ON THE ABSORPTION SPECTRA OF SALT SOLUTIONS OF SOME RARE EARTH ELEMENTS.⁽¹⁾

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It is the well known fact that some salts of rare earth elements yield highly characteristic absorption spectra, by means of which, therefore, they are very conveniently detected. Concering to this subject we have indeed plenty of literatures to be referred;⁽²⁾ notwithstanding I repeated the study of the absorption spectra of some rare earth salts, in order to know whether their spectra are influenced from each other by mixing them and further to investigate the absorptions in the ultraviolet region, which are wanting in the preceding studies.

Experimental.

1) Absorption Spectra of Chlorides of Lanthanum, Cerium, Praseodymium, Neodymium, Samarium and Erbium in the Visible Region.

Lanthanum chloride, being colourless, shows no absorption band in the visible part. Cerous chloride also shows no bands, but its end absorptions are extended to the region of the spectrum of comparatively long wave lengths: namely 10 cm. layer of its 0.05 mol aqueous solution absorbs even to 4200 Å (violet), and 0.2 mol solution (the same thickness of layer) absorbs to 4600 Å (blue violet). The aqueous solutions of praseodymium chloride, neodymium chloride, samarium chloride and erbium chloride absorb remarkably in visible part and they show very characteristic bands, which accord very well with the results attained by the works already published.

Brauner and others⁽³⁾ have studied the mutual influences of the absorption spectra of the solutions of rare earth salts, when they were mixed with each other. According to them, the spectra change distinctly their appearances by contamination of other salts. But in my present investigation, this was by no means the case; I studied, with the special care, the absorption bands 4441 Å of praseodymium, 5222, 5205, 5123 and 5091 Å of neodymium and 4071 and 4013 Å of samarium in mixing the salt solutions to each other or adding lanthanum chloride to each solution. These characteristic bands, however, remained always unchanged, and it was thus accertained that these elements may at least be detected by means of these absorption bands. (Fig. 1).

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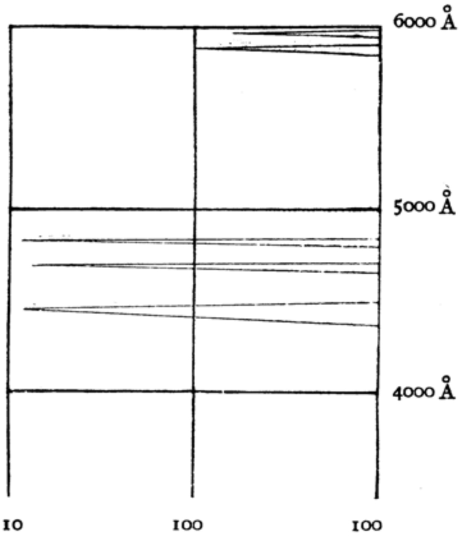
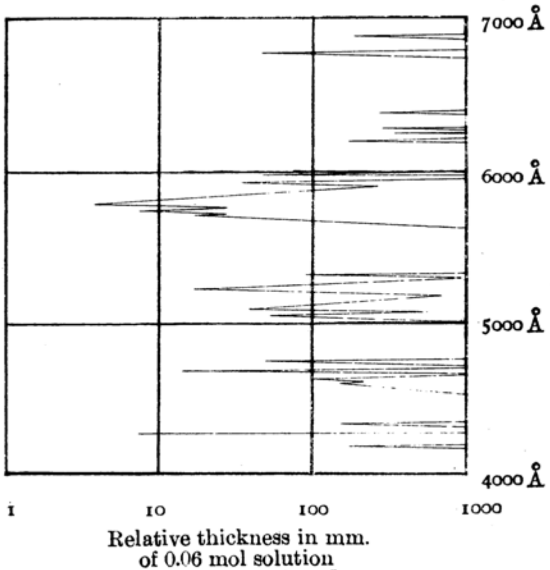
(1) Read before the Chemical Society of Japan, April 8, 1923.

(2) Compare "A Text Book of Inorganic Chemistry" by N. Friends, Vol. IV, p. 283, (1917).
W. Prandtl, *Z. anorg. Chem.*, 116 (1921), 96.
Z. F. Yntema, *J. Am. Chem. Soc.*, 45 (1923), 907.

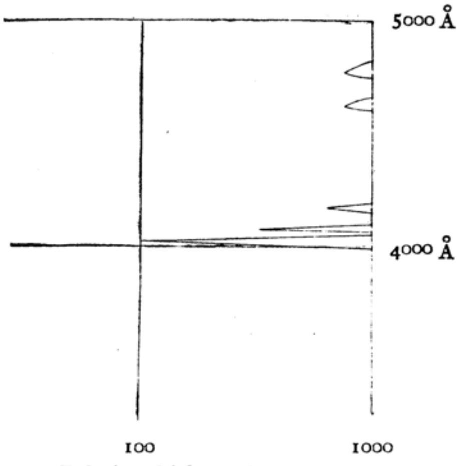
(3) B. Brauner, *J. Chem. Soc.*, 43 (1883), 278.
E. Demarçay, *Compt. rend.*, 126 (1898), 1039.



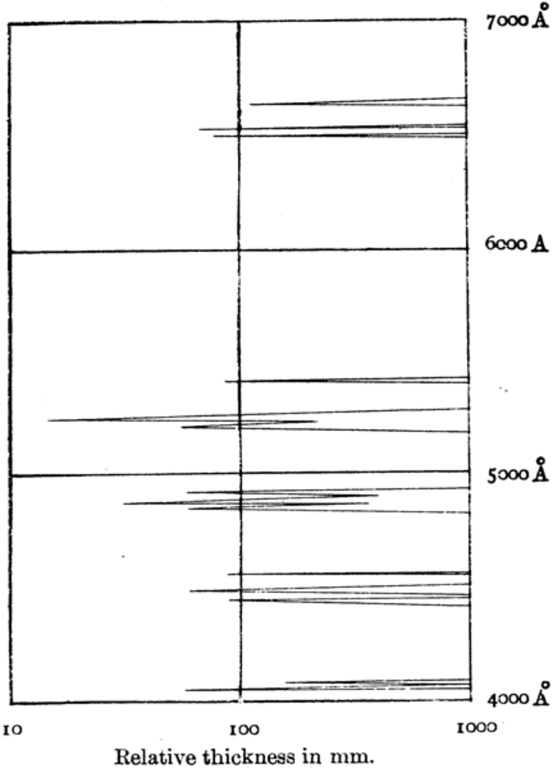
Praseodymium chloride.



Neodymium chloride.



Samarium chloride.



Erbium chloride.

Fig. 1.

2) Absorption Spectra in the Ultra-Violet Region.

Among chlorides of six rare earth elements above mentioned, only three, namely cerous chloride, samarium chloride and erbium chloride, show absorption bands in the ultra-violet region. As it will be seen in Fig. 2, cerous chloride possesses two bands, while both of samarium chloride and erbium chloride show only one in ultra-violet. The positions of their absorption maxima are given in the following table:

	Concentration in mol.	Thickness of liquid layer (cm.)	$\lambda(\mathring{A})$	ν
$CeCl_3$	0.01 0.001	2.8 4.8	3350 2469	2985 4050
$SmCl_3$	0.11	1.4	2600	3850
$ErCl_3$	0.2	5.6	2470	4050

Chlorides of praseodymium, neodymium and lanthanum absorb only continuously in ultra-violet (compare Fig. 2.)

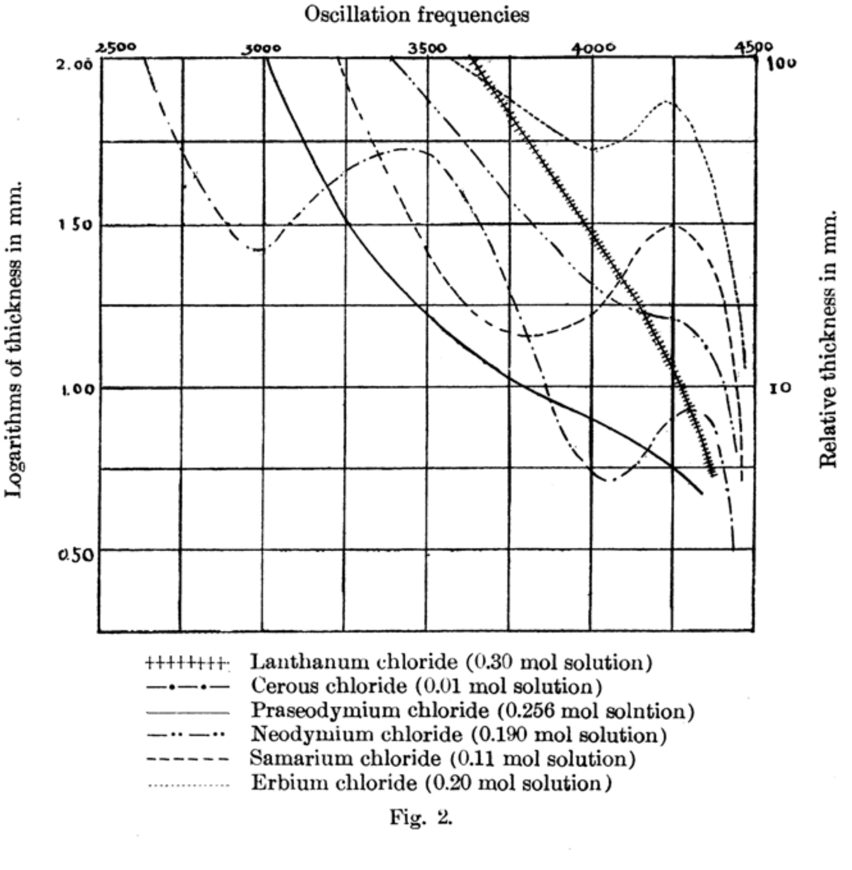


Fig. 2.

3) Application of Absorption Spectra for the Quantitative Determination of Some Rare Earth Elements.

The concentration of some rare earth salts in a solution may be determined by measuring the thickness of the liquid layer, at which a certain characteristic band of that element just disappears, provided that the limiting concentration (or the thickness of liquid layer) of disappearance of the same band at the certain thickness of liquid layer (or at the certain concentration) is previously known.

According to my present study, this method of analysis is especially suited for such the rare earths, that show absorption bands in the ultra-violet region, because the latters are, as a rule, far more wide and distinct than those of the visible part. For example, cerous chloride absorbs selectively very wide region of spectrum in ultra-violet; its analysis by using this method, therefore, will be scarcely hindered by the presence of other rare earth salts, which absorb likewise selectively in ultra-violet. In applying Beer's law, it was calculated from the experimental results that the quantity of cerous chloride in a given solution may be determined even when its fifty times so much praseodymium and samarium salts and its hundred times so much lanthanum and neodymium salts are simultaneously presented in that solution. In the actual case of mineral analysis, if the total quantity of the salts of lanthanum, praseodymium, neodymium and samarium do not exceed hundred times of that of cerous salt, the latter will be conveniently and rapidly determined by this spectroscopic method in performing as follows: the fraction of cerium group extracted from a given mineral will be changed into chlorides and the absorption spectra of that solution in various thicknesses of liquid layer are photographed on a same plate. The absorption curve will then be traced according to the Hartley-Baly's system and the thickness of liquid layer at the bottom of the absorption curve is measured. On the other hand, the absorption curve of cerous chloride of the known concentration will be prepared for the purpose of comparison, and on this curve, the thickness of liquid layer at bottom of the same absorption band is likewise determined. According to the Beer's law, the following simple relation will be given to denote the concentration of cerous chloride in the mineral extract:

$$c' = \frac{c\,l}{l'}$$

where c and c' mean respectively the concentrations of known and unknown solutions of cerous chloride, and l and l' are respectively the thicknesses of liquid layer of these solutions, at which the absorption bands just disappear.

For the purpose of the verification of this method, the following experiment was carried out: a solution, containing 0.02 gr. CeO_2 and 1.1240 gr. R_2O_3 (R= metals of Ce-group, Ce itself excluded) in a litre as chlorides, was prepared, and the absorption spectrogram of this solution was made as usual. The absorption curve showed that the bottom of the band, the wave lengths of which is found 2469 Å, appears at the thickness of 4.0 cm. of liquid layer, while in the control solution, which contains 0.017 gr. of CeO_2 as chloride in a litre, the bottom of the same absorption band was found at the thickness of 4.8 cm. of liquid layer. The quantity of CeO_2 in the first solution will, therefore, be calculated from the following formula.

$$\frac{4.8 \times 0.0170}{4.0} = 0.0204.$$

As for the ultra-violet absorption of samarium chloride, it is not interfered by that of lanthanum chloride, but when the quantities of the co-existing neodymium and praseodymium chlorides exceed respectively 3 and 1 times of that of samarium chloride, the characteristic absorption band at 2600 Å of the latter salt is no more of without influence. In the practice, therefore, the spectrogram of the solution of rare earths fraction extracted from a certain mineral will be carefully examined, and if the band of samarium 2600 Å be found therein, so we can at least conclude that the extract contains neodymium in the less quantity than 3 times that of samarium and praseodymium less than the equal quantity of samarium. In this case, therefore, the above mentioned method may be applied for the quantitative analysis of the latter element utilising its characteristic band.

Summary

1) The absorption spectra of chlorides of lanthanum, cerium (trivalent), praseodymium, neodymium, Samarium and erbium were studied and compared with the works published up to the present time.

2) In studying the ultra-violet absorptions of these salts, the existence of the following bands was confirmed:

3350 and 2469 Å in cerous chloride; 2600 Å in samarium chloride; 2470 Å in erbium chloride.

3) A method for the quantitative analysis for cerium and samarium by measuring their characteristic ultra-violet absorptions was described.

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