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ANALYTICAL SECTION

# ANALYSIS FOR OXIDE IN THORIUM METAL

PROBLEM ASSIGNMENT #7

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## ABSTRACT

To estimate the oxygen picked up by thorium in casting a rapid method of running the acid insoluble content of the metal was developed. The quickest procedure consists of reacting with mixed acids, fuming with perchloric and filtration to separate the "free" thorium from the "combined". The precipitate is ignited and weighed as thorium dioxide.



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## ANALYSIS FOR OXIDE IN THORIUM METAL

While it is possible to determine oxygen by vacuum fusion in graphite[1], a need has arisen in the production of thorium for a rapid method to ascertain the oxide content of the metal. The equipment necessary and the time required rule out the former method as a routine procedure.

## EXPERIMENTAL

A. Solubility of Thorium Metal

Thorium reacts vigorously with hydrochloric acid leaving a fine black powder. This residue seems to consist of finely divided thorium metal and oxide. Upon prolonged boiling with hydrochloric acid, the black residue dissolves leaving a white granular powder; three to five hours boiling with six normal hydrochloric acid is necessary. Similar results are obtained with (a) hydrochloric acid-hydrogen peroxide mixtures, (b) nitric acid, or (c) fuming perchloric acid. Hydrochloric acid solutions containing traces of fluosilicic acid, after long boiling, give complete solution. X-ray studies of the black residue have been made, but their results showed only strong metal and weak oxide lines. These findings are in agreement with previously reported work(1).

B. Hydrogen Evolution

Since the hydrogen liberated by solution of the metal in hydrochloric acid should be equivalent to the free metal content, hydrogen evolution procedures were tried. Errors could be caused by (a) any thorium hydride present, (b) hydrocarbons that might be given off, (c) undissolved thorium in the oxide and (d) any suboxide of thorium that might be oxidized. The error due to hydrocarbons can be minimized by converting the hydrogen to water by passing the evolved gas over copper oxide at 300°C. At this temperature most hydrocarbons should be untouched, while the water formed can be absorbed by calcium chloride or magnesium perchlorate and weighed. This should be more accurate than the more obvious procedure of measuring the volume of the gas in a water burette. On the first twenty-seven samples of metal submitted for analysis, the free metal content calculated from the volume of gas evolved averaged 95.8 per cent. Some values were as low as 84.8 per cent while others were as high as 101.7 per cent. Since these variations might be attributed to the possible errors previously mentioned, the procedure utilizing the oxidation to water should be preferred.

C. Acid Insoluble

Since thorium dioxide is relatively insoluble in hydrochloric acid, it seemed logical that a separation could be effected by reaction with hydrochloric acid alone. Numerous runs were made with this hypothesis as a basis; but the extensive boiling required led to a search for a more rapid method of solution. Several grams of the "HCl-insoluble" were prepared by boiling two hundred grams of thorium with

eight normal hydrochloric acid. The resultant white granular powder was washed well and dried at 115°. Samples of this were dissolved in nitric acid containing a trace of fluosilicic acid and the thorium then precipitated with oxalic acid. Filtration and ignition to the oxide showed the "HCl-insoluble" to be 88.45 ± 0.05 per cent thorium. This is slightly higher than the thorium content of thorium dioxide but the presence of some suboxide of thorium could account for the discrepancy. Little is known about the suboxide (or suboxides) of thorium, but there is X-ray data to show the probable existence of such a substance[2]. Using this white residue as a source of material, the effects of different acids were studied. It was found that the "HCl-insoluble" was little affected by nitric acid or nitric-hydrochloric acid mixtures; some solubility resulted from fuming with perchloric acid, the amount dissolved increasing slowly with longer fuming. Investigations with the metal showed there was no advantage in fuming samples longer than fifteen minutes; in this length of time, less than half a per cent of the oxide present was dissolved. In dissolving the metal, a mixture of acids was used; hydrochloric to disintegrate the massive metal, nitric to rapidly oxidise the black residue left from the hydrochloric, and perchloric to dissolve rapidly the yellowish residue left by the other two acids. Care should be exercised to see that samples are not allowed to fume to dryness since there is some evidence to show that thorium perchlorate may be decomposed by the heat of a hot plate. This would give a high value for the "perchloric acid-insoluble".

D. Recommended Procedure: Perchloric Acid Insoluble

Samples of thorium weighing about two grams are chosen; surface oxide may be removed by a brief treatment with warm one to one nitric acid containing a trace of fluosilicic acid. Samples can be ground and polished mechanically, if desired. The samples are allowed to react with a mixture of acids (10 ml 6 N HCl, 10 ml 9 N $HClO_4$, and 2 ml 16 N $HNO_3$) until all the massive metal is decomposed. The mixtures are placed on the hot plate and allowed to boil to fumes. After fuming for ten to fifteen minutes (during which time the solution changes from yellow to colorless) the samples are removed from the hot plate, cooled, diluted to about 100 ml and filtered through S and S white ribbon filter paper (or its equivalent). The residues are washed eight to ten times with thirty ml portions of dilute (1:100) HCl. The filtrates are occasionally cloudy through some peculiarity of thorium solutions. The filters are placed in weighed crucibles, charred and then ignited in the muffle at 950-1000°C to constant weight. The crucibles are removed, cooled in a desiccator and weighed. The weight of oxide can either be converted to metal to give "combined thorium" or the per cent "acid-insoluble" (oxide) can be calculated directly.

If total thorium is desired, the filtrate from the acid insoluble is heated almost to boiling, filter pulp and excess oxalic acid are added. When the solution is cool, it is filtered and the precipitate is dried, charred and ignited to $ThO_2$ as before. The weight of dioxide will give the "free metal" present and the sum of "free" and "combined" thorium will give the total thorium in the sample.

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REFERENCES

1. Templeton, Niedrach and Byerly, CC-2694 (March 14, 1945).

2. N. Baenziger, CC-1984 (Nov. 10, 1944).

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