CXCVI.—*The Ultra-violet Spectra of Praseodymium, Neodymium, Samarium, Europium, and Erbium.*

By JAMES HENRY GARDINER.

VERY little work has been done in the photography of the ultra-violet absorption spectra of the rare earths, possibly on account of the rarity of the elements themselves and of the difficulty of photography.

Having in my possession specimens of many of the rarer elements in a state of purity, I thought that it would be of interest to place on record photographic reproductions of the absorption spectra of some of them. The five named above were found to give well-defined absorption bands in the region under examination; these spectra are shown together with a photograph of the light used to produce them. Photographs of this character lose much of their value unless care is taken to ensure uniformity in the conditions under which they are produced.

The spectrograph used is of novel design and has been constructed

purposely for this class of work; it consists essentially of a pair of quartz "Cornu" prisms with plano-convex collimating and object lenses. The "comparison spectrum" that is given in each case is put into position without any movement of the film by passing the radiation into the spectrograph through an aperture in a metal disc which is fixed in front of the slit; this disc has holes of different sizes and in different positions and it can be moved so as to confine the radiation entering the instrument to any one of them at will.

For this work it was necessary to use a very narrow slit, and it was essential for purposes of comparison that there should be no variation from the width in any of the spectra. A thick brass plate with a slot 2 mm. wide and 10 mm. long was made, and by the point, slot, and plane method it could be accurately fixed in the optical centre of the quartz train; upon the flat surface of the plate, jaws of hard steel with accurately ground edges were clamped at the determined width of 0·03 mm. This device of a slit with jaws that are immovable removes any possibility of accidental variation in its width such as would arise if it were adjusted by a screw.

All the photographs given are made with the same slit. The light used for the absorption spectra was produced by passing a high-tension current between electrodes of metallic uranium, producing a spark very rich in ultra-violet radiation. The spectrum of uranium has such a great number of lines so close together that, for the present purpose, it may be regarded as continuous.

At the top of each absorption spectrum and slightly overlapping it, is projected the spark spectrum of an alloy of the metals zinc, cadmium, mercury, and tin. These elements give well-defined lines of which the wave-lengths are known to a great degree of accuracy; their values given on each photograph make it possible, by means of a simple interpolation curve, to find the value of any of the bands shown. The wave-lengths of the approximate centres of the bands are given, although the photographs themselves are of more value than tables of wave-lengths and descriptions of the bands.

It was considered essential that the strengths of the solutions, *i.e.*, the amounts of the element present in each case, should be comparable or at least accurately known. The rarity of the materials available, and the obscurity of the chemistry of some of them, made this a matter of difficulty, but after some preliminary work it was decided to take the crystalline nitrates which have the general formula of $R(NO_3)_3,6H_2O$ as the basis of the solutions. These salts are easy to prepare and are soluble in water. As in some cases only a fraction of a gram of the element was available, it was decided to make all solutions from a weighed quantity of the

salt with ten times its weight of water. The solutions were in all cases put into a cell made from a glass cylinder, 20 mm. long, closed at the ends with plates of thin quartz.

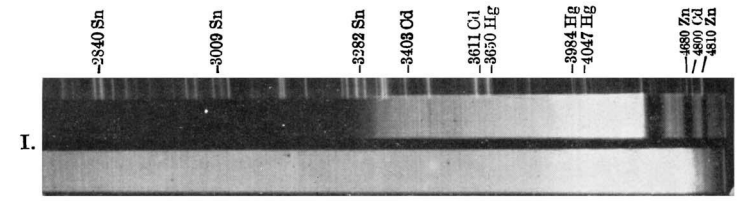
The procedure for the production of a photograph was as follows. By adjusting the aperture-disc so that the light passed into the upper part of the slit, an exposure was made to the light from the metallic alloy, and the disc was then rotated so as to present another opening slightly overlapping the first; the cell containing the solution was fixed in front of the slit, an exposure was given for 3 minutes to the uranium spark, the disc was again shifted so as to expose another part of the slit, and the solution was removed and another exposure given to the same light for the same time; this last exposure was considered to be advisable for reasons that will appear later.

In addition to the five elements that form the subject of this paper, 1 : 10 solutions of the nitrates of the following elements were made and their absorption spectra were photographed: lanthanum, ytterbium, gadolinium, terbium, thorium, cerium, and scandium. They did not show any absorption bands in the region under examination, *i.e.*, from 400$\mu\mu$ to the commencement of transmission, which in all cases was at about 350 $\mu\mu$. The elements giving absorption bands are described in the order of their atomic numbers.

Praseodymium.—This specimen was prepared some years ago by Thompson. The nitrate gives well-defined crystals dissolving easily in water to a brilliant green solution; the dried crystals, $Pr(NO_3)_3,6H_2O$, were used for the solution which was placed in the cell described above. The spectrum shows that it is quite free from neodymium and gives three well-defined bands at the least refrangible end; the approximate centres of the bands are 482$\mu\mu$, 468$\mu\mu$, and 442$\mu\mu$ (Fig. I).

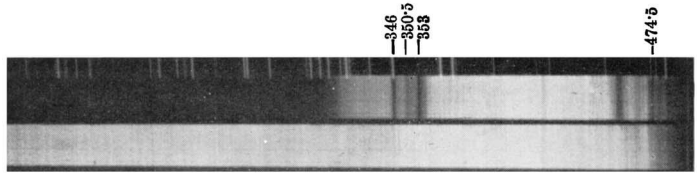
Neodymium.—This material was obtained from the Welsbach Co. in the form of deliquescent crystals of pale rose colour; it was recrystallised by keeping the solution over sulphuric acid and gave good crystals of $Ne(NO_3)_3,6H_2O$. The spectrum (Fig. II) shows that the material is not quite free from praseodymium, but the three bands corresponding to this element are very faint; the bands of neodymium, however, are definite, and in this region of the spectrum are represented by a very faint and narrow band midway between the two least refrangible bands of praseodymium, at 474·5$\mu\mu$, and a well-defined group of three bands which do not appear to have been recorded hitherto; the wave-lengths of their maxima are approximately:

353 $\mu\mu$. Centre of the strongest part of a band having a broad wing on its least refrangible side;



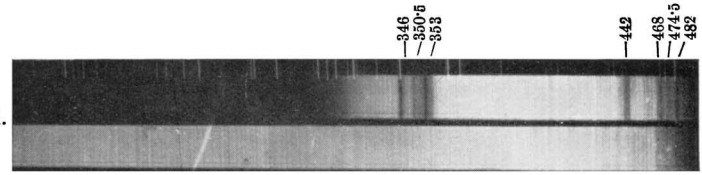
I.

Praseodymium.



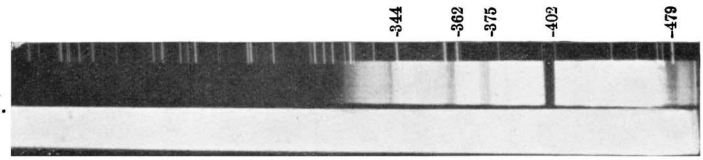
II.

Neodymium (impure).



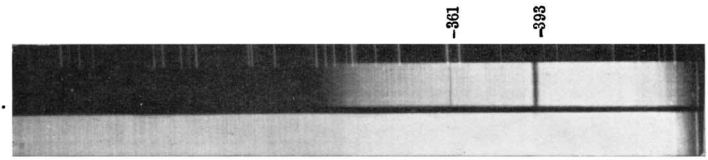
III.

Old Didymium (1884).



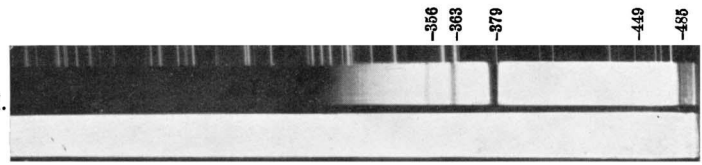
IV.

Samarium.



V.

Europium.



VI.

Erbium.

[*To face page* 1520.]

350·5 μμ. Brightest edge of a band, fading off at the most refrangible edge;

346·7 μμ. Centre of the most refrangible band.

An interesting confirmation of the allocation of the faint band at 474·5 μμ to neodymium is seen by reference to Fig. III, which is the absorption spectrum of a 1 : 10 solution of the nitrate of a specimen of didymium prepared, in the form of a dark brown oxide, by Cleve in 1884 — some 12 months before Welsbach announced his discovery of the complex nature of the substance. It can be seen that all the bands of praseodymium and neodymium are visible, including the faint one at 474·5 μμ.*

Samarium. — Samarium nitrate forms yellow crystals of $Sm(NO_3)_3,6H_2O$. The spectrum of its solution is characterised by a very strong band having sharp edges and by four other broad, but faint, bands; there is also an indication of a fifth band, but it is too faint to measure. As the spectrum as a whole did not seem to correspond to the description given by Demarcay (*Compt. rend.*, 1900, **130**, 1185), other photographs of it were made using stronger solutions, but the character of the bands did not change. The measurements of the approximate centres of the bands are (Fig. IV):

First faint band: 479 μμ. Centre of dominant band: 402 μμ.

Centres of other faint bands: 375 μμ, 362 μμ, 344 μμ.

Europium.—This element is one of the rarest of the yttria earths. The oxide of the specimen under examination was of a faint cream tint, whereas it is said to be light pink. The spectrum shows a strong but narrow band with a very sharp edge on the more refrangible side, and one other faint but equally sharp band; the wave-lengths of the approximate centres are 393 μμ and 361 μμ (Fig. V).

Another specimen of this earth from an unknown source gave exactly the same spectrum.

Erbium.—The material from which the nitrate was prepared was a pink oxide prepared by Cleve in 1885. The wave-lengths of the absorption bands as determined by various observers vary considerably, but in this case there was one dominant band accompanied by four others that are all very faint; the wave-lengths of the approximate centres are as follows (Fig. VI):

A strong band at 485 μμ; a very faint band at 449 μμ.

* In discussing the spectrum of neodymium, J. F. Spencer ("The Metals of the Rare Earths," 1919) states that a band with a maximum at 469 μμ coincides exactly with one of the praseodymium bands and that this has led to the view that these substances contain an undiscovered element. The photographs of Cleve's old didymium and of the later praseodymium and neodymium fail to justify this view, as all the bands of the old element in this region of the spectrum are accounted for

The dominant band, sharp on the least refrangible side, at 379 μμ.

A very faint band, which is crossed by a strong uranium line (from the source of light), at 363 μμ.

A very faint line at 365 μμ.

This element is said to be slightly radioactive and a photographic experiment was therefore made : the oxide was filled into a tube closed at the end by a sheet of aluminium foil 0·04 mm. thick, which was fixed on a photographic plate so that the oxide was separated from the sensitive surface by the aluminium, and it was shut up in a dark box for 7 days. On developing, a faint but decided impression was obtained, where the oxide had rested. A similar experiment made with europia also gave an indication of radioactivity, but much more feebly.

[*Received, January 27th,* 1926.]