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ABSTRACT

The methods of McWhan, Cunningham, and Wallmann were utilized to prepare lanthanide and actinide metals from fluorides which were made by precipitation from aqueous solution and (a) dried over P_2O_5 or in a vacuum, or (b) dried with heating in a stream of HF or of BrF_3 gas in the absence of avoidable water. The reduced metals were analyzed by the method of Markowitz and Mahony using helium-3 ions to convert oxygen-16 to fluorine-18. The latter was determined by coincidence counting of positron annihilation radiation. The method was checked using thorium and gold which were run as above and also by vacuum fusion.

Terbium trifluoride dried over P_2O_5 gave metal containing at least 2090 ppm oxygen. Thorium metal gave an average of 1394 ppm with a of 1320 ppm by vacuum fusion. Commercial lanthanum contained 970 ppm as analyzed directly--and 1000 ppm after being re-melted in barium vapor. Other "wet" precipitated trifluorides gave metals containing:

curium, 4470; americium, 5450 ppm. Terbium trifluoride "wet" precipitated and then dried for three hours at 600°C. under anhydrous HF gave at best 310 ppm oxygen and at best 260 ppm carbon.

The analysis of submilligram samples of such metal for their common anionic impurities was impossible until the development by Markowitz and co-workers of their scheme for carbon and oxygen activation analysis by bombardment with helium-3 ions. This scheme was adopted to the lanthanide-actinide problem by Green and Demildt and further modified by Ryan and Lowenhaupt. The method is readily adaptable to analysis of nitrogen. The activated targets were counted by multi-channel pulse height analysis or by coincidence counting of γ-rays from β^+ annihilation.

Small samples of the lanthanide and actinide metals are made conveniently by the reduction of the trifluorides with barium vapor at elevated temperatures.[1][2] Metals of quite low cationic impurity content have been made in this way[2] but the degree of contamination by oxygen, nitrogen, and carbon was unknown. The analysis of submilligram samples of such metals for their common anionic impurities was impossible until the development by Markowitz and co-workers[3] of their scheme for carbon and oxygen activation analysis by bombardment with helium-3 ions. Their scheme was adapted by Demildt[4] to work with active metals and further modified by the present authors. The method is readily adaptable to analysis for nitrogen. The activated targets were counted by multi-channel analysis or by coincidence counting of gammas from positron annihilation.

In an attempt to develop a preparative technique applicable to the production of small quantities of the rarer actinide metals, we have applied the helium-3 activation method to the analysis for oxygen, and in some cases carbon, in a number of small scale preparations of lanthanide and actinide metals. These were prepared from trifluorides made as detailed below.

In as far as the analytical technique was concerned, it was initially necessary to study the degree of reliability of the individual analysis and to determine whether a lower limit to the oxygen content was set by oxygen contamination during reduction or during the analytical procedure.

To answer the first question, a number of milligram samples of metallic thorium were analyzed for oxygen by the activation method. These samples were all taken from the same large piece of thorium metal foil, and a sufficient amount of this foil was submitted so that

analysis for oxygen by the vacuum fusion method could be made. Oxygen analysis results of 1160, 1170, 1240, and 1700 for an average of 1320 with an average deviation of 192 ppm were reported on four samples. The results of the activation analysis of this thorium foil are shown in Table 1.

TABLE 1. OXYGEN ACTIVATION ANALYSIS OF COMMERCIAL THORIUM FOILS.

Sample number	ppm O
1	1280
2	1100
3	1330
4	1460
5	1500
6	1460
7	1370
8	1390
9	1660
Average 1394 ppm	
Average deviation 112 ppm	

In order to investigate the possibility of oxygen contamination during sample preparation and encapsulation, milligram samples of pure gold were substituted for the active metals. These were sealed in platinum capsules and bombarded and counted in the usual way. If oxygen (as indicated by F^{18} counts) reached the gold via adsorption on platinum, imperfect inertion of the inert gloved box, imperfect

evacuation of the platinum capsule, etc., it could reach the metal under study in the same way. The low chemical affinity of gold for oxygen is not important, as the He^3 beam would drive resultant F^{18} atoms into the gold if oxygen were present anywhere inside the capsule.

Four portions of the same piece of foil gave 16, 98, 199, and 34 ppm oxygen respectively.(5) Three other portions submitted for vacuum fusion gave results of 21, 12, and 78 ppm O. J. W. Frazer and co-workers of the Lawrence Radiation Laboratory, Livermore, kindly performed the vacuum fusion analyses. No further investigation of the reasons for the large spread in values was made, since all were substantially less than the lowest values found for the metal preparations.

In order to investigate the importance of oxygen contamination from the crucible and vacuum system during reduction, the oxygen content of lanthanum metal before and after remelting in a standard reduction apparatus was investigated. Three samples of commercial lanthanum (Research Chemical Corp.) were analyzed by activation analysis and found to have an average oxygen content of 970 ppm with an average deviation of 215 ppm. Two samples of the same material were subjected to the usual reduction operation (exposure to Ba vapor in a vacuum) and remelted at 1150°C. The remelted material had an average oxygen content of 1000 ppm with an average deviation of 40 ppm. These results indicate that there was no significant oxygen contamination due to the preparative technique in the 1000 ppm range.

On the submilligram scale the mechanical manipulation of the starting trifluoride is facilitated if it is first precipitated from aqueous solution and then allowed to dry slowly to produce a hard

compact mass. Such "wet precipitated" trifluoride is known to contain about 1/2 molecule of water per molecule of trifluoride,[6] but weight changes on further drying suggest that this water is eliminated by high vacuum drying at about 150°C.[6] or by prolonged drying over P_2O_5 in a vacuum desiccator.

To study the completeness of drying, the oxygen content of terbium prepared from terbium trifluoride was studied as a function of the fluoride drying time. The results are given in Table 2. These results appear to indicate that considerable amounts of oxygen (presumably as water) remain in "wet precipitated" trifluoride even after very extended periods of drying over P_2O_5 or in high vacuum. Terbium was selected originally because the reduction conditions are similar to those used for curium.

On the assumption that most of the oxygen originated from water or oxyfluoride, a sample of wet precipitated TbF_3 was treated with

TABLE 2. OXYGEN CONTENT OF TERBIUM METAL MADE FROM "WET PRECIPITATED" TRIFLUORIDE.

TbF_3 drying conditions	O content of Tb Metal (ppm)
I. 9 days over P_2O_5	6400
II. 18 days over P_2O_5	3380
III. 27 days over P_2O_5 26 days at 10^{-7} mm	3070
IV. 27 days over P_2O_5 43 days at 10^{-7} mm	2090

commercial anhydrous HF. Four reductions were made using this material and the metal analyzed for both oxygen and carbon by activation. The results of these analyses are shown in Table 3. The oxygen content of these preparations was substantially lower than for those derived from physically dried trifluoride; however, the carbon contents were rather high. In an attempt to remove both water and organic impurities, several batches of TbF_3 were treated with BrF_3. The activation analysis results for metals prepared by this method are also shown in Table 3. These results indicate that this procedure is inferior to the simple HF treatment. For this reason, further TbF_3 preparations were made using anhydrous HF purified by multiple batch distillation to remove organic impurities. The results for samples derived from this material are shown in Table 3. The results for several samples of americium and curium preparations derived from physically dried trifluorides and from americium produced from AmF_3 treated with purified HF are also shown in Table 3.

Standardization: The oxygen content of silica, and the carbon content of silicon carbide, are assumed known, and presumably are constant under considerable heating, as during the bombardment. Portions of these compounds are encapsulated at the same time as the metal samples, and are rotated in the beam so that metals and standards receive equal exposure. However, silica and silicon carbide contain much more oxygen and carbon than does the metal under study. The gold and thorium foil provide checks near the oxygen content of interest. It has been suggested that further checks could be made using the non-stoichiometric compounds recently studied by L. L. Eyring.

TABLE 3. OXYGEN AND CARBON CONTENTS OF LANTHANIDE AND ACTINIDE METALS BY ACTIVATION ANALYSIS.

Sample	Treatment of wet precipitated trifluoride	O (ppm)	C (ppm)
Tb	HF* dried at 600° 3 hours	580	1470
Tb	HF* dried at 600° 3 hours	330	680
Tb	HF* dried at 600° 3 hours	310	750
Tb	HF* dried at 600° 3 hours	480	970
Tb	BrF_3 400° for 3 hours; H_2 300°-600°C for ten min	1440	1680
Tb	BrF_3 400° for 3 hours; H_2 300°-600°C for ten min	1770	1530
Tb	BrF_3 400° for 3 hours; H_2 300°-600°C for ten min	1500	1360
Tb	HF# dried, 600° for 2.5 hours	350	260
Tb	HF# dried, 600° for 2.5 hours	2200	390
Tb	HF# dried, 400°C for 1 hour 600°C for 3 hours	620	330
Tb	HF# dried, 400°C for 1 hour 600°C for 3 hours	490	600
Tb	HF# dried for 3 hours at 800°	730	410
Am	MeOH wash, vac dried 11 days at 10^{-6} mm Hg	5450	
Am	MeOH wash, vac dried 11 days at 10^{-6} mm Hg	980	
Cm	dried over P_2O_5	4070	
Cm	dried over P_2O_5	4470	

*Tank warmed to 25 psig then vented to 15 psig.

#HF purified by re-distillation.

In conclusion, it appears that the treatment of wet precipitated lanthanide and actinide trifluorides purified with anhydrous HF yield metal samples having oxygen contents of the order of 300-700 ppm and carbon contents of the order of 250-600 ppm.

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FOOTNOTES

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