

CHROMATOGRAPHIC SEPARATION AND IDENTIFICATION OF SOME INDIVIDUAL RARE EARTHS ON PAPER BY MEANS OF FLUORESCENCE

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The applications of fluorescence in inorganic analysis have hitherto been seriously limited by the presence of numerous interfering substances (activators, quenching substances and other substances that form fluorescent compounds with the reagent employed) and also by the poor selectivity of the organic reagents normally employed for the formation of fluorescent compounds.

Recent progress in separation techniques, however, and the extremely small quantities of an element that can be revealed by means of analyses based on fluorescence, encouraged us to work out simple and rapid methods for the separation of some elements from all interfering substances, and to initiate a study of the fluorescent properties of a number of inorganic compounds with a view to finding more sensitive and more selective reagents than those at present employed.

We have elsewhere¹ discussed the conditions governing the formation and the fluorescent properties of inorganic precipitates containing traces of uranium.

Treatment with zinc acetate followed by trisodium phosphate yields highly sensitive fluorescent spots with uranium (identification limit 10^{-3} μ). This test has also been used for rapid field determination of uranium in natural waters².

In the work described here, a series of fluorescent rare earth compounds was examined, some of which are already known from the literature (rare earth tungstates). A special study was made of the conditions governing the formation on paper of compounds that exhibit a characteristic, stable, fluorescence. Attention was also paid to the quenching of a large number of inorganic ions, and a description is given of a paper chromatographic technique for the separation of rare earths from interfering ions. Separation on paper was decided upon because of the rapidity and simplicity of this operation, and also because the lanthanide elements can be revealed directly, after separating the interfering substances, by spraying the appropriate reagents on the paper.

EXPERIMENTAL

Reagents

Rare earths. The solutions were prepared from rare earth oxides (Johnson, Matthey & Co, London). In the case of europium 99.995 % pure europium oxide (Johnson, Matthey Specpure) was used.

Tributyl phosphate. TBP (Fluka) 100 %.

Sodium tungstate (Merck). 15 % solution in water.

Ammonium oxalate (Merck). Saturated solution.

All other chemicals used were Merck analytically pure reagents.

Formation of fluorescent spots on filter paper

On a Whatman No. 1 paper was micropipetted 0.005 ml of a solution of known concentration of the ion under examination. After quick drying in hot air, the paper was sprayed with the appropriate reagents in order to form the fluorescent compound and then examined under U.V. light (280 m μ). The concentration of the solution was then reduced to the point of the maximum dilution at which the ion in question could still be revealed. The smallest quantity (by weight) of the ion that can be detected on paper is related to the volume taken for the test. The values given in Tables I and II are for volumes of 10⁻³ ml of solution, a volume which is still easy to measure and yields spots of about 0.3 cm diameter.

Procedure for the study of interference

The interference of various ions was studied by determining the quantity of a given ion that reduces the fluorescence by 50 %. The quantity in question may be found without difficulty by comparing the fluorescent spots obtained with 0.005 ml of solution containing, respectively,

(a) 50 γ /ml of the ion under examination,

(b) 50 γ /ml of the ion under examination plus a known amount of the ion being studied for interference,

(c) 25 γ /ml of the ion under examination.

The quantity of the interfering ion is varied up to the point where the intensity of the fluorescent light of spot (b) is equal to that exhibited by spot (c).

RESULTS

Studies were carried out on a series of reagents capable of producing fluorescent compounds on paper with the elements of the lanthanide series.

In Table I are listed the reagents giving positive results. For each reagent the colour of the fluorescent light and the identification limit on paper are given.

Of all the reagents examined, sodium tungstate gave the best results for traces of dysprosium, samarium and europium, while ammonium oxalate exhibited a certain selectivity for terbium and europium. Cerium forms weakly fluorescent compounds with sodium phosphate, sodium pyrophosphate and borax only. As regards the individual lanthanide elements, terbium can be readily identified with ammonium oxalate by means of spot tests on paper. In fact, with the reagent in question, as may be seen from Table I, only terbium and europium give appreciably fluorescent compounds. The two fluorescent spots are nevertheless clearly distinguishable, that of terbium being yellow-green and that of europium red. Dysprosium is likewise readily identifiable with sodium tungstate, in that it is the only lanthanide element giving off a whitish-pink fluorescent light with that reagent. Europium gives a highly sensitive reaction on paper with sodium tungstate (red fluorescence; identification limit 10⁻³ γ) but its identification is difficult in the presence of appreciable

TABLE I
SPOT TESTS OF RARE EARTHS BY MEANS OF FLUORESCENCE ON PAPER

Reagent employed	Spot test sensitivity and fluorescence colour*					
	Ce	Sm	Eu	Gd	Tb	Dy
Sodium tungstate	d.s.	0.01 γ (10 γ /ml) red	0.001 γ (1 γ /ml) red	i.s.	d.s.	0.002 γ (2 γ /ml) whitish pink
Ammonium oxalate	d.s.	2 γ (2000 γ /ml) red	0.025 γ (25 γ /ml) red	i.s.	0.025 γ (25 γ /ml) yellow-green	0.1 γ (100 γ /ml) whitish pink
Sodium ortho-phosphate	5 γ (5000 γ /ml) blue	i.s.	0.1 γ (100 γ /ml) red	i.s.	d.s.	i.s.
Sodium pyro-phosphate	5 γ (5000 γ /ml) blue	i.s.	0.5 γ (500 γ /ml) red	i.s.	d.s.	i.s.
Sodium molybdate	d.s.	i.s.	0.4 γ (400 γ /ml) red	i.s.	d.s.	i.s.
Borax	5 γ (5000 γ /ml) blue	i.s.	0.2 γ (200 γ /ml) red	i.s.	d.s.	i.s.
Ammonium vanadate	i.s.	i.s.	2 γ (2000 γ /ml) red	i.s.	i.s.	i.s.

* The values in parentheses are dilution limits; i.s. = invisible spot; d.s. = dark spot.

amounts of samarium, the latter, in fact, producing fluorescent spots of a similar colour (identification limit with tungstate $10^{-2}\gamma$). Thermo-quenching tests, however, showed that when the fluorescent spots of europium and samarium are warmed at the same time by means of hot air, as the temperature rises (from 30° to 80°) the colour of the fluorescence veers from red to yellowish orange in the case of samarium, while the red fluorescence of europium only weakens slightly.

With thermo-quenching, therefore, it is possible to identify europium and still obtain useful indications for identification of samarium.

According to POLLARD *et al.*³ and STEVENS⁴ lanthanum, lutetium and gadolinium may be identified with morin in that they are the only lanthanide elements that form fluorescent (yellow-green) compounds with that reagent, so that there are now seven lanthanide elements that can be revealed and identified by means of fluorescent techniques on paper. In addition, cerium (III) can be revealed and identified by fluorescence, though with a lesser degree of sensitivity (blue fluorescence with borax; identification limit 5 γ).

Separation of rare earths from interfering ions

A large number of ions interfere with the reactions described. Table II shows the quantities of the interfering ions, which quench the fluorescence of the spots obtained with sodium tungstate by 50 %.

In order to bring about a rapid separation of rare earths from the interfering ions, we applied simple paper chromatographic separation methods relying on the high degree of selectivity with which certain organic solvents extract lanthanide elements.

The procedure is as follows: 10^{-2} ml of the solution under examination is spotted on to a small strip of Whatman No. 1 paper at about 2–3 cm from one end. After drying, the end is dipped into the organic solvent and left there till the latter rises to a height of a few centimetres (approx. 2 or 3 minutes). The strip is then dried with

TABLE II
THE AMOUNTS OF VARIOUS ELEMENTS THAT QUENCH THE FLUORESCENCE
OF 0.25 γ OF EUROPIUM BY 50%

Element	Amount γ	Element	Amount γ	Element	Amount γ
Sr(II)	20	Ba(II)	5	Th(IV)	3
Cd(II)	10	Be(II)	5	Fe(III)	2
Zr(IV)	8	Bi(III)	5	Pb(II)	2
La(III)	5	U(VI)	5	Fe(II)	1
Ce(III)	5	Ce(IV)	4	Cr(III)	0.7
Hg(I)	5	Hg(II)	4	Cu(II)	0.2
Tl(I)	5	Y(III)	4	Ni(II)	0.2

hot air and the desired reagents sprayed on it in order to form the fluorescent compound. Of the different solvents employed, the best results were obtained with 100% TBP saturated with concentrated HNO_3 . This solvent extracts quantitatively on paper all the lanthanides provided one has taken the precaution to add a drop of aluminium nitrate as salting-out agent at the starting point. Some sixty inorganic cations were studied (among them all the interfering ions listed in Table II) under the conditions described, and only U(VI), Th(IV), Zr(IV) and Ce(IV) accompanied the rare earths to the solvent front.

From Table II it can be seen that thorium and uranium do not interfere with the fluorescence test provided they are present in only small amounts, yet they may be easily separated from the rare earths by means of ascending chromatography with mesityl oxide. The latter solvent, in presence of HNO_3 , extracts uranium, thorium and other tetravalent elements, leaving the rare earths at the starting point. Therefore, in order to separate on paper the group of rare earths from the other elements the following procedure may be adopted: first elute with mesityl oxide- HNO_3 to a height of about 20 cm. Dry and elute again with TBP- HNO_3 up to 15 cm. The rare earths will be well separated (Fig. 1). Their presence may be revealed with sodium tungstate or ammonium oxalate.

Separation of individual lanthanide elements on ion-exchange paper and identification by means of fluorescence

With TBP as solvent the rare earth group can be separated from most inorganic elements, but the individual lanthanide elements cannot be separated.

In earlier work⁵ we separated mixtures of La, Ce, Nd and Sm by ascending chromatography on paper impregnated with zirconium phosphate. The eluent used was a strong acid such as HClO_4 , which was employed to demonstrate the complexing

power of zirconium phosphate. Separation of lanthanides with a higher atomic number was, however, not possible by such means. To separate mixtures of La, Ce, Sm, Eu, Tb, Dy and Lu (the only lanthanide elements at present detectable by means of fluorescence on paper) we utilised the well-known complexing power of

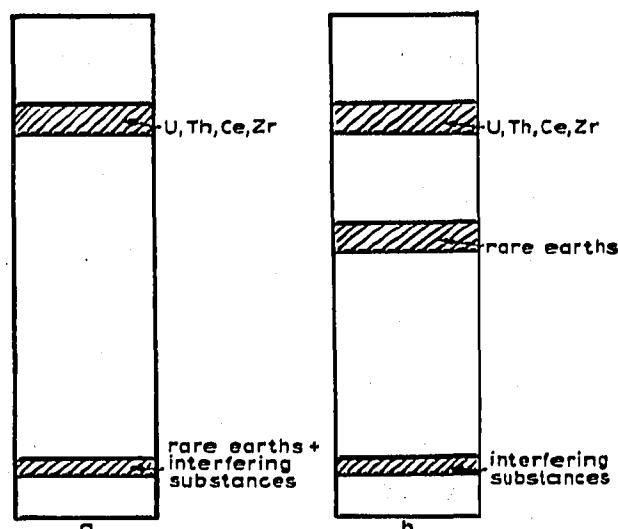


Fig. 1. (a) Elution with mesityl oxide-HNO₃ (first step). (b) Elution with TBP-HNO₃ (second step).

lactic acid, the complexes formed with the lanthanide elements being separated on ion-exchange paper. We employed strips of Amberlite SA-2 ion-exchange papers (manufactured by Rohm & Haas). The separations were effected by descending chromatography with 10% lactic acid as eluent.

The findings are given in Fig. 2*. In all probability better results might be obtained with other eluents such as ethylenediaminetetraacetic acid solution. The separations obtained, however, are sufficient to permit the identification of the individual lanthanide elements in a rare earth mixture, not only by their position relative to one another but also by the colour of the fluorescence produced with the specific reagents employed, and, again, by thermo-quenching.

If there are other interfering ions present in the rare earth mixture these should be separated with TBP, as described earlier, before attempting separation of the individual rare earths by ion exchange. The separation may be carried out by first extracting uranium, thorium, cerium and zirconium with mesityl oxide-HNO₃, and then extracting the rare earths with TBP-HNO₃.

The rare earths are then put in water and the individual elements are separated by ion-exchange chromatography.

Extractions with mesityl oxide or TBP may also be performed directly on ion-exchange paper, as already described for non-impregnated paper, in which case the problem remains of eliminating TBP from the paper before proceeding with the next ion-exchange separation by means of elution with complexing acids. This is possible with carbon tetrachloride once the strips have been made alkaline with sodium carbonate in order to reduce losses of rare earths into the CCl₄. This procedure may

* It should be noted that on ion-exchange paper the sensitivity of fluorescence tests is somewhat reduced.

find useful application in the rapid qualitative isolation of rare earths from such minerals as monazite.

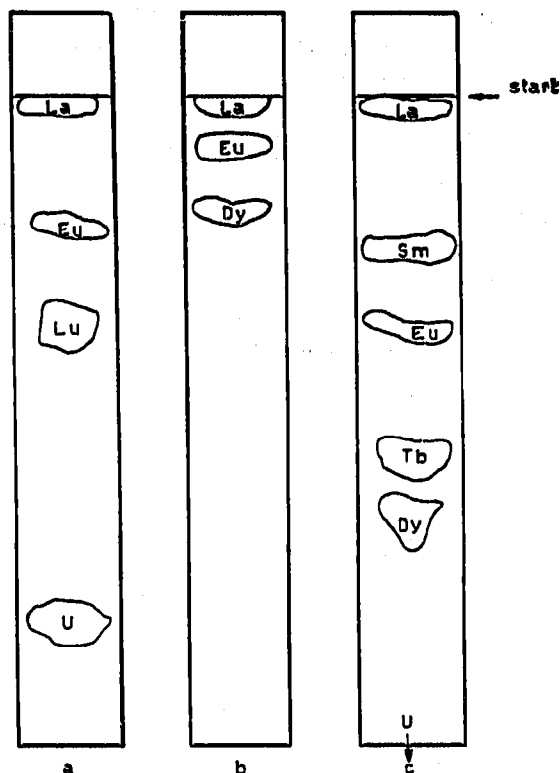


Fig. 2. (a) Separation of La, Eu, Lu and U(VI) by descending chromatography. Elution with aqueous lactic acid; pH = 3; time 2 h. (b) Separation of La, Eu, Dy; pH = 2.4; time = 3 h. (c) Separation of La, Sm, Eu, Tb, Dy and U(VI); pH = 1.5; time 28 h.

CONCLUSION

Identification test by means of fluorescence on paper showed a high degree of sensitivity and were to some extent specific for individual rare earths, such as Sm, Eu, Dy and Tb. With simple separations on paper the tests may be conducted even in presence of interfering ions.

In addition to the application in detecting individual earths in various compounds, minerals included, the test described may be usefully adopted in chromatography and electrophoresis in order to show the position of these elements on filter paper. Reagents normally employed to reveal rare earths on paper (Thoron, 8-hydroxyquinoline and morin) are less sensitive and not very specific.

SUMMARY

The conditions for the formation of some U.V. fluorescent rare earth compounds were studied. It is possible to detect by fluorescence some rare earth ions on paper with high sensitivity. The spot tests employed are moreover very specific for Eu, Sm, (sodium tungstate as reagent; red fluorescence; identification limit: Eu $10^{-3} \gamma$; Sm $10^{-2} \gamma$), for Dy (sodium tungstate as reagent; whitish pink fluorescence; identification limit: $2 \cdot 10^{-3} \gamma$) and for Tb (sodium oxalate as reagent; yellow-green fluo-

rescence; identification limit $2.5 \cdot 10^{-2}\gamma$). Separation of the rare earth group from interfering substances was carried out by extracting with mesityl oxide (which removes tetravalent cations) followed by extraction with tributyl phosphate-HNO₃. The individual rare earths were separated on Amberlite SA-2 ion-exchange paper employing aqueous lactic acid as eluent.

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