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[Contribution from the Chemical Laboratory of the University of Illinois]

OBSERVATIONS ON THE RARE EARTHS. XXV. EXAMINATION OF CERTAIN RARE EARTH MATERIALS FOR ELEMENT NUMBER 72

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Considerable interest has attached to the question of the possible presence of element number 72 in rare earth minerals, and especially in the more soluble fractions of the yttrium group, because of the assertion of Urbain that the element celtium was found in such material. This investigation was undertaken for the purpose of furnishing more information pertaining to this interesting question.

Inasmuch as both zirconium and thorium, the two most closely related homologs of element number 72, are often found in varying percentages in rare earth minerals, it seems reasonable to suppose that element number 72, which comes between zirconium and thorium, should likewise be present. It is a well-known fact that the usual procedures employed for the separation of the rare earths concentrate the thorium and zirconium content in the most soluble fractions of the series. Wherefore, it is not improbable that element number 72 might also be present in these same fractions.

X-Ray Analysis

With this possibility in mind, an x-ray analysis[2] was made of the oxide material prepared from the most soluble fractions of two different crystallization series of the yttrium group. The L-series spectra in the region of the $L\alpha_1\alpha_2$ doublet for element number 72 was photographed but the most intense $L\alpha_1$ line was not visible on the plates. This would indicate that if this element were present, its concentration must be less than one part in one thousand, which we believe is the limiting concentration detectable by our method of x-ray analysis.

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

[2] Harris, Yntema and Hopkins, This Journal, **48**, 1594 (1926).

Arc Spectrum Analysis

The arc spectrum lines in the ultraviolet region are already well known for element number 72.[3] Using an E-1 model Hilger quartz prism spectrograph, we have measured the wave lengths of twenty-five of the most prominent and easily recognized lines of this element in order that they may be used for comparison. These selected lines are free from coincidence with all but a very few of the minor arc spectrum lines of the rare earths, zirconium, thorium and other probable interfering elements.[4] The material used to obtain this arc spectrogram was a mixture of the oxides of zirconium and element number 72, containing approximately 30% of the latter element.[5]

The wave lengths which we measured and the intensities as we observed them are given in the first column of the accompanying table, while the corresponding values as noted by Hansen and Werner are listed in the second column.

The arc spectrograms of eight rare earth preparations were examined, not only for these lines of element number 72, but also for the major lines of both zirconium and thorium. The first, second, third and fourth preparations were materials obtained at various steps in the working up of some original gadolinite from Hitterö, Norway. The presence of most of the rare earth elements and thorium was readily established. No evidence was obtained for the presence of either zirconium or element number 72.

The fifth and sixth preparations were phosphate precipitates obtained from the soluble end fractions of the two yttrium group series which were used in the x-ray analysis. The seventh preparation was a similar precipitate obtained from the soluble end fractions of a cerium group series. In these three materials thorium was found present but the presence of zirconium and element number 72 could not be established.

Preparation No. 8 was a solution of nitrates obtained from some potassium double sulfate residues. This rare earth–potassium double sulfate residue was the accumulation of many years' work, obtained by treating the most soluble fractions of various yttrium group series with potassium sulfate to remove the cerium elements along with zirconium and thorium. The arc spectrogram of this material revealed the presence of much thorium and no zirconium. The evidence with regard to element number 72 is presented in the third column of the accompanying table. The intensity symbols used in this connection have the following meanings: ab—absent; 0—a faint, yet distinctly perceptible line; and the other

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[3] Hansen and Werner, *Nature*, **112**, 618–619 (1923).

[4] For the arc spectrum lines of these elements, see H. Kayser, "Handbuch der Spectroscopie," Hirzel, Leipzig, **1908–1912**, Vols. IV, V and VI.

[5] This material was given to us by Dr. F. H. Driggs of this Laboratory.

numbers indicate proportionally increasing intensity. We feel that the probable presence of element number 72 is indicated in this material.

TABLE I

WAVE LENGTHS OF THE MOST READILY DISTINGUISHABLE LINES IN THE ARC SPECTRUM OF ELEMENT NUMBER 72

Holton and Hopkins		Hansen and Werner		Potassium double sulfate residues	
3428.37	1	3428.39	5	3428.37	ab
3417.33	1	3417.36	5	3417.33	ab
3352.03	2 (Ti)	3352.03	6 (Ti)	3352.03	0
3332.73	2	3332.74	6	3332.73	1
3312.88	1	3312.86	6	3312.88	ab
3253.71	2	3253.70	6	3253.71	0
3194.21	2	3194.20	6	3194.21	1
3176.83	2	3176.86	6	3176.83	0
3134.73	2	3134.77	6	3134.73	ab
3109.12	2	3109.14	6	3109.12	ab
3101.34	1	3101.42	6	3101.34	1
3080.66	1	3080.77	6	3080.66	ab
3072.92	6 (Ti)	3072.94	6	3072.92	1
3067.35	2	3067.39	6	3067.35	ab
3057.07	3	3057.04	5	3057.07	0
3016.79	4	3016.77	6	3016.79	ab
3000.07	1	3000.12	5	3000.07	ab
2982.70	1	2982.74	5	2982.70	0
2950.69	2	2950.72	5	2950.69	ab
2929.64	2	2929.66	5	2929.64	0
2919.61	2	2919.61	6	2919.61	0
2909.94	1	2909.91	5	2909.94	0
2898.70	2	2898.79	5	2898.70	0
2898.23	3	2898.31	6	2898.25	1
2866.37	5	2866.37	5	2866.37	1
2861.68	4	2861.72	6	2861.68	1
2861.04	4	2861.04	6	2861.04	0
2773.39	4	2773.42	6	2773.39	0

Summary

1. The method of x-ray analysis failed to show the presence of element number 72 in the most soluble fractions of rare earth elements of the yttrium group.

2. Arc spectrum analysis showed the presence of thorium and failed to show the presence of zirconium (1) in gadolinite from Hitterö, Norway, (2) in the most soluble fractions of rare earth elements from both the yttrium and cerium groups, (3) in an accumulation of potassium double sulfate residues obtained from the soluble end fractions of various yttrium group series.

3. Arc spectrum analysis failed to show the presence of element number 72 in any of the aforementioned rare earth materials except the last.

4. Arc spectrum analysis indicated the probable presence of element number 72 in the potassium double sulfate residues from the yttrium group.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

REACTIONS IN LIQUID HYDROGEN SULFIDE. III THIOHYDROLYSIS OF CHLORIDES[1]

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In the two previous papers from this Laboratory concerning liquid hydrogen sulfide as a reaction medium[2,3] it has been shown that while liquid hydrogen sulfide has, in many ways, more the properties of an organic solvent than water has, nevertheless there are some reactions that bring out its close relationship with water. One of these is its reaction with chlorides, especially those of the elements of the fifth group in the periodic table. This reaction, which corresponds to hydrolysis in water systems and ammonolysis in ammonia systems, has been designated as thiohydrolysis. While the above mentioned chlorides are the most reactive, other chlorides have been studied in order to make the series complete.

Most of the truly metallic chlorides, except $AlCl_3$, $FeCl_3$, $HgCl_2$ and $ZnCl_2$, are quite insoluble and non-reactive, but the more non-metallic chlorides are not only very soluble but many of them are quite reactive. An attempt has been made to bring about these reactions and to examine the products formed to show how complete is the thiohydrolysis.

Experimental

The liquid hydrogen sulfide was prepared in an apparatus very similar to that used by Quam.[2] The chlorides, after careful purification, were placed in heavy-walled, well-annealed glass tubes of about 10cc. capacity which had been dried by washing with alcohol and ether and then heating in an oven while passing a current of dry air through them. The liquid hydrogen sulfide was transferred directly from the generator to these after they had been cooled in a freezing mixture of ether and solid carbon dioxide contained in Dewar bulbs.

The reactions were allowed to take place at that temperature (about −77°) and at the same time other tubes were sealed at this temperature and then permitted to come to room temperature at which they were kept for a week or more, if necessary, for any slow reaction to take place. After the reaction had taken place at either temperature the excess of liquid hydrogen sulfide and any volatile substances were permitted to evaporate

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[1] This paper is from a portion of the work presented by A. W. Ralston in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Iowa State College.

[2] Quam, THIS JOURNAL, **47**, 103 (1925).

[3] Quam and Wilkinson, *ibid.*, **47**, 989 (1925).