Preparation Of Homogeneous Thorium Oxide Powders For Development Of Certified Reference Materials

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Abstract

In view of the growing importance of Thorium Oxide (ThO_2) as a fuel in nuclear power reactors, it is essential to develop Certified Reference Materials (CRMs) for trace level assay of ThO_2 in order to validate analytical methods and also to assess the performance of an individual chemical laboratory. The present paper discusses the preparation of four batches of homogeneous Thorium Oxide (ThO_2) powders on kilogram levels including a batch of ThO_2 and Natural UO_2 mixed oxide with varying amounts of impurities and also developing them as CRMs based on round robin tests.

1.0 INTRODUCTION :

The mineral Monazite, which is a precursor for the manufacture of Thoria (ThO_2) is available in abundance in the beach sands of Southern India. The chemical processing of Monazite leads to generation of thorium concentrate which is finally converted to Thorium Oxide after separation of rare earths. Thorium Oxide is used as a flux flattener to control the initial reactivity in Pressurised Heavy Water Reactor (PHWR) and also as a blanket material for production of U^{233}.

Characterisation of thorium oxide for chemical purity forms an important and essential step for its quality assurance.

In order to meet the above mentioned purpose, a programme was initiated at Nuclear Fuel Complex (NFC) for in-house preparation of four batches of homogenous ThO_2 CRMs on kilogram level with varying amounts of impurity contents including one batch of mixed oxide containing thorium and natural uranium oxide.

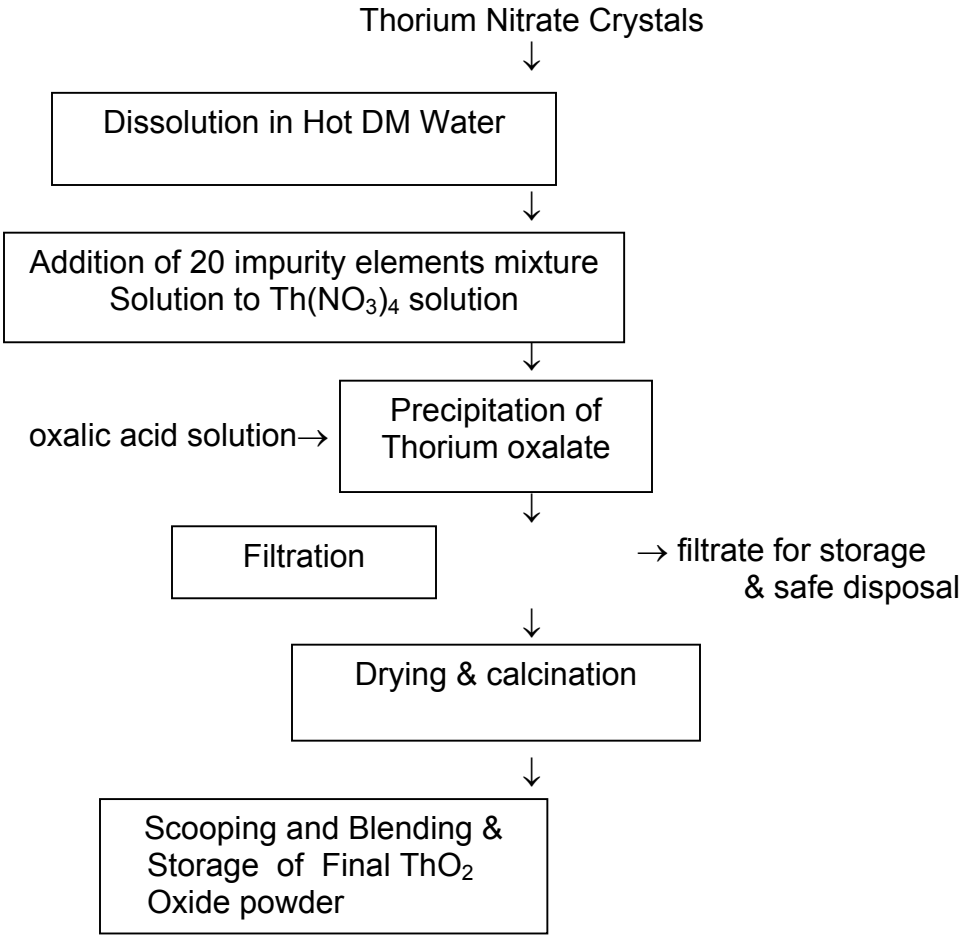
The powders that were produced at NFC include :

a) Thorium Oxide having impurities at base level (ThO_2-B)
b) Thorium Oxide having impurities at single specification level (ThO_2-S)
c) Thorium Oxide having impurities at double the specification level (ThO_2-D)
d) Thorium Oxide + Uranium Oxide (mixed oxide) having a composition of97.5 wt% of ThO_2+2.5 wt% of UO_2 and impurities at single specification level (ThO_2-MOS)

Also, the nodal procedure to analyse these materials has been developed and standardised at NFC [1] and the same was distributed to participating chemical laboratories along with sample materials for Round Robin Tests.

2.0 EXPERIMENTAL

2.1 Preparation of homogenous ThO_2 powders: A brief flow sheet for the preparation of homogeneous Thorium Oxide (ThO_2) powder for the development of Certified Reference Material (CRM) is outlined below:



Description of the process: A batch of thorium nitrate crystals ($Th(NO_3)_4.5H_2O$) was dissolved in hot DM water. Subsequently, all the desired impurities at the required levels were added in the form of acidic solutions, after considering their retention behaviour during oxalate precipitation. Afterwards, excess of oxalic acid solution were added to the tank with constant stirring. In the case of mixed oxide preparation, Uranyl Nitrate Pure Solution (UNPS) was added to thorium nitrate solution prior to mixing of oxalic acid solution. After precipitation, thorium oxalate slurry was drained out of the tank and filtered hot. Thereafter, wet thorium oxalate precipitate was dried and calcined.

The basic chemical reactions involved in the above process are as follows:

$$Th(NO_3)_4 \cdot 5H_2O + 2H_2C_2O_4 \cdot 2H_2O \rightarrow Th(C_2O_4)_2 + 4HNO_3 + 7H_2O \quad \text{----- (1)}$$

$$Th(C_2O_4)_2 + O_2 \xrightarrow{\Delta} ThO_2 + 4\,CO_2 \quad \text{----- (2)}$$

Homogenisation, storage and distribution: The resultant thorium oxide powders were homogenised in a double cone mixer situated in an enclosure for different times. Afterwards, the powders were discharged directly into double walled polythene bags which were in turn stored in SS containers. Finally, samples from the powders were distributed to all the participating laboratories for Round Robin Tests for analysis of impurities by a nodal analytical procedure.

2.2 Analysis of Thorium oxide powders by a Nodal procedure : Prior to the analysis of thorium oxide powders for trace metal assay by Inductively Coupled Plasma – Atomic Emission Spectrometric (ICP-AES), the matrix was separated from the analyte elements using each of the two extractants. In the first method, four contacts with 40% TBP / CCl_4 / 5M HNO_3 followed by two contact with 0.2M TOPO/CCl_4/5M HNO_3 were employed. Where as the second method involves five extractions with 30% Cynex/Xylene/4M HNO_3. After the separation, residual thorium and the concentration of analytes were determined by ICP-AES.

3.0 RESULTS & DISCUSSION:

3.1 Preparation of the Powders: All the four batches of homogenous ThO_2 powders were prepared through the solution route. This involves the addition of 20 impurities at different levels as mentioned above to the thorium nitrate solution followed by oxalate precipitation [2]. Subsequently, thorium oxalate precipitate was thermally dried and calcined in air to give thorium oxide powder. Thermo Gravimetric – Differential Thermal Analysis (TG-DTA) technique was employed to know the calcination temperature of thorium oxalate. The Specific Surface Area (SSA) of ThO_2 powder varies from 19.5 m^2/gm to 4.3 m^2/gm depending upon the calcination temperature [3].

Out of four batches prepared, first batch contains impurities at base level, i.e. without addition of impurities to thorium nitrate solution, second batch contains impurities equal to that of specification limits whereas the third batch contains double the level of specification limits. Finally, the last batch is a mixed oxide containing impurities equal to that of specification limits.

Prior to the bulk preparation, preliminary studies were conducted on laboratory scale to assess the extent of retention of added impurities in the final calcined product. The laboratory scale experiments were conducted in a similar conditions as that of plant scale. Before analysing the ThO_2 powder, moisture content was estimated in the wet thorium oxalate precipitate. It is observed that there is a considerable reduction in concentration of many elements added except rare earths, Cd, Ca upon oxalate precipitation from the base value present in thorium nitrate. The percentage recovery of these elements in the final ThO_2 powder through the oxalate precipitation route is in between 15% to 20%. Whereas for calcium, it is around 45% and more than 80% for rare earths and Cd. It indicates that majority of the elements are not co-precipitated along with thorium oxalate whereas rare earths and Cd are almost co-precipitated and calcium is partially co-precipitated.

Then, the only way to retain these elements in thorium oxalate and thereby in the final ThO_2 is by adjusting the levels of impurity elements added initially to thorium nitrate solution taking the moisture content in thorium oxalate into account.

3.2 Homogenisation, storage and distribution : The time for homogenisation was arrived only after analysing the different portions of sample obtained through cone and quartering of the powder discharged from the double cone mixture. After the homogenisation, the powders were discharged directly into double walled polythene bags which were in turn stored in SS containers. Then, the powder samples were distributed to all the participating laboratories for Round Robin Tests.

3.3 Round Robin Tests: A proposal for conducting Round Robin Tests in order to serve the purpose of obtaining ThO_2 CRMs was taken up involving a large number of analytical laboratories.

During the analysis, matrix removal is essential in view of spectral interferences encountered in ICP-AES measurements. In our experiments, relatively higher amounts of residual thorium was observed in cynex extraction procedure compared to TBP-TOPO extraction method. In the TBP-TOPO method, CCl_4 was used as the diluent, which being denser, resulting the organic phase at the bottom of separating vessel enabling its effective separation. Whereas in the cynex procedure, xylene was used as the diluent, which is being lighter than the aqueous phase, resulting organic phase at the top of the aqueous phase making it difficult to separate the two phases by

separating funnel. Because of this problem there may be higher residual concentration of thorium in aqueous phase in the cynex extraction procedure.

Compilation and statistical treatment of analytical data from all participating labs was presented in the form of a report [4]. From the report it is seen that there is no significant differences in the results obtained from various labs. In addition, the elemental concentrations obtained as median values are classified into three categories based on IAEA specified criteria [4] such as

(i) Recommended value with satisfactory degree of confidence (Class-A)
(ii) Recommended value with acceptable degree of confidence (Class-B)
(iii) Uncertified Information Value (Class-C)

Based on this classification, the overall classification of the analyte elements in all the four samples is given in below in Table I. From the table it is clear that, out of 20 elements added as impurities, up to 17 elements have got the status of Class-A which is testimony to the homogeneity of the powders made at NFC. Further, more number of elements getting Class-C status in case of ThO_2-B sample is attributed to variations associated with analytical measurements of low concentrations.

TABLE I : CLASSIFICATION FOR THE ANALYTES IN FOUR SAMPLES

Sample	Elements	Class	Elements	Class
ThO_2 –B	Al,Ca,Cr,Cu,Mg,Mn,Mo,Ni Sm,V	A	B,Be,Cd,Ce,Dy,Er, Eu,Gd,Fe,Sb	C
ThO_2 -S	Al,Cd,Ce,Cr,Cu,Dy,Er,Eu, Fe,Gd,Mg,Mn,Ni,Sb,Sm,V	A	B,Be,Ca,Mo	C
ThO_2 - D	Al,Ca,Cd,Ce,Cr,Cu,Dy,Er, Eu,Fe,Gd,Mg,Mn,Ni,Sb, Sm,V	A	B,Be,Mo	C
$(Th,U)O_2$ –MOS	Al,Ca,Cd,Ce,Cr,Cu,Er,Eu, Mg, Mn, Ni, Sm, Sb, V	A	B, Be, Dy, Fe, Gd, Mo	C

The results of the analysis carried out in our laboratory along with the median values obtained in the statistical treatment of entire data from all participating labs is shown below in Table II.

It is clear from the table that the values obtained by our lab are in good agreement with overall median values. In case of boron, large variations are seen in the results from different labs whereas in case of Be, Dy, Er, Eu, Sb median values could not be calculated as values were not exactly quantified.

TABLE II : ELEMENTAL CONCENTRATIONS(IN PPM) IN FOUR ThO_2 SAMPLES ALONG WITH OVERALL MEDIAN VALUES OBTAINED IN ROUND ROBIN TESTS

S.No.	Element	ThO_2-B		ThO_2-S		ThO_2-D		ThO_2MOS	
		NFC value	Median value	NFC value	Median value	NFC value	Median value	NFC value	Median Value
1.	Al	7.3	6.24	43	39.2	71	63.5	46	36
2.	B	0.3	0.78	3.6	1.58	0.4	1.4	0.3	1.24
3.	Be	<0.5	-	<0.5	0.36	<0.5	-	<0.5	-
4.	Ca	68	71.4	342	343	589	591	503	472
5.	Cd	<0.1	0.03	1.1	1.03	2.0	2.0	1.5	1.3
6.	Ce	0.85	0.9	6.4	5.4	12.4	11.6	7.9	7.24
7.	Cr	10	7.7	8.8	7.38	16.0	13.3	25	19.6
8.	Cu	3	3	71	67.2	133	118	87	73
9.	Dy	<0.1	-	0.4	0.3	0.68	0.6	0.4	0.31
10.	Er	<0.1	-	0.3	0.3	0.7	0.57	0.35	0.3
11.	Eu	<0.1	-	0.12	0.11	0.3	0.23	0.10	0.12
12.	Fe	67	51.4	96	81.8	159	138	178	136
13.	Gd	<0.1	0.14	0.5	0.47	0.7	0.7	0.5	0.5
14.	Mg	4	4.5	153	170	72	70	41	36.3
15.	Mn	4	3.2	5.3	4.56	8.5	7.33	7.0	6.12
16.	Mo	1.5	1.08	27	21.7	58	48.9	29	21.4
17.	Ni	14	12	33	34	73	64	43	40
18.	Sb	<0.5	-	2.1	2.2	5.0	4.53	2.1	1.92
19.	Sm	0.15	0.17	0.95	0.7	1.40	1.33	1.1	0.92
20.	V	<1	0.2	3.4	3.0	7.6	5.87	4.0	3.45

4.0 CONCLUSION

Based upon Round Robin Tests, it is concluded that all the four batches of ThO_2 powders prepared at NFC are homogeneous and can be considered as Certified Reference Materials (CRMs).

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