MLM-1863

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MASTER

***Mound Laboratory Chemistry
and Physics Progress Report:
July-September 1971***

May 5, 1972

AEC Research and Development Report

MOUND LABORATORY

Miamisburg, Ohio

operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company

for the

U. S. ATOMIC ENERGY COMMISSION

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Foreword

The Mound Laboratory Chemistry and Physics Progress Report, issued quarterly, is intended to be a means of reporting items of current technical interest in research and development programs. Since this is an informal progress report, the results and data presented are preliminary and subject to change.

These reports are not intended to constitute publication in any sense of the word. Final results either will be submitted for publication in regular professional journals or will be published in the form of MLM topical reports. Questions concerning the material compiled here should be directed to W. T. Cave, Director, Nuclear Operations.

Previous reports in this series are:

MLM-1829	MLM-1751
MLM-1815	MLM-1726
MLM-1792	MLM-1612
MLM-1767	MLM-1609

Table Of Contents

Page

SEPARATION CHEMISTRY

Residue Adsorption	6
------------------------------	---

The residue adsorption behavior of a high-specific-activity (HSA) source of ^{113}Sn and ^{113m}In was found to be significantly different from that of a low-specific-activity (LSA) source of the same nuclide with respect to the volatility of SnCl_4 and the desorption of ^{113m}In . Preparation of two ^{113m}In generators from the HSA source, one on powdered unfired Vycor and the other on silica gel, is described. The silica gel generator gave higher yields and purity of the ^{113m}In . An irreducible minimum amount of ^{113m}In was left on both generators when they were repeatedly leached with dilute HCl; this behavior is attributed to the crystal structure of the adsorbed stannic oxide.

Thorium-229 Recovery	13
--------------------------------	----

A method for separating thorium-229 from uranium-233, incorporating ion exchange from nitric acid solution onto AG-50W X 12 cation exchange resin, is being studied. It was found that pressed uranium dioxide-graphite powder compacts could be converted to U_3O_8 by air oxidation at 870°C . The weight of the U_3O_8 "ash" was greater than that corresponding to the uranium content, and the identity of the diluent was not determined.

Uranium-234 Recovery	13
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A batch of uranium, containing at least 10 g of uranium-234, was treated by a double homogeneous oxalate precipitation, then by an anion exchange technique. One fraction of the uranium product solution had the plutonium contamination lowered to 1500 ppm (by weight).

INORGANIC CHEMISTRY

Further Studies on Removing Molybdenum from Coated Ceramic Oxide Particles	15
--	----

Molybdenum may be removed from molybdenum-coated thorium dioxide by the use of aqueous solutions of hydrogen peroxide and potassium ferricyanide. Reaction begins when the mixture is gently

heated, and considerable heat is generated after the reaction is initiated, when peroxide is used. When the ferricyanide method is used, water and sodium hydroxide are added, and the solution is boiled with vigorous stirring. Both methods remove the major portion of the molybdenum coating.

ANALYTICAL CHEMISTRY

Determination of Oxygen Content of Polyethylene Containers Used in Neutron Activation Analysis.	17
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The oxygen content of polyethylene containers used in neutron activation analysis was determined by comparison to data obtained from four Mylar standards containing 0, 2.04, 2.81, 8.42 and 16.73 mg of oxygen. A polyethylene-container-material value of 0.77 mg was obtained for the actual sample. Nine additional randomly chosen containers were analyzed, showing a value of 0.7 ± 0.2 mg of oxygen.

Determination of Thorium in Plutonia by X-Ray Fluorescence	17
--	----

X-ray fluorescence techniques are being evaluated as a replacement method for the involved spectrophotometric procedure for determining thorium in plutonia. Encouraging results are presently being obtained on solid samples of plutonia containing known amounts of thorium, although precision is poor in the lower thorium concentration ranges.

Determination of Tritium Concentrations and Percent Tritium as Tritiated Water in Effluent Samples.	20
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Additional effluent samples were taken for the determination of tritium concentration by gas proportional counting, and for the determination of the percent tritium as tritiated water. Data are given for the accuracy evaluation of determining tritium in air by gas proportional counting.

REFERENCES	22
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Separation Chemistry

RESIDUE ADSORPTION

The results of an investigation of the residue adsorption behavior of ^{113}Sn and $^{113\text{m}}\text{In}$ were described in the last quarterly report.¹ The study was performed with a source of relatively low specific activity (~ 250 g/Ci). Since it was of interest to determine the effect of inert Sn on the adsorption/desorption characteristics of the system, a fresh source of higher specific activity (~ 1 g/Ci) was obtained and the various parameters previously tested were reexamined.

Several significant differences immediately became apparent. The volatility of SnCl_4 , which was a severe problem with the low-specific-activity (LSA) source, was found to be relatively insignificant when the high-specific-activity material (HSA) was evaporated to dryness. Furthermore, desorption of $^{113\text{m}}\text{In}$, which began with the LSA source only after the HCl concentration reached 0.1N or above, became significant in the HSA source with HCl concentrations as low as 0.001N. In view of these surprising differences, the entire investigation was repeated.

The HSA source was obtained from New England Nuclear Corp. and, after suitable dilution with 6N HCl, contained approximately 0.1 μCi of ^{113}Sn and 0.1 μg of inert tin (as SnCl_2) per drop, based on data supplied by the vendor. The procedures used were essentially those previously described¹ except that gamma-counting was limited to the area under the 393-keV photopeak of $^{113\text{m}}\text{In}$, instead of to the total of all gamma energies above 315 keV. (This change was made to minimize the error due to the high and erratically fluctuating gamma background in the laboratory.)

Because of the problems encountered with the LSA material, a preliminary series of experiments was carried out to determine the extent of losses due to volatilization of SnCl_4 and the effectiveness of various reagents in suppressing these losses. In addition, it was desirable to know to what extent these reagents interfered with the subsequent desorption. After evaporation to dryness, therefore, the adsorbates were leached first with 0.5 ml of H_2O and then with 0.5 ml of 0.01N HCl. In both cases, the adsorbate was heated for 2 min at 95°C in the presence of the desorbent before the solution was removed and counted. The results of these tests are given in Table 1.

The effect of adding inert tin was next investigated. Varying amounts of tin, as SnCl_2 in 6N HCl (1 mg Sn/ml), were combined with one drop of HSA ^{113}Sn and one drop of 0.001M Na_3PO_4 . The mixture was evaporated to dryness at 100°C and a second evaporation was performed after 0.25 ml of water was added to the residue. The residual amount of ^{113}Sn was determined and the residue was leached with water and then with 0.01N HCl, both heated to 95°C for 2 min before desorption. The results of this series are given in Table 2.

Table 1

SUPPRESSION OF SnCl_4 VOLATILITY AND DESORPTION OF ^{113m}In

Reagent Added	Volume (ml)	Residual ^{113}Sn (%)	Desorbed by H_2O (%)		Desorbed by 0.01N HCl (%)	
			^{113m}In	^{113}Sn	^{113m}In	^{113}Sn
None	0.00	99.4	0.7	2.2	72.7	8.1
H_2O	0.05	95.3	1.6	3.1	79.9	8.8
H_2O	0.25	98.4	0.4	0.9	68.8	3.1
0.0002M Na_3PO_4	0.25	100.3	1.3	1.6	89.2	13.0
0.001M Na_3PO_4	0.05	99.3	2.4	2.5	85.5	7.0
0.001M $(\text{NH}_4)_2\text{HPO}_4$	0.05	100.3	0.2	0.9	81.3	5.8
0.002M $(\text{NH}_4)_2\text{HPO}_4$	0.25	100.3	37.4	37.9	89.6	19.5
1N HNO_3	0.05	93.0	1.1	2.0	74.1	2.5
3N HNO_3	0.25	100.6	6.9	9.0	77.8	26.8
6N HNO_3	0.05	100.1	1.9	2.4	73.3	10.3
0.001N HClO_4	0.10	96.9	0.3	1.0	83.2	2.4
10^{-10} M Na_2EDTA	0.05	97.7	1.0	3.5	(lost)	
10^{-8} M Na_2EDTA	0.05	96.7	8.9	6.8	80.2	8.0
10^{-6} M Na_2EDTA	0.05	97.3	2.1	4.3	62.1	3.2
10^{-4} M Na_2EDTA	0.05	98.0	6.2	7.3	81.0	6.7
2×10^{-4} M Na_2EDTA	0.25	100.7	98.1	96.1	—	—
10^{-3} M Na_2EDTA	0.05	99.3	95.8	94.8	—	—

Table 2

EFFECT OF INERT TIN ON THE VOLATILITY AND DESORPTION OF ^{113}Sn

Sn Added (μg)	Residual Sn (%)	Desorbed by H_2O (%)		Desorbed by 0.01N HCl (%)	
		^{113m}In	^{113}Sn	^{113m}In	^{113}Sn
0	100.9	2.4	2.1	87.9	7.5
25	95.4	4.2	2.4	8.8	1.7
50	84.7	7.7	9.0	5.9	1.9
100	76.7	4.4	3.8	1.2	0.2

A series of tests was now performed in which the effects of the acidity and of the desorbent anion were examined. The procedure used was similar to that previously described.¹ The ^{113}Sn was adsorbed on the walls of a glass vial in the presence of phosphate ion and the residual phosphate was removed with hot water. Each vial was then leached repeatedly with 0.5 ml (two 0.25-ml portions) of varying concentrations of a mineral acid heated for 2 min at 95°C. The results are summarized in Figures 1 to 4 (solid lines).

It was observed that, after the desorbates had stood for some time at room temperature, large fractions of the desorbed ^{113}Sn and $^{113\text{m}}\text{In}$ remained adsorbed in the receiver vial when the desorbing solution was removed. This suggested that improved separations might be made if the desorbent, instead of being heated and immediately removed, were left in contact with the adsorbed ^{113}Sn for a longer time at room temperature. Accordingly, a second series of experiments was performed in which 0.5 ml of a given desorbent was added to the adsorbate, after which the vial was stoppered and left at room temperature (ca. 25°C) overnight. The solutions were then removed and gamma-counted. The results, represented by the broken lines of Figures 1 to 4, indicated that resorption did, indeed, occur and that the separation factors (ratio of $^{113\text{m}}\text{In}$ to ^{113}Sn in the desorbate) were enhanced. However, the $^{113\text{m}}\text{In}$ yield was significantly reduced (Table 3).

Table 3

$^{113\text{m}}\text{In}$ YIELDS AND SEPARATION FACTORS WITH 0.01N ACID DESORBENTS

Acid	Desorbent Heated at 95°C and Removed		Desorbent at 25°C Overnight	
	Yield (%)	Separation Factor	Yield (%)	Separation Factor
HCl	86.0	4.4	76.4	36
HNO ₃	79.7	7.5	57.0	41
HClO ₄	67.8	13.0	45.8	38
H ₂ SO ₄	--	--	62.6	19

Assuming equal yields and separation factors at each stage, it would require two stages of desorption with 0.01N HCl, for example, to produce a separation factor greater than 1000, with a yield of nearly 60%. Unfortunately, the short half-life of $^{113\text{m}}\text{In}$ (99.8 min) precludes the use of more than one stage of desorption from a vial. On the other hand, if the ^{113}Sn were adsorbed on powdered glass or silica, a column type of operation could be carried out. Powdered unfired Vycor was available for this purpose.

The bottom of a 2-dram vial was covered with 88 mg of Vycor which had been collected on a 100-mesh standard sieve. To this was added 2 μCi of ^{113}Sn in 0.05 ml of 6N HCl and one drop of 0.01M $(\text{NH}_4)_2\text{HPO}_4$. The solution was evaporated to dryness at 100°C and 2 drops of water were added to the residue. The vial was again dried at 100°C and gamma-counted.

The Vycor was transferred (as a slurry in 0.5 ml of water) to a small column previously prepared by plugging the end of a medicine dropper with glass wool. After the Vycor was transferred, the vial and column were washed with water and then with 0.05N HCl. Gamma-counting showed that only 5% of the ^{113}Sn remained in the original vial and only 0.2% of the ^{113}Sn had passed through the column in the washings.

FIGURE 1 - Desorption of tin-113 and indium-113m by HCl.

FIGURE 2 - Desorption of tin-113 and indium-113m by HNO_3 .

FIGURE 3 - Desorption of tin-113 and indium-113m by H_2SO_4 .

FIGURE 4 - Desorption of tin-113 and indium-113m by HClO_4 .

Desorption was carried out alternately with 0.5-ml portions of water and various concentrations of HCl. The results (Table 4) are expressed as percentages of the equilibrium amounts of ^{113}Sn and $^{113\text{m}}\text{In}$ before desorption. (Precision indices are not shown but it should be noted that the ^{113}Sn equilibrium counting rates were often only 1 count/sec or less above background, which was typically 8 ± 0.3 counts/sec but which fluctuated unpredictably during the course of a day and was sometimes as high as 13 counts/sec. Thus, the internal standard deviations for the ^{113}Sn values were in the range of $\pm 50\%$ and the separation factors had correspondingly large uncertainties.)

Table 4
DESORPTION OF $^{113\text{m}}\text{In}$ AND ^{113}Sn FROM A VYCOR COLUMN

Time Since Last Desorption (min)	HCl Concentration (N)	$^{113\text{m}}\text{In}$ Desorbed (%)	^{113}Sn Desorbed (%)	Separation Factor ^a
321.1	0.01	10.0	0.007	1440
1063.5	0.01	10.2	0.006	1763
3.0	(H ₂ O)	1.9	0.004	483
373.4	0.02	41.7	0.01	3669
1025.0	0.02	57.1	0.01	5581
2.6	(H ₂ O)	4.6	0.005	856
412.1	0.03	53.7	0.008	7035
1123.0	0.03	75.3	0.01	5129
2.9	(H ₂ O)	2.4	0.005	518
315.9	0.04	55.1	0.02	2885
1132.6	0.04	80.5	0.03	3044
3.1	(H ₂ O)	2.2	0.01	205
307.0	0.05	55.1	0.04	1454
4394.1	0.05	86.6	0.08	1231
3.0	(H ₂ O)	0.8	0.02	45

^aRatio of the counting rates of $^{113\text{m}}\text{In}$ and ^{113}Sn in the desorbate.

It is apparent from the data in Table 4 that significantly higher $^{113\text{m}}\text{In}$ yields were obtained when the column was left overnight or longer in contact with a film of desorbent remaining from the preceding desorption. However, the ^{113}Sn contamination was also increased under these conditions, so that there was no significant improvement in the separation factor.

It was noted in the previous report¹ that there seemed to be an irreducible residual amount of ^{113m}In which remained incorporated in the SnO_2 crystal lattice when the LSA ^{113}Sn was adsorbed on the walls of a glass vial. The same appears to be true of the HSA material adsorbed on powdered Vycor. When the column was leached repeatedly with 0.5-ml portions of 0.05N HCl, approximately 20% of the ^{113m}In could not be desorbed (Table 5). The fifth through tenth desorptions in Table 5 were made at short and approximately equal intervals in an effort to strip all of the ^{113m}In from the column. The fifth and sixth desorptions removed the immediately available ^{113m}In , approximately 75% of the total initially present, while each of the next four desorbed only 5-6% of the total, corresponding approximately to the total amount (5.7%) which would have been produced by the decay of ^{113}Sn during the time between desorptions. Nevertheless, 21.4% of the ^{113m}In was found on the column when it was gamma-counted immediately after the tenth desorption.

Table 5
DESORPTION OF ^{113m}In WITH 0.05N HCl FROM A VYCOR COLUMN

Time Since Last Desorption (min)	^{113m}In Desorbed (%)	^{113}Sn Desorbed (%)	Separation Factor ^a	Residual ^{113m}In on Vycor Column (%)
1018.6	64.1	0.03	2112	NC ^b
3.2	11.1	0.04	254	27.6
420.5	83.8	0.04	1863	NC
2.9 ^c	1.8	0.02	109	18.9
1352.1	58.6	0.03	1947	NC
5.2	15.1	0.04	383	NC
7.0	6.7	0.04	153	NC
8.0	6.4	0.04	160	NC
7.8	5.8	0.04	139	NC
8.2	5.5	0.05	118	21.4
4028.6	85.6	0.06	1336	NC
3.4 ^c	1.8	0.01	124	15.9

^aRatio of the counting rates of ^{113m}In and ^{113}Sn in the desorbate.

^bNC = not counted.

^cH₂O desorption.

To determine the loading capacity of 100-mesh Vycor powder, a new column was prepared by the same method, except that 100 μ g of inert tin as SnCl_2 in 6N HCl was added before evaporation. It was found that 68 μ g of tin could be adsorbed on 49 mg of Vycor powder. Desorption with various concentrations of HCl gave disappointing results; only 43% of the ^{113}In was desorbed with 0.05N HCl along with 0.1% of the ^{113}Sn . Even 0.1N HCl desorbed only 56% of the ^{113}In along with 0.7% of the ^{113}Sn .

A third column was prepared with 160 mg of 100-200 mesh silica gel as the adsorbing surface; this column gave excellent yields and separation factors (Table 6). The data clearly show that the volume of desorbent is of less significance than the contact time. After desorption with an acid desorbent, the column was allowed to drain completely and to regenerate for several hours. When the residual desorbent was washed from the column with water, the yields and separation factors were typically equal to or better than those obtained by the preceding desorption with acid.

Table 6
DESORPTION OF ^{113}In AND ^{113}Sn FROM A SILICA GEL COLUMN

Time Since Last Desorption (min)	Desorbent (0.5 ml)	^{113}In Desorbed (%)	^{113}Sn Desorbed (%)	Separation Factor ^a	^{113}In Left on Column (%)
1160.0	0.05N HCl	93.4	0.16	734	-
3.2	H ₂ O	1.9	0.01	162	6.5
388.5	0.1N HCl	71.1	0.02	3784	24.0
4140.8	0.1N HCl	96.2	0.12	983	5.7
1212.1	H ₂ O	89.0	0.04	2233	12.6
297.4	0.01N HCl	50.3	0.02	3924	39.7
1120.4	H ₂ O	74.0	0.00 ^b	-	27.3
420.5	0.02N HCl	72.4	0.007	10453	24.9
1064.3	H ₂ O	86.5	0.01	7343	14.8
366.4	0.03N HCl	75.3	0.00 ^b	-	19.5
1098.9	H ₂ O	88.3	0.01	9166	13.1
341.9	0.04N HCl	74.2	0.002	43236	19.2
5332.5	H ₂ O	88.1	0.01	7513	13.3
440.0	0.05N HCl	80.1	0.00 ^b	-	17.2
1016.7	H ₂ O	88.2	0.002	46646	13.2
400.1	0.06N HCl	71.4	0.01	6266	24.6
1442.3	H ₂ O	81.9	0.01	7401	18.2
5435.3	0.1N HCl	81.8	0.01	5929	-
2.7	0.1N HCl	9.8	0.01	731	11.2
329.6	H ₂ O	80.6	0.02	4073	11.8
1068.5	0.2N HCl	82.5	0.04	1995	-
2.6	0.2N HCl	9.7	0.15	67	10.8
377.1	H ₂ O	83.4	0.13	629	11.3
1030.8	0.1N HNO ₃	68.2	0.003	21008	-
2.5	0.1N HNO ₃	14.1	0.005	2848	20.1
398.0	H ₂ O	80.5	0.002	33661	15.7
1021.4	0.1N HClO ₄	65.0	0.004	16232	-
2.6	0.1N HClO ₄	22.3	0.008	2808	15.4
408.0	H ₂ O	78.8	0.01	8181	16.2

^aRatio of the counting rates of ^{113}In and ^{113}Sn in the desorbate.

^bUndetectable.

It was possible, in some cases, to strip the column of all but 5-10% of the ^{113m}In , indicating that the stannic oxide was deposited on the silica surface in a configuration approximating a monomolecular layer. Under such conditions, any atom of ^{113}Sn converted to ^{113m}In would be exposed to the acid environment and would be available for desorption, whereas a ^{113m}In atom formed in the interior of a polymolecular layer would remain trapped as an impurity in the stannic oxide crystal. It should be possible to optimize the separation (or any separation based on residue adsorption) by controlling the conditions under which the adsorbate is deposited on the surface. Future work is being directed toward this objective. (H. W. Kirby)

THORIUM-229 RECOVERY

Several uranium-thorium test separation runs were made on milligram-size samples of UO_2 -graphite materials received from Gulf General Atomic. The results indicate a uranium-232 content of 2.2 ppm and an age since last thorium separation of 6 yr.

A recheck of a proposed ion exchange method of uranium-thorium separation was made. The uranium-thorium was to be loaded from 1.5M HNO_3 on AG-50W X 12 cation exchange resin, resulting in no retention of uranium and complete retention of thorium. The thorium would then be eluted with an ammonium acetate-acetic acid solution. In the tests, using the Gulf General Atomic uranium, which was free of fluorides, both the uranium and the thorium loaded, although the thorium apparently displaced the uranium. Additional work will be done using higher HNO_3 concentrations for loading, thereby reducing the tendency of the uranium to stick.

A York-Scheibel 1-in. (2.5-cm)-diameter, laboratory liquid-liquid extraction column was operated to calibrate instruments and gain experience. Water and TOPO-AMSCO, without solute, were used for the tests. From the preliminary tests, it appears that maximum column throughputs approximate the manufacturer's specifications, and it is expected that the column will operate satisfactorily for actual separations. Tests with depleted uranium in nitric acid and DSBPP-DEB (di-sec-butyl phenylphosphonate in diethyl benzene) will be started as soon as stainless steel safety cans for handling acidic flammable liquids are received.

Of the uranium-233 received from Gulf General Atomic, approximately 150 g were in the form of pressed pellets of UO_2 -graphite, canned in six welded aluminum "rods" approximately 1.5 in. (3.8 cm) in diameter and 3 ft (91 cm) long. These rods were disassembled and the approximately 10 kg of pellets obtained were placed in lead-shielded "bird cages" for temporary storage in the criticality storage vault. Oxidation tests were run on several of the pellets with the lowest uranium concentration. The oxidation rate became significant above 700°C and, above this temperature, was more dependent upon the amount of air allowed to enter the muffle than on the temperature. Tests were run at temperatures up to 870°C . In one run, 3.33 g of "ash" were obtained from the oxidation of 323 g of pellets. Based on Gulf General Atomic data, 1.47 g of U_3O_8 should have resulted. The identity of the additional material has not been established. (M. R. Hertz)

URANIUM-234 RECOVERY

The uranium-234 batch designated A12 originated from special processing of nearly 500 g of aged plutonium-238 heat source fuel. The fuel was dissolved, then the plutonium was precipitated with oxalic acid. Uranium-234, along with most of the impurities, remained in the filtrate. The oxalate filtrate solution was evaporated to a very small volume before the plutonium was precipitated by the usual homogeneous oxalate precipitation method. Some impurities appeared to have been precipitated along with the plutonium oxalate, so the plutonium was dissolved and precipitated a second time.

The combined oxalate supernatant solutions, containing 0.29 g of plutonium and at least 10 g of uranium-234, were evaporated to destroy the oxalate and remove part of the excess nitric acid. Additional nitric acid was neutralized with sodium hydroxide before the solution was salted with aluminum nitrate. The salted feed solution was passed through an anion exchange column, and was followed by an aluminum nitrate wash to remove impurities, a 7M HNO₃ wash to remove the uranium, and a 0.35M HNO₃ wash to elute the plutonium. The first two fractions collected, containing the impurities and aluminum nitrate, were difficult to analyze by alpha counting, but appeared to still contain 5 g of uranium-234. The next two fractions contained over 6 g of uranium-234 contaminated with approximately 1500 ppm (by weight) of plutonium-238. The plutonium fraction contained no detectable amount of uranium-234. The high uranium value in the raffinate solutions was attributed to overloading the capacity of the resin, and these solutions will be reprocessed for recovery of the uranium. The uranium fraction has been evaporated in preparation for the next purification step. (P. E. Figgins)

Inorganic Chemistry

FURTHER STUDIES ON REMOVING MOLYBDENUM FROM COATED CERAMIC OXIDE PARTICLES

In manufacturing processes involving the coating of plutonium dioxide with molybdenum, it is sometimes desirable to remove the molybdenum from the plutonium dioxide so that the latter may be easily recovered by dissolution in nitric acid. This stripping may be done, for example, in a melt of potassium hydroxide and potassium nitrate.² Two methods for attacking metallic tungsten and, therefore, perhaps metallic molybdenum, are suggested by Rieck.³ These methods involve treatment of the metal with hydrogen peroxide or with an aqueous solution of potassium ferricyanide and sodium or potassium hydroxide. Three 10-g samples of molybdenum-coated thorium dioxide containing 15.2 wt % molybdenum were treated with hydrogen peroxide, or hydrogen peroxide and oxalic acid, as described elsewhere.³ The amount of peroxide was a 100% excess of the theoretical amount of peroxide required to oxidize the molybdenum completely and such that the hydrogen peroxide concentration was 5-10 wt % of the stripping solution at the end of the reaction:

The reaction of molybdenum with dilute hydrogen peroxide begins when the reaction mixture is gently heated, and generates considerable heat as it progresses. With 30% hydrogen peroxide, the reaction of molybdenum is so rapid and violent as to constitute a potential safety hazard. The reaction medium gradually becomes acidic due to the presence of yellow precipitated molybdic acid:

Sample #1, when treated one time with hydrogen peroxide as above and washed with water, and then with dilute sodium hydroxide in a filter funnel, retained 450 μg of molybdenum per g of thorium dioxide, corresponding to removal of more than 99% of the original molybdenum. Sample #2 was treated two times with hydrogen peroxide as above and retained 60 μg of molybdenum per g of thorium dioxide. Sample #3 was treated three times as above, except that the hydrogen peroxide solution was saturated at room temperature with oxalic acid. Sample #3 retained 75 μg of molybdenum per g of thorium dioxide. These experiments were repeated exactly as above with thorium dioxide coated with molybdenum to the extent of 15.8% of total weight. Exactly as above, Sample #1 retained 80 μg , Sample #2 retained 80 μg , and Sample #3 retained 75 μg of molybdenum per g of thorium dioxide.

In another series of experiments, samples of molybdenum-coated thorium dioxide (each weighing 5 g) were treated with ferricyanide and sodium hydroxide as described in Table 7.

Table 7

PROPORTION OF INGREDIENTS IN STRIPPING SOLUTION,
AND AMOUNT OF MOLYBDENUM REMAINING IN
MOLYBDENUM-COATED THORIUM DIOXIDE AFTER TREATMENT
WITH THE STRIPPING SOLUTION

Sample No.	Volume of Water in Stripping Solution (ml)	Weight of NaOH (g)	Weight of $K_3Fe(CN)_6$ (g)	Theoretical Excess of $K_3Fe(CN)_6$ (%)	Molybdenum Remaining in Stripped ThO_2 (%)
1	50	10	25	50	0.17
2	50	5	25	50	0.005
3	50	5	25	50	0.005
4	37	4	18	8	4.3

Since the weight of each sample was 5 g, and since each sample contained 15.8% molybdenum, each sample contained about 0.8 g of molybdenum metal. Since molybdenum metal and ferricyanide react according to Equation 3:

each sample required a minimum of about 16.6 g of $K_3Fe(CN)_6$. The composition [i.e., proportions of water, NaOH and $K_3Fe(CN)_6$] of the stripping solution is also shown in Table 7. Each sample was stirred and heated gently with the stripping solution until the solution boiled. Boiling, with vigorous stirring to agitate the dense oxide material in the bottom of the reaction beaker, was then allowed to continue for about 10 min. The oxide material was then washed thoroughly with water by decantation and filtration, dried, and analyzed. Table 7 indicates that this method may be quite effective for stripping molybdenum from coated ThO_2 provided a sufficient excess of the ferricyanide is present.

Both the ferricyanide and hydrogen peroxide methods have the advantage that high temperatures are not required for the stripping process. Both methods suffer disadvantages, however. Neither method works well with chunks or fragments of molybdenum-coated compacted ThO_2 , (i.e., for these methods to be effective, the material to be stripped must be in powder or granular form). So much heat is generated by the peroxide method that the reaction may get out of control unless the peroxide is less than 30% concentration in the reaction vessel. Moreover, the heat may decompose the excess H_2O_2 , resulting in the generation of oxygen gas. This may be undesirable inside an alpha box. The ferricyanide method requires so much potassium ferricyanide per sample that the method may be uneconomical compared to other methods of removing molybdenum from ThO_2 . (G. L. Silver)

Analytical Chemistry

DETERMINATION OF OXYGEN CONTENT OF POLYETHYLENE CONTAINERS USED IN NEUTRON ACTIVATION ANALYSIS

In an effort to evaluate the oxygen content of polyethylene containers used in neutron activation analysis, standards containing 0 (blank), 2.04, 2.81, 8.42 and 16.73 mg of oxygen were prepared using 1/4-mil Mylar sheet⁴ containing 33.3% oxygen, from the formula $(C_{10}H_8O_4)_n$. The Mylar was cut to fit the inside dimensions of the container, rolled onto a glass stirring rod, inserted into the container, and then released, giving a snug fit to the inside surface.

A monitor was prepared similarly, but with 1.5 times the oxygen content of the highest standard, to obtain better counting statistics. The monitor was placed in one of the two pneumatic sample transfer tubes and kept in that particular tube throughout the analyses. Then each time a determination was made, both standard and monitor were irradiated with the same neutron flux.

To correct for variations in neutron flux between determinations, the ratio of counts of the standard to the counts of the monitor (after subtraction of background), were plotted as a function of oxygen content. From the experimental curve, the solid line in Figure 5 (the ratio of counts of the blank standard to the counts of the monitor) lies above zero, due to the apparent oxygen content of the blank. This value was obtained by drawing a parallel curve (broken line) to pass through the origin.⁵ The lateral separation of the two curves indicates the apparent oxygen content of the container, which was 0.77 mg. This value was added to each standard and a linear regression analysis of the data points showed an intercept of practically 0 mg of oxygen and a population correlation coefficient of +0.9999.

A series of nine additional polyethylene containers was randomly selected, including some containers used in previous analyses. These were analyzed using the monitor, and their values were obtained from the corrected oxygen curve. An average value of 0.7 ± 0.2 mg of oxygen was obtained at the 95% confidence limit.

An attempt will be made to determine the oxygen content of small hollow steel containers, using a similar technique. (R. D. Hamman and E. B. Nunn)

DETERMINATION OF THORIUM IN PLUTONIA BY X-RAY FLUORESCENCE

In an attempt to avoid lengthy and involved thorium and plutonium separation techniques prior to the x-ray fluorescence determination of thorium in plutonia, efforts were made to determine the thorium without separation of the plutonium. A 100-ml sample (plutonia containing a small quantity of thorium) was placed in the cavity of a microscope slide and mixed with a few drops of collodion. After the collodion was dried, a

0.005-in. (0.013-cm) thick piece of polystyrene was placed over the sample and securely taped in place. The slide was removed from the alpha box in a small polyethylene bag which was thermally sealed, and then sealed in a second plastic bag. (Containment integrity of plutonia was found to be satisfactory by this technique for at least 30 days.)

FIGURE 5 - Comparison of experimental and corrected curves.

Because of encouraging data from this sample, a series of thorium standards was prepared by spiking high-purity plutonium nitrate (prepared by dissolving high-purity plutonia with nitric acid) with known quantities of thorium nitrate. The thorium and plutonium were co-precipitated as the hydroxides with ammonium hydroxide and the hydroxides were converted to oxides by ignition at 900°C. Two series of standards were prepared for 1-min counts on the x-ray fluorescence spectrophotometer (chromium source and lithium fluoride crystal). Table 8 shows the fluorescence ratio data of the thorium $L\alpha_1$ to the plutonium $L\alpha_1$, and the data relating these ratios to percent thorium are shown in Figure 6. Background uncertainties result in the graph not passing through the origin and cause poor precision at the lower thorium concentrations.

X-ray fluorescence data were obtained on one sample (147 OX-62) with which thorium had previously been determined by the existing spectrophotometric method. An x-ray fluorescence result of 0.53% thorium compared favorably with the spectrophotometric result of 0.57% thorium. (H. A. Woltermann and S. A. Tomes)

Table 8

Th($L\alpha_1$) TO Pu($L\alpha_1$) RATIOS

Standard	Thorium (%)	Analysis Date	Th/Pu Ratio
1A	0	6/14	0.00180
		6/14	0.00180
2A	0.1	6/14	0.00679
		6/17	0.00853
2B	0.01	6/15	0.00631
		6/17	0.00548
3A	0.5	6/14	0.0172
		6/17	0.0178
		6/18	0.0178
3B	0.5	6/15	0.0182
		6/17	0.0171
4A	1.0	6/14	0.0320
		6/17	0.0331
		6/18	0.0326
4B	1.0	6/15	0.0324
		6/17	0.0329
5A	1.5	6/14	0.0483
		6/17	0.0476
5B	1.5	6/15	0.0466
		6/17	0.0475

FIGURE 6 - Th $L\alpha_1$ /Pu $L\alpha_1$ compared to thorium concentration.

DETERMINATION OF TRITIUM CONCENTRATIONS AND PERCENT TRITIUM AS TRITIATED WATER IN EFFLUENT SAMPLES

Additional effluent samples were taken to compare tritium concentrations as determined by gas proportional counting to Kanne chamber values. The percent tritium as tritiated water in some of the effluent air samples was also determined by the "freeze-out" method described previously⁷ and was compared to values obtained using a bubbler sampler.⁸

In order to evaluate the accuracy of the gas proportional counting method of determining tritium concentrations in air, samples of tritiated water which had been standardized against National Bureau of Standards (NBS) tritiated water, were converted to hydrogen,^{9,10} diluted with methane, mixed with room air, and counted. Table 9 shows the experimental values determined by proportional counting compared to the concentrations calculated from the NBS standard. The estimated maximum inaccuracy of the NBS standard was given as $\pm 1\%$; thus, acceptable accuracy of the gas proportional counting method is indicated. This is in agreement with earlier studies in which tritium gas was diluted in methane for proportional counting.⁹

Table 9

DETERMINATION OF TRITIUM CONCENTRATION IN AIR SAMPLES PREPARED BY DILUTION OF TRITIATED HYDROGEN FROM STANDARD TRITIATED WATER

Sample No.	Tritium Concentration in Prepared Air Sample (dis/min/cm ³)		
	Calculated from Standard	Average Experimental Concentration	Individual Experimental Concentrations
1	2.23×10^3	2.23×10^3	2.24×10^3 2.22×10^3 2.21×10^3 2.25×10^3 2.25×10^3 2.19×10^3
2	1.87×10^3	1.81×10^3	1.80×10^3 1.81×10^3
3	2.24×10^3	2.16×10^3	2.14×10^3 2.22×10^3 2.17×10^3 2.11×10^3

A number of 2-liter samples of exhaust air were taken for gas proportional counting to determine the tritium concentration. The percent tritium as tritiated water in some of these samples was also determined by freezing the water out of the sample as previously described. Results are given in Table 10. The two proportional gas counting tritium concentrations given for the sample of 6/1/71 actually represent two samples. In this case, two 2-liter samples were taken. One was counted within 30 min after sampling, the other was allowed to remain in the flask overnight before counting. The purpose of this delay in counting was to determine whether any of the tritium adsorbed

to the walls of the flask upon standing for a considerable period of time. From the concentrations obtained for the two samples, it can be seen that less than 10% loss of activity occurred.

Table 10

TRITIUM CONCENTRATIONS AND PERCENT TRITIUM
AS TRITIATED WATER IN EFFLUENT SAMPLES

Date	Tritium Concentration ($\mu\text{Ci}/\text{m}^3$)		Ratio of Kanne to Proportional	Tritium as HTO (%)	
	Kanne	Proportional		Bubbler	Freeze-out
4/26/71	23.7	12.4	1.9	15	29
5/12/71	28.8	4.90	5.9	37 ^a	47
5/24/71	33.3	6.45	5.2	35 ^a	44
6/1/71	43.2	9.07, 8.63 ^b	4.9		
6/2/71	16.7	9.52	1.8		
6/2/71	34.2	11.1	3.1		
6/17/71	-- ^c	5.1		82	67

^aSome tritiated water (determined by the freeze-out method) was found beyond the bubbler.

^bThe second number was determined by allowing the sample to remain in the 2-liter flask overnight before counting.

^cNo accurate Kanne value was available.

Bubbler samplers were also used to determine the percent tritium as tritiated water in the exhaust air. This system consisted of two gas-washing bottles connected in series, the first containing 250 cc of water and the second containing 50 cc of water, through which the gas passed at a rate of about 10 liters/min for 20 min. The tritiated water trapped by the bubbler was then counted by liquid scintillation counting. Ninety-three percent of the tritium collected was in the first bubbler, which is similar to the results observed by Valentine.⁸ Four results using the bubbler method are given in Table 10 and show fairly good agreement with the freeze-out results.

As in previous measurements of the effluent, Kanne values are higher than values obtained by gas proportional counting of grab samples. As suggested previously, the presence of alpha activity in the exhaust air could account for this discrepancy.⁷ Sampling could also be a problem, since the gas samples for proportional counting were not taken at the same location where the Kanne chambers take samples.

Future samples for gas proportional counting will be taken where the air just leaves the Kanne chamber; this will help to minimize sampling errors. The percent tritium as tritiated water will be determined at this same location by both the bubbler and the freeze-out methods. Also, an attempt will be made to develop a system that could convert all of the tritium in the 2-liter gas sample to tritiated water for liquid scintillation counting. This system would enable a more rapid determination of total tritium concentration, and of percent tritium as tritiated water, than does the gas proportional counting method. (C. T. Bishop, M. M. Bolton, M. L. Curtis, T. M. Flanagan, R. D. Hamman and R. L. Ryan)

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