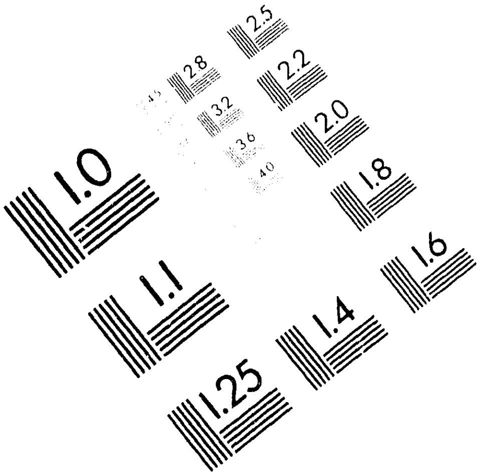

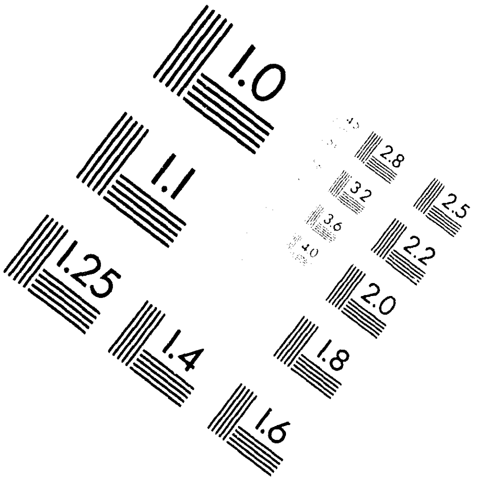

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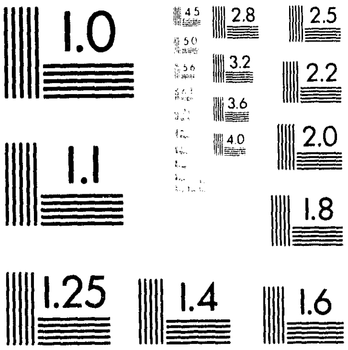

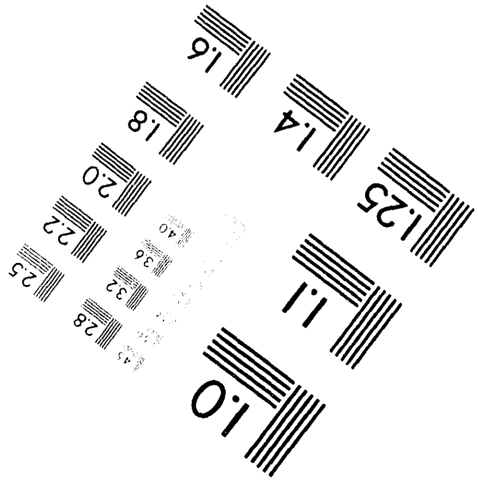

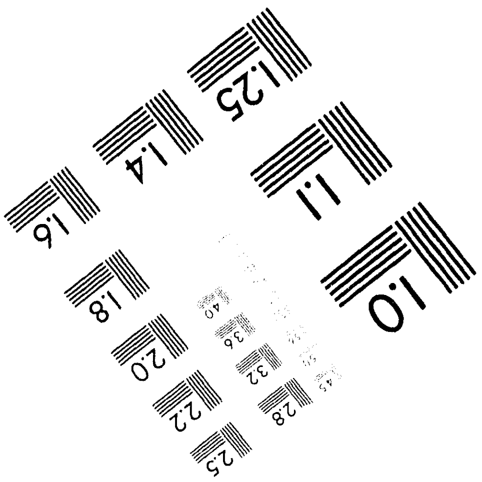

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MEASUREMENT PROCEDURES FOR PURIFIED BIRCH

by

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August 14, 1961

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MEASUREMENT PROCEDURES FOR PURIFIED BIRCH

INTRODUCTION

Since start-up of the neptunium recovery and purification program at HAPO, the neptunium has been subjected to the following process steps:

1) Production of crude neptunium nitrate by the Redox and Purex plants.

2) Production of purified neptunium nitrate, using an anion exchange process, in research and development facilities operated by CPD's Process Chemistry Operation.

3) Production of neptunium oxide (NpO_2) by Process Chemistry.

4) Mixing the NpO_2 powder with aluminum powder and incorporation in an aluminium-clad target element, done by the Plutonium Metallurgy Operation of Hanford Laboratories.

5) Irradiation of the target elements in the Savannah River reactors.

6) Chemical reprocessing of the irradiated target elements at Savannah River to recover the desired plutonium-238 and the unconverted neptunium.

As frequently happens to between-contractor transfers, neptunium material balances between Hanford's NpO_2 and Savannah River's recovered neptunium have sometimes been poorer than expected. Because of wide spread interest in this problem, it was deemed desirable to put on record a description of the measurement techniques which have been used at Hanford for NpO_2 and the

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improvements which have been made in the analytical methods. The measurement methods used for purified nitrate are also described.

SUMMARY AND CONCLUSIONS

Purified neptunium, either oxide or nitrate, is analyzed by 1) controlled potential coulometry, 2) TTA extraction and alpha counting, and 3) X-ray absorption. An average of the results from the three analytical methods has been found to be the best estimate of the neptunium content. Total alpha count corrected by alpha energy analysis is used only as a "referee" or to detect gross errors. The weight of neptunium oxide is determined with a triple beam balance accurate to better than 0.1 per cent. The volume of neptunium nitrate solutions are determined by weight and specific gravity.

The following observations have been made regarding the analysis of purified neptunium produced to date:

1) Long term averages of neptunium oxide assays as determined by coulometry, TTA extraction and alpha count, and X-ray absorption show a four per cent range. Improved analytical techniques are reducing the range between methods; for example the last two runs showed an average range of only 1.7 per cent between methods.

2) The theoretical values of 0.88104 and the first long term average of 0.8617 used to convert weight of oxide to SS weight were probably within 1 or 2 per cent of the real value.

3) The "F" factor 1.31×10^{-9} g/c/m, used to convert alpha counts to grams, is reasonably correct.

DISCUSSION

Crude neptunium nitrate produced by the Purex and Redox plants is sampled and weighed into product removal (PR) cans in a manner similar to that used to remove product plutonium from the separation plants.(5)(6) The neptunium content of the crude nitrate is analyzed by either controlled potential coulometry(1), TTA extraction and alpha counting (2), or by both methods. SS material accountability records are kept on neptunium from the time the material is removed from the separations plants.

In the ion exchange facility the crude neptunium is adjusted to feed composition and purified by variations of established flowsheets.(7) All waste solutions generated during the purification are sampled and analyzed for neptunium and plutonium. Neptunium is analyzed by TIOA-TTA extractions(2) and plutonium by alpha count. Waste solutions containing less than 35 mg Np/l and less than 35 mg Pu/l are discarded to underground waste storage.

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When neptunium oxide is to be produced, as was the case prior to April, 1961, and in July, 1961, the purified nitrate produced by the ion exchange process is checked for gross impurities, precipitated as an oxalate and calcined to the oxide. A composite sample of the oxide made from each batch of purified nitrate is analyzed for neptunium, uranium, thorium, plutonium, and metallic impurities. Two portions of the composite sample are weighed into 25 ml volumetric flasks on a five-place analytical balance accurate to 0.1 mg. The oxide is dissolved in nitric acid and the solution made to volume. Aliquots of the dissolved oxide are used for the analyses, except for metallic impurities which are done spectrographically on a portion of the composite sample. In the past, neptunium in the samples of dissolved oxide was analyzed by 1) total alpha count corrected by alpha energy analysis(3), 2) two different TTA extraction methods with alpha count(2), 3) X-ray(2), 4) controlled potential coulometry(1), and 5) by-difference, where all other impurities are analyzed for and subtracted out. Table I lists the results of the oxide analyses. A and B represent the two separate portions from the composited oxide. The specific activity of "F" factor used to convert Np^{237} alpha counts to grams was 1.31×10^{-9} g/c/m. The column headed "Range" lists the maximum range observed between the different analyses on a particular sample. Notice that in general the range has become less for more recent runs showing better agreement between analytical methods.

Because of tight shipping schedules for fabricated neptunium oxide target elements, it was necessary to fabricate the elements before analyses of the oxide were complete. Enough neptunium oxide for three elements was weighed in a tared high-temperature polyethylene wide mouth four ounce bottle. Either a standard laboratory platform balance or a triple beam balance accurate to 0.1 gram was used for the weighings. The balances were checked with a stainless steel check weight at least once a day. In the element fabrication step the amount of oxide for these elements was again weighed, thoroughly mixed with the proper amount of aluminum powder, divided into three portions and again weighed, packed in an aluminum billet, and extruded as an element rod. The weight of neptunium in each element was determined by the weight of the oxide-aluminum mixture packed into the billet before extrusion.

In the early stages of the program, it was assumed that the oxide was pure NpO_2 and the theoretical value of 0.88104 was used to convert weight of oxide to weight of metal or SS weight. Later, as oxide assay data began to accumulate, it appeared that 0.88104 was high; therefore, an average of a number of assays, as determined by the controlled potential coulometer, was used. The average assay used was 0.8617. The long term average of the assays, to date, now shows a value of 0.8720 as can be seen in Table I.

Total alpha count, or direct mount as it is sometimes called, corrected by alpha energy analysis gave consistently high results. The high bias is believed to be due to difficulty in correctly estimating the plutonium alpha contribution by alpha energy analysis. In other words, using plutonium free neptunium oxide, a high bias was not observed for the direct alpha counting measurement. Until this difficulty is resolved, the direct alpha counting measurement is recommended only as a back-up method.

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TABLE I

ANALYSIS OF NpO_2

		Per Cent Neptunium					
Oxide Batch	AT AEA	TTA 1	TTA 2	X-Ray	Coulometer	By Difference	Range
20	91.25						
21	73.6						
22A	85.65						
22B	88.06						
23	87.55					87.22	0.33
24A	86.55	90.89		84.22			6.67
24B	95.49	85.37		84.23		87.40	11.26
25A	94.78	88.60		86.99	85.83		7.79
25B	-	86.25		86.25	86.90	87.63	1.38
26A	88.40	-		84.20			4.20
26B	90.43			86.18		87.26	4.25
27A	98.29			85.23			13.06
27B	90.84			85.07		87.39	5.77
29A	91.30	88.21		84.13	85.84		7.17
29B	89.78	89.62		89.92	86.65	86.16	3.76
30A	88.45	89.90		81.78	86.52		8.12
30B	89.78	91.66		77.46	86.44	87.78	14.20
31A	86.34	84.05		74.65	86.81		12.16
31B	90.74	77.73		81.97	85.61	87.02	13.01
32A	84.24	87.05		82.52	84.35		4.53
32B	89.24	85.87		81.25	86.14		7.99
33A	86.57	84.12		82.97	85.91		3.60
33B	91.23	84.04		83.12	86.82	87.97	8.11
35A	90.65	63.55		80.40	85.33		27.10
35B	91.76	88.75		78.26	86.41		13.50
36A	91.09		88.21	88.63	88.21		2.88
36B	91.72		88.42	88.69	87.50		4.22
37A	90.50		85.36	85.26	89.03		5.24
37B	91.67		83.73	85.72	88.02		7.94
38A	87.66		87.34	81.04	88.69		7.65
38B	91.36		87.21	81.71	88.44		9.65
39A	90.02		88.33	85.84	88.33		4.18
39B	88.45		87.71	85.21	88.14		3.24
41A	89.29		89.71	86.83	87.67		2.88
41B	91.71		89.14	89.42	87.40		4.31
42A	88.66		87.97	84.39	89.36		4.97
42B	88.48		93.38	85.26	88.41		8.12
43A	89.79		88.46	86.61	88.54		3.18
43B	89.33		89.20	85.61	87.32		3.72

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		Per Cent Neptunium					
Oxide Batch	AT AEA	TTA 1	TTA 2	X-Ray	Coulometer	By Difference	Range
47A	90.61		87.47	87.21	88.12		3.40
47B	90.42		88.84	87.36	87.68		3.06
48A	88.39		88.40	87.75	86.78		1.61
48B	89.45		87.92	88.97	87.05		2.40
n	42	16	18	38	32	9	
$\bar{X}$	89.51	85.35	88.16	84.53	87.20	87.31	
s^2	12.7661	45.4626	3.6796	13.3209	1.1232	0.2738	

TTA-1 is designated as method NpA-1a in Redox laboratory manuals.

TTA-2 is designated as method NpA-5d in Redox laboratory manuals.

The first TTA extraction method, in which the neptunium is extracted into TTA from a nitrate system and a portion of the organic is mounted for alpha counting, gave low results and poor precision. Much better precision and higher results were obtained with the second TTA method. In this method, the neptunium is extracted into TTA from a chloride solution, stripped back into an aqueous phase, and a portion of the aqueous mounted for alpha counting. Coulometric results agreed within 1.1 per cent of the results obtained by the second TTA method. X-ray results appeared to be a little low, probably because of the large correction that must be made due to the high acid concentration needed to dissolve the oxide. The results obtained from the by-difference method, where all impurities are analyzed for and subtracted out, is not as desirable as a direct assay method because of the lack of specificity.

When purified neptunium nitrate is shipped, as was the case in January, April, and May, 1961, a sample of the nitrate is analyzed for neptunium by 1) TTA extraction and alpha counting, 2) controlled potential coulometry, and 3) X-ray absorption. An average of the results from the three methods is used as the best estimate of the neptunium assay. Total alpha count corrected by alpha energy analysis is used to detect gross errors. Table II shows the assays of the four batches of neptunium nitrate that has been shipped to Savannah River. Coulometric analyses were not available for Batches 40 and 44 so the neptunium assay is based on TTA extraction and alpha counting and X-ray only.

On loading the purified nitrate out, 3 to 3.5 liters are transferred to a tared one-gallon polyethylene bottle and weighed on a laboratory platform balance. The precision of the weighings are better than ± 0.05 per cent. The volume of the solution in each bottle is determined by a weight-specific gravity relationship.

As yet there is not sufficient data for the choice of a single preferred analytical method. The best estimate of neptunium assay is probably obtained by using the average of the TTA extraction, X-ray, and coulometer analyses.

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TABLE II

ASSAY OF NEPTUNIUM NITRATE

Batch	Assay g/1	% of Assay		Coulometer
		TTA-2*	X-ray	
40	49.93	101.9	98.1	-
44	39.51	100.7	99.3	-
45	35.44	101.5	102.7	95.8
46	35.18	99.3	100.0	100.6
Avg		100.9	100.0	98.2

* TTA-2 is designated as NpA-5d in Redox laboratory manuals.

Considering everything, the factors used to convert weight of neptunium oxide or neptunium nitrate to SS weight were never more than 1 or 2 per cent in error except in one instance.(4) The assay of future shipments of neptunium from the Research and Engineering Facility in 222-S Building will in all likelihood continue to be based on the average of the TTA extraction, X-ray, and coulometric analysis. When the permanent facility is completed in the Purex plant, official neptunium assays will probably be run on the coulometer with the X-ray and the TTA method used for back-up.

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