Summary

1. Fractionation of cerium group material as double magnesium nitrate concentrates element No. 61 between neodymium and samarium.

2. All fractions contain so small a proportion of No. 61 that its detection by X-ray analysis is difficult.

3. The absorption bands of Element No. 61 are masked by the broad bands of neodymium and samarium.

4. Fractionation as bromates reverses the order of solubilities, interposing gadolinium between No. 61 and samarium and terbium between No. 61 and neodymium. Under these conditions absorption bands probably due to the presence of Element No. 61 become plainly visible.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OBSERVATIONS ON THE RARE EARTHS
XXIII. ELEMENT NO. 61
PART TWO. X-RAY ANALYSIS

BY J. ALLEN HARRIS[1] WITH L. F. YNTEMA AND B. S. HOPKINS

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In order to justify the assumption that the absorption bands obtained by the investigators, as outlined in Part I, were due to the presence of Element 61 an X-ray spectrograph of the Uhler type was constructed in this Laboratory. A tube was also constructed on which many helpful suggestions were received from Professor Manne Siegbahn who was at the University of Illinois at that time, and to whom the investigators are indeed grateful. The bulb was of the cold cathode type, the cathode being of pure aluminum and the target of copper. Both were connected to the bulb by means of ground-glass joints which permitted their ready removal at any time, and were water-cooled. The average potential applied was about 30,000 volts with an average current of from 8 to 10 ma. Its source was the 220v. power line of the University. In view of the voltage required to excite the K series and the limitations of our equipment, it was decided to photograph the L emission spectra only.

Much difficulty was encountered in keeping the rare earth oxides on the target during the bombardment with cathode rays. The oxides showed a marked tendency to fly off during the long exposures which we were compelled to make, so it was found impossible to apply the oxides in powder form. The method of fusing the oxide to the perforated surface of the target[2] gave better results but even this method was not entirely satis-

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[1] From a thesis submitted in partial fulfilment for the requirements of the degree of Doctor of Philosophy at the University of Illinois.

[2] THIS JOURNAL, 46, 37 (1924).

factory for long exposures. The problem was finally solved by attaching to the face of the target a copper plate in the center of which there had been cut a depression about 15 mm. in diameter. The edges of this depression were undercut so the diameter was greater at the bottom than at the top. The rare earth oxide was compressed into a pellet which was just large enough to fit into the depression on the copper plate. The oxide was then fused in an electric arc using the plate as one electrode and a copper rod as the other. In this manner we secured a button of oxide which was ground down to the level of the copper plate, furnishing a permanent target capable of withstanding long bombardment. A new copper plate was used whenever the sample was changed. A long exposure on one of these targets failed to yield any copper lines, from which we assume that the button of rare earth oxide was the sole source of X-radiation. The button failed to give a qualitative test for copper.

Owing to the relatively low energy input, the crystal was rotated over an arc of but 30′, so that only a small portion of the series could be photographed at one time. For this reason it was decided to rotate over the angle for $L\alpha_1$ of Element 61 as calculated from Siegbahn's precision values, for the first exposures.

The first three exposures were made using the sample taken from the least soluble fractions of the double magnesium nitrate series S_{1-6}. In the first two of these exposures the distance from our crystal to the plate was 15.41 cm. so that we encountered considerable air absorption. The second plate was rejected as we found that the plate holder had worked loose and thus might have been moved, although the line checked exactly with the first plate. The remaining exposures were made after our spectrograph had been remodeled cutting down the distance from crystal to plate to about 8.81 cm. This allowed of a dispersion of about 0.5 mm. between the $L\alpha_1$ and $L\alpha_2$ of samarium. In all cases we used the Sm $L\alpha_1$ line as our reference and checked the deviation from the theoretical value for 61 $L\alpha_1$ against the Sm $L\alpha_2$ or Nd $L\alpha_1$ lines. In every case our value for the 61 $L\alpha_1$ line was well within the limits of error of measurement with our apparatus.

The second series of exposures were on a sample taken from fractions of the bromate series which first gave the 5816 Å. absorption band, while the last sample to be examined was taken from the CT series of bromates which had been concentrated much more than had the previous sample. In this case we rotated over the angle for the $L\beta_1$ line of 61, and obtained a line considerably stronger than we had obtained for the $L\alpha_1$ line in the previous sample. This indicates that we had effected a concentration of Element 61 in the CT series. There is also an indication of a line corresponding to the $L\beta_3$ of No. 61 on our last plate, but as this is at the edge of the area of general radiation covered by our oscillation it cannot definitely be considered. Our tube cracked before we were able to expose for the $L\alpha_1$ on this plate.

In Table I we have listed the wave lengths of the lines we have obtained, the value given in every case being that obtained at the initial reading of our plates. In all cases our lines were faint, indicating that our material is not in a very concentrated form. Our plates have in all cases been verified by disinterested observers. The lines were measured by means of a Hilger dividing engine, the center of the lines having been marked as closely as possible previously. The values calculated deviated from precision values always in the same direction as did those of the Sm $L\alpha_2$ or Nd $L\alpha_1$ which were measured and calculated as checks. This, then, indicates that our deviation is due to our limits of accurate measurement.

TABLE I

WAVE LENGTHS OF LINES OBSERVED

Date	Fraction	Time of exposure	Observed wave lengths in Å. $L\alpha_1$	Observed wave lengths in Å. $L\beta_1$	Deviation from calculated values
Dec. 16	S_{1-6}	$16^1/_4$ hrs.	2.2800		+0.0023
Jan. 2	S_{1-6}	$24^1/_4$	2.2800[a]		+ .0023
Jan. 24	S_{1-6}	$8^3/_4$	2.2786		+ .0009
Feb. 10	BT_{14-15}	$12^1/_2$	2.2803		+ .0026
Feb. 22	BT_{14-15}	$16^3/_4$	2.2786		+ .0009
Mar. 6	BT_{14-15}	15	2.2730		− .0047
	Av. value		2.2781		
	Value calcd. from Siegbahn		2.2777		
	Deviation		0.0004+		
Mar. 13	CT_{11}	$10^1/_2$ hrs.		2.0770	+0.0040
Value calcd. from Siegbahn				2.0730	

[a] Plate rejected. Loose plate holder.

We have taken into consideration all possibilities other than Element 61 that might give rise to lines in this region, such as a lag during oscillation, defects in the crystal, and lines of other elements in the first, second and third orders. We used three different calcite crystals during our analysis, so it is improbable that all three would show identical defects. All lines other than those of element No. 61 that occur in the regions investigated, as well as those whose second and third order spectra might interfere have been also listed in Table II. We had no source of chromium or vanadium since our target was of copper, and our slits were of lead with the exception of the last two exposures when our front slit was polished steel. Our original series had been carefully purified of all lanthanum, cerium and praseodymium, and the exhaustive fractionation subsequently would eliminate all possibility of these being present. The fractionation had been continued for a long time after the last absorption line of praseodymium had disappeared which assures the absence of this element as well as lanthanum and cerium both of whose double magnesium nitrates are less soluble than that of praseodymium.

TABLE II

LINES POSSIBLE IN THIS REGION OTHER THAN ELEMENT 61

Wave length	Element	Series		Wave length	Element	Series
2.270	La	Lβ_7				
2.273	Cr	Kα_3				
2.277	Ce	Lβ_6	Lines of first order in this region	2.067	Cr	Kβ_2
2.277	La	Lβ_9		2.072	Ba	Lγ_4
2.280	Va	Kβ_1		2.080	Cr	Kβ_1
2.285	Cr	Kα_1		2.082	Ho	Lρ
2.285	La	Lβ_{10}				
2.285	Va	Kβ'				
				1.030	Hg	Lβ_3
1.129	W	Lγ_5	Second order lines possible	1.037	Tl	Lβ_4
1.133	Ir	Lβ		1.038	Hg	Lβ_2
1.135	Ta	Lγ_1		1.038	As	Kβ_2
1.138	Ir	Lβ_3		1.038	Br	Kα_1
1.140	Pt	Lβ_4		1.038	Au	Lβ_5
				1.042	Br	Kα_2
0.745	U	Lβ_4	Third order	0.664	Cb	Kβ_1
0.749	Cb	Kα_2		0.688	Zr	Kβ_2
0.752	Th	Lβ_3		0.700	Zr	Kβ_1
{2.277	61	Lα_1		{2.073	61	Lβ_1

Barium is the only probability in the case of the 61 Lβ_1 line since we used barium bromate during our conversion to the bromates, but since this salt crystallizes in the least soluble fractions and is removed, it is highly improbable that it would be present in the fractions analyzed, in amounts sufficient to give rise to the weak γ_4 line. There are no elements that could be present in our material to give rise to lines of the second and third order even had we been using an energy input sufficiently great to make lines of these orders visible on our plates. Mercury is eliminated, as liquid air was always used between the pump and the bulb. On our last plate we had a rather sharp edge of radiation close to our 61 Lβ_1 line that might possibly be due to the second order of the K absorption limit for bromine.

We propose the name of Illinium with symbol Il for this element in honor of the State of Illinois and of our University.

We wish to acknowledge our appreciation of the valuable assistance rendered by Professor H. C. Kremers and Mr. W. B. Holton during the course of this investigation.

Summary

We base our claim to the discovery of a new element on three different lines of evidence.

1. The presence of lines in the arc spectrum of materials prepared in

this Laboratory common to both samarium and neodymium and stronger in intermediate fractions. These consist of 130 lines in the red and infra red, and five lines toward the violet.

2. The presence in our intermediate fractions of absorption bands which become stronger as the characteristic bands of neodymium and samarium become weaker. The bands at 5816 Å. and 5123 Å. are especially prominent and their positions confirm the belief that there is a systematic drift in the absorption bands of the rare earth group.

3. The presence of lines in the X-ray emission spectrum corresponding closely to the theoretical positions for $L\alpha_1$ and $L\beta_1$ of Element 61. The mean value obtained for $L\alpha_1$ agrees within 0.0004 Å. of the value calculated from Siegbahn's precision values. The single reading obtained for $L\beta_1$ varies by 0.0040 Å. from the calculated value.

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OBSERVATIONS ON THE RARE EARTHS. XXIV. A THEORY OF COLOR

BY L. F. YNTEMA

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Rare earth ions are characterized in most cases by extremely sharp absorption bands in the visible spectrum and in the small portion of the ultraviolet that has been explored. The striking similarity in chemical properties exhibited by members of this group is due to a similarity in arrangement of the outer, or valence electrons. Differences in physical properties, such as colors of compounds, must be due to differences in the arrangement in inner levels or shells. According to Bohr[1] the addition of an electron takes place in the fourth level. Thus lanthanum (57) is assigned the arrangement 2–44–666–666–441–(2) and lutecium (71) the arrangement 2–44–666–8888–441–(2). In both instances the number of electrons in the fourth shell is such that it may be considered complete. Neither element has absorption bands, as far as is known. However, most of the elements of atomic number between 57 and 71 do have absorption bands.

The accompanying chart shows the frequency/mm. of the absorption bands of the rare earths for most of the region for which data are available.[2]

The length of each line is made equal to 4-log of the equivalent thickness of the last appearance. This arbitrary method of plotting affords a means of showing the most persistent bands as the longest lines.

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[1] Bohr, *Nature*, **112**, 29 (1923).

[2] THIS JOURNAL, **45**, 907 (1923).