the basic salts $Na_3[Ln(SO_3)_2(OH)_2]$ and $Na_3[Ln(SO_3)(OH)_4]$ and finally $Ln(OH)_3$.

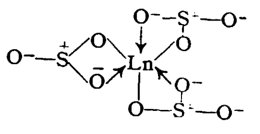
The evidence thus available is suggestive of the initial formation, not of bisulphite, but of the complex anion $[Ln(SO_3)_3]^{3-}$ and this should be readily detected by ion-exchange techniques. On using an anionic resin giving chloride ions on exchange, three chloride ion equivalents were found to be replaceable by one equivalent of lanthanon " bisulphite " solution (Table 1) :

$$3Cl_{resin} + H_3[Ln(SO_3)_3] \longrightarrow Ln(SO_3)_{3\,resin} + 3HCl$$

TABLE 1. *Uptake of lanthanons by anion-exchange resins.*

[100 ml. of " bisulphite " solution equiv. to 1 g. of $Ln(OH)_3$ equilibrated with 25 g. of Deacidite FF.]

pH	Ln	Uptake (%)	Cl^- in eluate (g.)	Ratio, $Cl_{elut.}/Ln_{abs.}$	pH	Ln	Uptake (%)	Cl^- in eluate (g.)	Ratio, $Cl_{elut.}/Ln_{abs.}$
5·3	La	100	0·458	2·92	6·2	La	99·9	0·420	3·03
	Yb	100	0·515	3·07		Nd	100	0·600	3·20
5·6	La	100	0·425	3·06		Yb	99·9	0·505	3·14
6·0	Nd	99·8	0·590	3·11					



The possible presence in the " bisulphite " solution of such compounds as $H_2[Ln(SO_3)_3]^-$ and $H[Ln(SO_3)_3]^{2-}$ cannot be disregarded, but the constancy of the exchange value between the critical pH values supports the view that the lanthanon trisulphito-ion, $[Ln(SO_3)_3]^{3-}$, is the main component of lanthanon " bisulphite " solutions. A possible configuration of this ion would consist of three four-membered chelate rings (see inset), and such a weakly chelated structure could account for the spectroscopic observations and for the lability of the ion under the influence of heat or reduced pressure.

Oxidation of Lanthanon Trisulphito-complex.—Solutions of these lanthanon compounds are readily oxidised by air or oxygen to the sulphates (Fig. 3). The rate of oxidation of the yttrium solution occupies an anomalous position between those of neodymium and samarium. This is out of conformity with the serial order of simple ionic size, but is consistent with the formation of complex compounds (Marsh, *J.*, 1947, 1084; 1951, 1337, 1461; Vickery: " Chemistry of the Lanthanons," Butterworths, London, 1953). Unlike the lanthanon complexes previously studied, however, the stability of the trisulphito-complex decreases with increase in atomic number of the lanthanon. It is evident from the oxidation curves that, under the conditions of these experiments, oxidation to sulphates occurs without the intermediate formation of sulphites. For example, there is no inflexion in the oxidation curve for the yttrium compound suggesting a change from the covalent to the ionic form which would place it in its normal serial position near holmium. Further, lanthanon sulphites are only sparingly soluble and if formed would have been precipitated. Whether or not this oxidation is a chain reaction cannot be deduced from the evidence available but the overall reaction may be represented by

$$4H_3[Ln(SO_3)_3] + 3O_2 \longrightarrow 2Ln_2(SO_4)_3 + 6SO_2 + 6H_2O$$

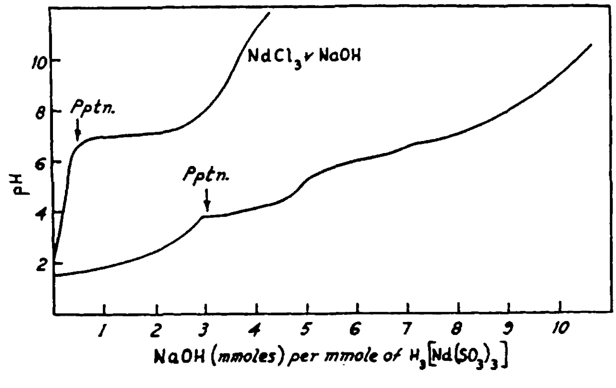
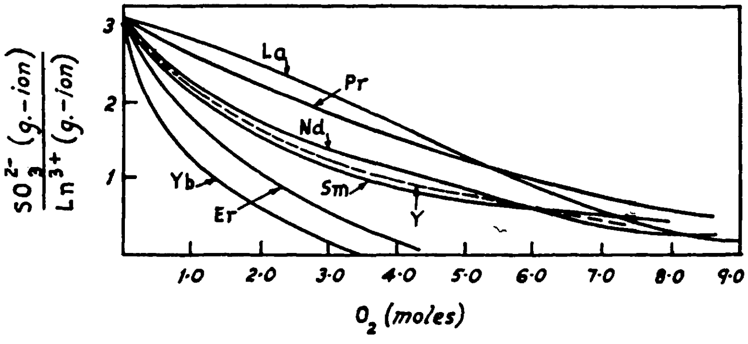


FIG. 2. *Titration of* $H_3[Nd(SO_3)_3]$ *against* NaOH.

FIG. 3. *Oxidation of lanthanon trisulphito-complexes in* 0·1M-*solution at* 20°.



Lanthanon Sulphites.—These may be prepared from solution of the trisulphito-complexes by partial removal of sulphur dioxide by heat or reduced pressure. Sulphites of the heavy lanthanons are readily precipitated at 45°, but those of the light lanthanons not below 70°. This difference in temperature suggested a means of separation but attempts to apply it were unsuccessful because of occlusion of light lanthanons in the heavy lanthanon sulphite precipitate even when the temperature was kept at 50°. Whether precipitated by reducing the pressure or by heating, the sulphites are microcrystalline, but their habit could not be defined microscopically. By either method of precipitation they formed hydrates as follows:

Lanthanon	La	Ce	Pr	Nd	Sm	Gd	Dy	Er	Yb	Y
Water of crystn. (moles)	4	5	5	4	3	8	8	8	8	4

Lanthanon sulphites are sparingly soluble in water at 20°, the solubilities ranging from *ca.* 0·2 g./l. for the lanthanum to 0·6 g./l. for the ytterbium salt. They are decomposed by mineral acids and aqueous oxalic acid with evolution of sulphur dioxide. By passage of this gas through aqueous suspensions of the sulphites they are readily dissolved but they are not converted into carbonate or otherwise affected by passage of carbon dioxide. They dissolve in ammonium acetate solutions and are not reprecipitated from these solutions by addition of acid (cf. acetatosulphate complexes; Vickery, *J.*, **1950**, 1101). This should not, however, be interpreted as indicating the strength of the complex formed, for doubtless the sulphites are completely decomposed at high acidities.

Double Sulphites.—As normally prepared by addition of alkali sulphite to hot, nearly neutral lanthanon chloride solutions, the precipitated double sulphites correspond to the formula $x\text{Ln}_2(\text{SO}_3)_3,y\text{R}_2\text{SO}_3,z\text{H}_2\text{O}$, in which x, y, and z vary as with the double sulphates but are normally in the ratio 1 : 1 : 2 or 1 : 1 : 4. In cerium sodium sulphite, however, the ratio is commonly 1 : 2 : 4. The double sulphites may also be prepared by heating or evacuating a solution containing the trisulphito-complex and sodium sulphite. Double sulphites prepared by the first method are crystalline; by the second, gelatinous. They are slightly soluble in water, values at 20° for the crystalline sodium salts being: for lanthanum (1 : 1 : 2) 0·4 g./l. and for ytterbium (1 : 1 : 4) 3·3 g./l. Solubilities of the corresponding potassium salts were 1·4 and 5·3 g./l. respectively, and for the ammonium salts 2·2 and 10·4 g./l. These values are only approximate, since slow hydrolysis occurs when these compounds are suspended in water.

The double sulphites dissolve in ammonium acetate solution but the resulting complex, in contrast to the analogous complexes formed by the double sulphates, does not yield a precipitate on addition of acid. Metathesis of the solid double sulphites to hydroxide or oxalate is readily accomplished.

Separation of Lanthanons by Homogeneous Double Sulphate Precipitation.—Double sulphates are precipitated by oxidation of the solution obtained by adding sulphite to an acid solution of lanthanon chloride. Oxidation may be effected by air, oxygen, or hydrogen peroxide and catalysed by the additions of such ions as Cu^{2+}, Mn^{2+}, and Fe^{2+}. This reaction was investigated as an improved technique of double sulphate separation and it was found that, although oxidation by air or oxygen was easy to control, yet the use of hydrogen peroxide or catalysts gave unduly high rates of oxidation and made fractionation difficult.

The pH range through which this reaction can be effected is quite narrow. Provided the pH of the mixture be kept between 1·3 and 2·0 by addition of hydrochloric acid, M-sodium sulphite solution (pH 9·4) can be added to M-lanthanon chloride solution without evolution of sulphur dioxide or precipitation of lanthanons. Below pH 1·3, satisfactory oxidation of sulphite has not been obtained; above pH 2·0 lanthanon double sulphites are precipitated. Since it is desirable to work in a solution containing as little acid as possible, a pH range of 1·6—1·8 was adhered to,* and to ensure precipitation of heavy lanthanon double sulphates, sodium chloride was added to the solution (Marsh, *Nature*, 1949, **163**, 998).

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* At this acid level the formation of HSO_3^- rather than SO_3^{2-} ions might be expected. However, the addition of sodium hydrogen sulphite solution to one of lanthanon chloride effected precipitation at pH 1·7, and even when the pH was kept at 1·3—1·5 oxygenation produced no precipitate of lanthanon double sulphate—possibly under these conditions bisulphite ions are oxidised directly to bisulphate which would not precipitate the lanthanons.

In separations based on this homogeneous double sulphate precipitation, two aspects were examined: a comparison of the conventional double sulphate separation of the light and heavy lanthanon groups, and the effectiveness of separating individual members. The separations achieved are shown in Table 2. An enhanced degree of separation of light from heavy lanthanons is evident, but within the lighter group separations were confined to a good concentration of samarium in the tail fractions. In the middle lanthanon fractions good concentrations of gadolinium and dysprosium were obtained. In view of the relatively high concentrations of erbium and ytterbium in the initial material their accumulation is not noteworthy. In general, fractionation by this homogeneous method is most effective in separating the middle lanthanons, samarium to dysprosium, and thus also in giving enhanced separations of both light and heavy lanthanons.

TABLE 2. *Lanthanon separation by double sulphate fractionation.*

Fractionation of 150 g. of oxide of original composition: Pr, 8; Nd, 35; Sm, 8; Gd, 5; Dy, 2; Er, 10; Yb, 12 (as Ln_2O_3) %.

	Homogeneous pptn. Ln_2O_3 (%)								Heterogeneous pptn. Ln_2O_3 (%)							
No.	Wt. (g.)	Pr	Nd	Sm †	Gd	Dy	Er	Yb	Wt. (g.)	Pr	Nd	Sm †	Gd	Dy	Er	Yb
1	17·2	9·9	32	—	—	—	—	—	15·9	12·5	39·3	—	—	—	—	—
2	22·3	16·2	70·9	—	—	—	—	—	17·3	17·9	55·0	0·6	—	—	—	—
3	22·3	17·1	73·1	0·9	—	—	—	—	19·2	18·3	64·5	2·1	—	—	—	—
4	15·2	12·5	62·5	21·0	1·2	—	—	—	15·5	13·3	76·5	7·7	1·3	0·6	—	—
5	10·0	8·0	38·0	51·0	20·0	1·0	—	—	12·5	8·0	60·0	23·0	1·5	0·8	4	2·4
6	8·6	2·3	17·0	25·5	30·2	1·1	23·2	—	13·4	2·2	23·0	27·6	19·3	2·2	11·2	6·7
7	7·6	—	2·6	5·2	30·2	5·3	40·5	15·8	14·9	0·7	8·0	18·1	15·4	5·4	19·4	16·1
8	12·6	—	—	2·4	15·1	7·1	27·8	23·8	16·1	—	1·8	5·6	11·8	6·8	23·0	23·6
9	14·3	—	—	—	0·7	7·0	22·3	22·3	11·9	—	—	4·4	8·4	3·4	32·0	33·6
10	9·6	—	—	—	—	1·0	18·0	49·0	8·4	—	—	—	—	2·0	23·0	45·7
11	6·0	—	—	—	—	1·6	8·3	50·2	5·1	—	—	—	—	1·9	11·7	56·7
12 *	2·5	—	—	—	—	—	12·0	84·1	3·1	—	—	—	—	2·0	10·0	67·8

* Final oxalate precipitate. † Probably high, owing to the presence of Fe^{3+}

Separation of Lanthanons by Anion–Cation Conversion of Trisulphito-complexes.—In addition to the homogeneous conversion of lanthanon double sulphites into double sulphates, a further method has been devised based on the different rates of oxidation of the anionic complexes $[Ln(SO_3)_3]^{3-}$ to the corresponding sulphates (Fig. 3). (This process is part of the subject matter of Australian Patent Appln. 14,772/52.)

Fractionation was effected by a succession of partial oxidations followed at each stage by adsorption of the sulphates on a cation-exchange resin. The sulphates were subsequently stripped from the resin by a solution of sodium ethylenediaminetetra-acetate, and the resin regenerated by sodium chloride. Oxidation was effected by molecular oxygen with the solution buffered to pH 5—7. The heavy lanthanons separated first, and the results given in Table 3 indicate an excellent concentration of ytterbium and appreciable separation of dysprosium and erbium. The lighter lanthanons are also extracted in the order of decreasing atomic numbers (Table 4). Good concentrations of samarium were obtained, and praseodymium was concentrated with residual lanthanum towards the tail fractions with some separations from neodymium.

TABLE 3. *Separation of heavy lanthanons by anion–cation conversion.*

	Dy	Er	Yb		Dy	Er	Yb
Original	6	18	20		—	—	—
Fraction 1	—	6	62	Fraction 5	15	57	10
„ 2	—	18	60	„ 6	26	41	—
„ 3	3	25	51	„ 7	24	27	—
„ 4	9	39	31	„ 8	18	10	—

Separations of the lanthanons by this technique do not compare, in purity of product, with those obtained by conventional ion-exchange techniques. On the other hand, this new technique is not limited by the capacity of the resin to effect this conversion; the resin

TABLE 4. *Separation of light lanthanons by anion–cation conversion.*

	Pr	Nd	Sm
Original	10	50	15
Fraction 1	—	10	52
„ 2	—	18	48
„ 3	2	26	50
„ 4	—	42	31
„ 5	10	66	16
Fraction 6	12	79	9
„ 7	15	82	2
„ 8	28	63	—
„ 9	40	58	—
„ 10	48	38	—
„ 11	52	30	—

functions solely as a collector of sulphate already produced. This method has the advantage that larger quantities of lanthanons can be handled with greater facility, yielding concentrates which, after second or third fractionations, are of a quality comparable with those obtained by other methods.

EXPERIMENTAL

Materials and Analytical Methods.—Lanthanon hydroxides used in the preparative work were of >98% purity. The neodymium oxide was of "Specpure" quality. The lanthanon mixtures were prepared from various sources: the light lanthanons were obtained chiefly from monazite, some cerium and lanthanum having been removed; the heavy lanthanons were extracted from South Australian davidite, and freed from much yttrium. Sulphur dioxide, oxygen, and nitrogen were of commercial quality. The anion-exchange resin was Deacidite FF in the chloride form, and the cation-exchange resin was Dowex-50 in the sodium form.

Spectrophotometric measurements were made with the Unicam and the Beckman D.U. instruments, and electrometric titrations were followed on a Cambridge pH meter. Lanthanons were determined as oxide after ignition of the oxalates, and sulphite was determined iodometrically. The degree of hydration of the simple and double sulphites was determined by drying first in a vacuum-desiccator (conc. H_2SO_4) and then in an air-oven at 110°. During this treatment insignificant oxidation of the solid sulphites occurred; even after 24 hours' exposure to the atmosphere in an open dish, solid neodymium sulphite contained only 1·1% of SO_4^{2-}. Solubilities were roughly determined by shaking an excess of the salt with distilled water for 24 hr., filtering the suspension, and evaporating an aliquot part of the filtrate to dryness in platinum under an infrared lamp.

The *neodymium salt* obtained at pH 3·8 by titrating the solution containing the trisulphito-complex with sodium hydroxide (Fig. 2) was microcrystalline and anhydrous. Sulphite was determined iodometrically, lanthanons as oxalates, and sodium as the zinc uranyl acetate salt [Found: SO_3, 52·8; Ln_2O_3, 37·2; Na, 14·9. $Na_3Ln(SO_3)_3$ requires SO_3, 53·2; Ln_2O_3, 36·8; Na, 15·4].

The charges on the trisulphito-complex were determined by shaking 25 g. of Deacidite FF resin with 100 ml. of a solution of the complex containing the equivalent of 1 g. of Ln_2O_3 for 24 hr. in an atmosphere of nitrogen. Equilibrium was assumed to have been reached after this period, and the resin was filtered off, and, from the combined filtrate and washings, lanthanons were precipitated as oxalates, and chloride as silver chloride (Table 2).

Oxidation rates were determined by use of the apparatus shown in Fig. 4. Sulphur dioxide was passed at 20 ml./sec. through 250 ml. of a 0·1M-slurry of lanthanon hydroxide in the central reaction cell for 3 min., by which time all lanthanons had dissolved. After passage of nitrogen through the solution at 30 ml./sec. for 30 min. to remove excess of sulphur dioxide, the sulphite content of the solution was determined iodometrically. Oxygen was then passed through the solution at 20 ml./sec., and 2 ml. samples were collected and titrated in an atmosphere of nitrogen first at 3-min. intervals but at longer intervals as oxidation progressed. In calculating the results shown in Fig. 3 corrections were made for the samples removed. The temperature was maintained at 20° ± 1·5° by circulating water through the jacket of the cell.

Separation of Lanthanons by Homogeneous Double Sulphate Precipitation.—Hydrochloric acid was added to 1500 ml. of 10% $LnCl_3$ solutions to reduce the pH to 1·4. Sufficient sodium sulphite was added to produce later a suitable amount of double sulphate without increasing the pH above 1·8: 30 g. of $Na_2SO_3,7H_2O$ generally yielded 8—10 g. of double sulphate, and up to 60 g. of the anhydrous sulphite could be added before pH adjustment with acid was necessary; the pH was finally adjusted to 1·6—1·8 by addition of sodium sulphite or hydrochloric acid and the solution was heated to 80° whereat oxygen was passed through the solution at 20 ml./sec. until precipitation reached sufficient proportions. After the precipitate had been filtered off oxygen was again passed through the filtrate, further sodium sulphite being added if necessary, and the sequence of filtration and further oxygenation repeated.

In Table 2, the efficiency of double sulphate fractionation by this homogeneous method is compared with that obtained by the normal heterogeneous procedure. The latter was carried out by the simple intermittent addition of anhydrous sodium sulphate to 10% $LnCl_3$ solution at 80—90° and pH 2·5, the solution being saturated with sodium chloride and well stirred. Double sulphate fractions obtained by either mode of precipitation were converted into hydroxides, washed free from alkali, ignited to oxide, and analysed spectrophotometrically by using the extinction coefficients and wavelength data given by Moeller and Brantley (*Analyt. Chem.*, 1950, **22**, 433) and Wylie (*J. Soc. Chem. Ind.*, 1950, **69**, 143). Analyses for gadolinium are subject to the ±10% error noted by Moeller and Brantley but other values have been appropriately corrected for interfering ions.

Separation by Anion–Cation Conversion.—This separation can be carried out as either a batch, or a cyclic process, but the former is less satisfactory because of the necessity of handling a large bulk of liquid in an inert atmosphere. All results recorded here were obtained by a cyclic process conducted in the equipment shown in Fig. 5. A slurry of lanthanon hydroxides contained in the main reaction vessel *B* was dissolved by sulphur dioxide admitted through one branch of the triple manifold *A*. After dissolution, nitrogen was passed through another branch of the manifold to displace the excess of sulphur dioxide before introduction of oxygen through the third branch of the manifold. Oxygenation having proceeded for an appropriate time, nitrogen was again introduced to give an inert atmosphere, whilst the partially oxidised solution was led *via* the main tap *C* and the distribution head *D* into one of the " collector " columns F. The ground-in adaptors to these columns, *E*, carried three additional inlets for wash-water, sodium " enta " stripping solution, and brine regenerant solution.

FIG. 4. *Apparatus for measuring rate of oxidation.*

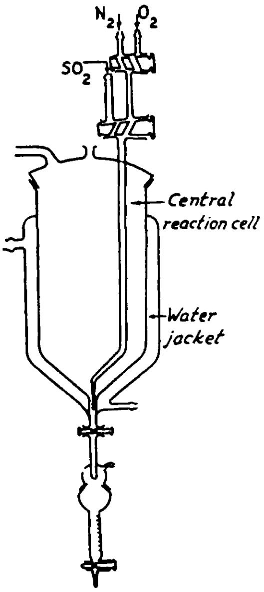
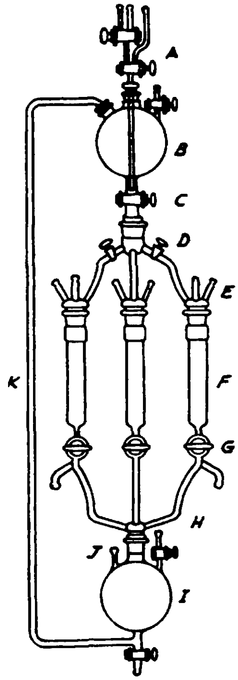


FIG. 5. *Apparatus for separation of lanthanons by oxidative anion–cation conversion.*



After passing through the columns, the unoxidised solution was directed by the two-way tap *G* to the collector head *H* and thence to the receiving vessel *I*. When finally collected in *I*, the solution and washings from the columns were blown by nitrogen pressure *via J* up the return line *K* to the main reaction vessel *A* for further oxygenation. During this return of the solution to *A* and further oxidation, the collector column was being stripped of its adsorbed lanthanons by 5% sodium " enta " solution at pH 8—8·5, washed free from excess of stripping solution, regenerated with sodium chloride solution, and then washed free from excess of chloride. All these solutions were directed from the columns by the tap *G* to an external receiver. These treatments of the collector column invariably required more time than was required for return of the lanthanon solution to *A* and its further oxidation, so it was necessary to direct the re-oxidised lanthanon solution to a second column for extraction of the second fraction of lanthanon sulphate. In practice six collector columns were operated in rotation.

Sulphur dioxide, nitrogen, and oxygen were measured through flow-rate manometers, and the stripping and regenerant solutions were dispensed from aspirators on a shelf 18″ above the main reaction vessel. The whole assembly was erected inside a steel framework of supporting bars and platforms at the appropriate levels.

The selectivity of the anion–cation conversion is related to the dilution of the lanthanon solution; for maximum efficiency the concentration of the solution should be between 0·5 and 6·0% and preferably between 3 and 4%. Below 0·5% the complex undergoes some hydrolysis.

To ensure complete removal of cation from solution, an excess of exchange resin must be used; this can be determined from the capacity of the resin, the oxidation curves, and the duration of oxidation. The resin must be used in the sodium form; a hydrogen resin would, on exchange, depress the pH of the solution to below that at which the complexes are stable. Time of contact between solution and resin is also of importance.

In a typical run the operating conditions were : sulphur dioxide at 50 ml./min. was passed through 4 l. of hydroxide slurry containing 140 g. of $Ln(OH)_3$. On completion of solution, nitrogen was passed at 30 ml./min. for 2 min. and then oxygen at 20 ml./min. for 20 min. to give a maximum yield of 8 g. of Ln^{3+}. After this oxygenation, nitrogen was again passed for 2 min. and the solution was then passed through the exchange column, containing 250 g. of resin, at 1500 ml./hr. After the column had been washed with 100 ml. of water the lanthanon solution plus washing was blown back to the reaction vessel for further oxygenation. The resin column was stripped by the slow (5 ml./min.) passage of the stripping solution, washed with 500 ml. of water, and then regenerated by the slow passage of 2 l. of 2% sodium chloride solution, again followed by washing. The lanthanons contained in the stripped fraction were recovered by precipitation as oxalate after acidification of the solution to pH 3.

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