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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-1751	MLM-1606
MLM-1726	MLM-1603
MLM-1612	MLM-1531
MLM-1609	MLM-1526

Summary

SEPARATION CHEMISTRY

Thorium-229 Recovery One shipment of 4.5 mg of thorium-229 was made to the Heavy Elements Research Pool at ORNL. An additional uranium-thorium separation run on 62 g of uranium-233 is nearly complete.

The uranium-233 purification waste raffinate obtained from Nuclear Fuel Services and found to be useless for thorium-229 recovery because of high natural thorium content, is being disposed of through the waste disposal facility. Seventeen of the original 42 26-gal (98-liter) drums have been processed. (Page 6)

Airport Cake Residues The ionium-rich "St. Louis Residues" are being processed by the Cotter Corporation in Colorado. Fourteen samples were collected during a visit to the plant, and are being analyzed for ionium and protactinium content. Preliminary ionium analyses indicate the ionium is being dissolved in the head-end step and tends to follow uranium through the process. Gamma spectral analysis indicates that a major portion of the protactinium is to be found in a "crud" layer formed in the solvent extraction step. This "crud" material seems to be a potential source of multigram quantities of protactinium. (Page 6)

INORGANIC CHEMISTRY

Instability of Heptavalent Plutonium in Water Solutions The potential of the Pu(VII)/Pu(VI) couple may be sufficiently positive to oxidize water in usual concentrations of acid and alkali. Methods of obtaining heptavalent plutonium are suggested. (Page 11)

ANALYTICAL CHEMISTRY

Liquid Scintillation Counting of Plutonium-238 The methods of alpha assay presently in use were compared on the basis of sensitivity, time required for analysis, accuracy, and cost. Calorimetry, 2π and 4π proportional counting, Logac, and liquid scintillation counting were compared. The results indicate that liquid scintillation counting is the ideal method for routine analysis of alpha emitters such as plutonium-238. (Page 12)

Preparation of Tritiated-Hydrogen Gas Standards Three samples of dry tritiated-hydrogen gas were produced from standard tritiated water by reduction with amalgamated magnesium. The samples were counted and used to evaluate the counting efficiency of proportional counting tubes. More standards will be necessary so that a better value for the efficiency and the absolute accuracy of tritium gas proportional counting may be determined. (Page 19)

X-Ray Fluorescence of Thorium Oxide-Uranium Oxide Mixtures A technique was developed for preparing x-ray samples by placing the thorium oxide-uranium oxide mixture on the outside surface of the aluminum pan and securing it in position with cellophane tape. This eliminates the need for mixing the oxides with gum arabic binder. A sample of 5-15 mg of pure oxide is sufficient to give a relative standard deviation ranging from 0.04 to 0.75% for five successive 24-sec counting periods of the selected characteristic x-ray fluorescence lines of thorium and uranium. (Page 20)

Separation Chemistry

THORIUM-229 RECOVERY

Purification of 4.5 mg of thorium-229, the pooled products of the last two uranium-thorium separation runs¹ on a total of 120 g of uranium-233, was completed and the thorium-229 was shipped to the Heavy Elements Research Pool at ORNL.

The current uranium-thorium separation run, on 62 g of uranium-233 which had been dissolved during the previous quarter,¹ is under way. The uranium-233 has been removed from the thorium-229 by extraction with di-sec-butyl phenylphosphonate (DSBPP) in diethyl benzene (DEB) using the continuous extraction-stripping apparatus previously described. The thorium-229 is being purified by extraction into tri-n-octyl phosphine oxide (TOPO).

The Nuclear Fuel Services waste raffinate from uranium-233 purification, from which it had been planned to extract the 300 mg of contained thorium-229, was found to be useless because of a natural thorium content of more than 100 kg. Seventeen of the 42 drums of this material on hand have been disposed of through the Mound Laboratory waste disposal facility. The rate has been limited to one drum per day to ensure that all radioactive material is removed by the facility. (M. R. Hertz)

AIRPORT CAKE RESIDUES

For a number of years, the waste material known as the "St. Louis Residues" or "Airport Cake" has been acknowledged to be the largest and best source of ionium (thorium-230). It was also felt that this material would contain appreciable amounts of protactinium. When it was learned that these residues were being processed by the Cotter Corporation of Canon City, Colorado, arrangements were made to visit the plant and to observe their process. During the visit, 14 samples were collected throughout the process; they are being analyzed for protactinium and ionium.

The Cotter mill operates two separate processes: a carbonate leach process, operating on domestic uranium ores, and an acid leach process,

operating on the St. Louis Residues. A simplified flowsheet of the Cotter processes is shown in Figure 1.

St. Louis Residues are dried in St. Louis and shipped to Colorado in railroad cars. The residue goes through a crusher and a ball mill before being leached with sulfuric acid at 190°F (88°C). After filtering and washing, the filter cake is sent to the waste tailings area. The filtrate, at a pH of approximately 1, contains uranium, copper, cobalt, and nickel values in the grams-per-liter range. Copper is recovered first by precipitating and filtering as copper sulfide. Uranium is recovered in a multi-stage mixer-settler, using di-2-ethylhexyl phosphoric acid as the extracting agent and sodium carbonate as stripping agent. The uranium, which is often contaminated with appreciable amounts of iron, is introduced into the middle of the carbonate leach process. The uranium from both processes is eventually recovered as yellow cake.

The raffinate from the solvent extraction contains cobalt and nickel values which are recovered by adjusting the pH to 2.5-3.0 and precipitating the sulfides. The filtrate from this precipitation is sent to the waste tailings area. A "crud" material usually forms in the first extraction stage and must be periodically removed. A sample of this material was obtained. Samples taken from the Cotter process are indicated on the process flowsheet (Figure 1) and are listed in Table 1 along with a short description.

The first analysis performed on the Cotter samples was to obtain gamma spectra using a multichannel analyzer and a sodium iodide detector. This technique uses the 68-keV peak of ionium and the 27 and 300-keV peaks of protactinium-231 to identify the presence of these isotopes; the 300-keV peak of protactinium-231 can be used for quantitative determinations. Gamma spectra of the first three samples (COT-1, COT-2, COT-3) showed the presence of other gamma emitters, probably radium-226 and daughters, so that the characteristic peaks of protactinium and ionium were nearly masked. After copper sulfide precipitation, the spectra showed only protactinium and ionium and, after solvent extraction and cobalt/nickel sulfide precipitation, the spectra showed nearly pure protactinium, but at decreasing levels. Later, by comparing these samples to a protactinium standard, the protactinium-231 content of the copper sulfide filtrate (COT-3) was estimated to be 12 µg/gal. This figure is subject to considerable error (estimated ±50%) and probably cannot be considered representative because of the variable composition of the St. Louis Residues.

Gamma counting indicated that about 75% of the protactinium "disappeared" in the solvent extraction step, with the raffinate containing the other 25%, but essentially no protactinium was found in the other two streams (COT-7 and COT-9). However, the gamma spectrum of the "crud" sample (COT-8) showed that it contained a large quantity of protactinium and this is apparently where the "missing" protactinium is going. The Cotter personnel report that the formation of crud is an intermittent problem, but that occasionally the crud builds up to the point where

ACID LEACH PROCESS

CARBONATE LEACH PROCESS

() Sample number for the location at which a sample was taken.

FIGURE 1 - Simplified flowsheet of Cotter processes.

Table 1

SAMPLES FROM COTTER CORPORATION RECOVERY PROCESS

<u>Sample Number</u>	<u>Description</u>
COT-1	6x6 Ball Mill Discharge--A slurry (in water) of the St. Louis residue as it comes out of the ball mill and just prior to leaching. Dried before analysis.
COT-2	#3 Acid Filter Cake--Solids remaining after leaching which are sent to tailings area. Dried before analysis.
COT-3	#1 Filtrate--Filtrate from sulfuric acid leach which is sent to copper recovery.
COT-4	Copper Thickener Overflow--Supernatant solution from copper sulfide precipitation.
COT-5	Cobalt/Nickel Thickener Overflow--Supernatant solution from cobalt/nickel precipitation, which is sent to waste.
COT-6	Solvent Extraction Raffinate
COT-7	Pregnant Carbonate--Carbonate strip solution containing uranium.
COT-8	Crud and Pregnant Organic--The crud has been separated by filtration and the two fractions are being analyzed separately.
COT-9	Stripped Organic
COT-10	Co/Ni Sulfides--Moist filter cake. Dried before analysis.
COT-11	Cu Sulfide--Moist filter cake. Dried before analysis.
COT-12	Yellow Cake--Calcined uranium product from both acid leach and carbonate leach processes.
COT-13	#3 Tail Thickener Overflow--Liquid waste from carbonate process.
COT-14	#3 Filter Cake--Solid waste from carbonate process.

it must be removed from the extraction cell. A second sample of crud, representing material which had been removed from the cell and set aside, was obtained and the gamma spectrum showed that this material was also very rich in protactinium.

Gamma spectra indicated that a major portion of the dissolved ionium was being extracted in the solvent extraction step, and then was being stripped along with the uranium. However, the gamma spectra could not be treated quantitatively. Work is in progress to determine ionium by a previously developed method² which involves coprecipitation of the purified thorium fraction with a small amount of cerium fluoride carrier, which is then mounted on a planchet and alpha counted. Preliminary results indicate that the acid leach solution (COT-3) contains over 2 mg/gal and the carbonate strip solution (COT-7) contains over 16 mg/gal. By way of comparison, the richest solution found in a previous survey of sources of ionium was 0.12 mg/gal.² Further discussion of the fate of ionium in the Cotter process will be deferred until more data are available.

It is not yet possible to evaluate the feasibility of recovering ionium from the Cotter process. The evidence indicates ionium is being dissolved in the leach step, follows the uranium through the extraction and stripping steps, and is passed into the carbonate leach circuit. It is presumed that the ionium either follows the uranium through the carbonate process and winds up in the yellow cake, or is rejected with the solid wastes.

The best source of protactinium from the Cotter process is the crud material. This is a by-product and seems to have little value other than for the protactinium it contains. Because of the variable nature of the crud formation, it is not possible to accurately estimate production rates, but it seems reasonable to expect multigram quantities of protactinium. This material is at least an order of magnitude richer in protactinium than the starting material of a previous protactinium recovery program. (P. E. Figgins)

Inorganic Chemistry

INSTABILITY OF HEPTAVALENT PLUTONIUM IN WATER SOLUTIONS

If the form of heptavalent plutonium is PuO_5^{3-} as has been proposed,³ and if the potential of the couple

is about 0.95 V in 1M hydroxide, then heptavalent plutonium should be capable of oxidizing water so that heptavalent plutonium solutions in which the plutonium is present as PuO_5^{3-} should not be permanently stable. Figure 2 shows a section of a predominance region diagram for water. This diagram also contains a line illustrating the potential behavior of the Pu(VII)/Pu(VI) couple in water solution. This line lies much outside the region of stability of water, suggesting that the best methods of obtaining heptavalent plutonium might include oxidation of hexavalent plutonium in a molten oxide or hydroxide, in a non-aqueous solvent, or in water by complex formation. (G. L. Silver)

FIGURE 2 - Potentials of the system $\text{O}_2/\text{H}_2\text{O}$ and $\text{PuO}_5^{3-}/\text{PuO}_2(\text{OH})_2$.

Analytical Chemistry

LIQUID SCINTILLATION COUNTING OF PLUTONIUM-238

Liquid scintillation counting has been used for alpha assay at Mound Laboratory since 1963, but has not been generally adopted as a routine analytical procedure. The methods of alpha assay presently in use (calorimetry, 2π and 4π proportional counting,⁴ Logac,⁵ and liquid scintillation counting) were therefore examined to compare their usefulness for process control, particularly for ^{238}Pu analyses. Sensitivity, accuracy, time required for analysis, and cost were considered.

Calorimetry is a very accurate method where applicable. For a high-wattage sample (30 Ci) on a Mound Laboratory standard calorimeter the precision (probable error) is 0.0005% and the accuracy (probable error) is 0.0020%. For a 45-mCi sample the probable error is 0.1%.⁶ Large sources can be measured without dilution and sampling. The disadvantage of the method is that comparatively large amounts of radioactivity are required for measurement, and so it is insensitive when compared to counting techniques.

Samples ranging from approximately 0 to 10^6 dis/min can be counted by 2π proportional counting,⁶ if corrections for coincidence losses are made. The geometry is 50%, but uncertainties are present because of back-scattering and self-absorption. These effects can be determined and corrected for, but for highest accuracy an absorption study would have to be made for each slide, and this is too time-consuming for routine analytical work. Alpha particles can be counted in the presence of betas by distinguishing against the betas with the voltage setting.

At Mound Laboratory 4π proportional counting is performed on solutions mounted on 1/8-mil (0.0003-cm) thick stainless steel foil. Scattering and absorption effects are determined for each sample. This method is not applicable to solutions which would react with the steel, and is generally too time-consuming for routine analytical work. Likewise, 4π counting performed on samples mounted on thin film, while excellent for standardization, is tedious and time-consuming for routine analytical work.

For high-level assay (5×10^4 to 5×10^9 dis/min), the Logac can be used. This counter is ideal for many applications. Sample thickness for high

specific activity alpha emitters is not critical, and back-scattered particles do not penetrate the Mylar window between the low geometry attachment and the proportional counter.

There are some disadvantages to this method of analysis. Sample preparation must be carried out in a closed hood, and there is always danger of contaminating the hood during mounting and particularly during drying of the samples. For this reason, there is danger of cross contamination of samples of different activity levels prepared in the same hood. There is also danger of contaminating the counting area with these high-activity slides. The sample deposit must be confined to a small area in the center of the slide. For ^{210}Po (half-life 138 days), self-absorption is not a problem, but for ^{238}Pu (half-life 87.8 yr) self-absorption introduces an error if activity levels exceed about 1.5×10^7 dis/min per slide. With isotopes of longer half-life, sample thickness becomes more critical. The problem is compounded by the fact that the samples, after drying, are not deposited uniformly.

With liquid scintillation counting, many of the problems inherent in the other measurement techniques, as applied to routine analytical work, are overcome. Sample preparation involves measuring aliquots of the sample into counting vials and adding 20 ml of scintillator solution (the exact amount is not critical). The tedious work involved in slide preparation is eliminated, namely: 1) choosing an electroconducting slide material which will not react with the acid in which the sample is dissolved; 2) obtaining a thin, uniform sample deposit centered on the slide; 3) drying the sample without losing volatile material; and 4) covering with a protective coating of collodion. The danger of contaminating the sample preparation area is minimized and, since the sample is in a closed vial while being counted, it cannot contaminate the counting area.

Since the sample is dissolved in the counting solution, self-absorption does not occur. Care must be taken to assure that the radionuclide stays in solution, however. Because of the very short range of the alpha particles in the scintillator solution, loss of pulses due to alphas emitted close to and toward the sides of the vial is negligible in a standard 25-ml counting vial.

Coincidence losses with alpha emitters are also negligible. Counts made on samples containing increasing amounts of ^{210}Po show no coincidence loss even at counting rates exceeding 2.6×10^6 dis/min.

Chemical quenching is easily avoided. Samples of ^{238}Pu , dissolved in 10 ml of 0.35N HNO_3 with 10 ml of gel phosphor added, were counted with 100% efficiency. Likewise, a sample of ^{210}Po containing 20 ml of scintillation solution showed no decrease in count when 5 ml of 0.1N HCl was added.

Counting efficiency and geometry are both 100%. This has been verified by several cross checks between liquid scintillation counting and other

assay methods. The most recent of these compared calorimetry, low-geometry alpha and liquid scintillation counting.

A solution containing approximately 60 mCi/ml of ^{238}Pu in 0.35N HNO_3 was used for the cross check. The solution was first analyzed for ^{241}Am (the daughter of ^{241}Pu) by gamma pulse height analysis, and was found to contain 557 ppm by weight compared to ^{238}Pu . The americium was removed by ion exchange and the isotopic ratios of the plutonium fraction were determined by mass spectrometry. The original sample was used for the alpha cross check. The composition of the cross check sample is shown in Table 2.⁷ It is important to know the isotopic ratios for calorimeter measurements, since the disintegration energy of the nuclides determines the heat generated in the decay process. For Logac and liquid scintillation counting, the total alpha disintegration rate is measured. The isotopic ratios and half-lives determine that 99.9% of this will be due to ^{238}Pu . For liquid scintillation counting, where beta decay must also be considered, the ^{241}Pu content is significant. Because of the 13-yr half-life, the beta disintegration rate of the sample is 1.5% of the total alpha.

Four 1-ml aliquots of the solution were pipetted into calorimeter cans, allowed to dry, and then measured in a standard calorimeter. Results are given in Table 3.⁶

Three separate 10^4 dilutions (25 μl to 250 ml) were made of the same solution. Three 10- μl aliquots of each dilution were pipetted onto 1-in. square (2.5 x 2.5-cm) stainless steel slides and measured by Logac counting. Three 10- μl aliquots of each dilution were also pipetted into vials for liquid scintillation counting. Results of these measurements are shown in Tables 4 and 5 and a summary of the cross check is given in Table 6. The almost exact agreement between Logac and calorimeter is no doubt fortuitous, since the calorimeter results include errors in pipetting four 1-ml aliquots, and the Logac results include errors in dilution, in pipetting the 10- μl aliquots, and in counting statistics. The liquid scintillation counting results include these same sources of error. Thus, liquid scintillation counting shows excellent agreement with an assay based on a heat measurement, and with the absolute alpha counting method based on a geometric calibration.

An analysis of the time required for the sample preparation and measurement in the cross check is shown in Table 7. The time required for the Logac analyses is not typical for Logac counting since, in order to avoid more than one dilution level for Logac and liquid scintillation counting, the slides were made low level for the Logac and required 2-hr counting times per slide plus long background determinations. Had the solution been diluted by a factor of 10^2 instead of 10^4 , the instrument time for nine slides would have been 1 hr and the operator time 1 hr. Even under these conditions, liquid scintillation counting clearly is the least time-consuming both for sample preparation and measurement. Either 2π or 4π proportional counting of nine samples each would have required 3 to 4 days of instrument and operator time for absolute alpha analysis.

Table 2

COMPOSITION OF CROSS-CHECK SAMPLE

<u>Isotope</u>	<u>Half-Life (yr)</u>	<u>Radiation</u>	<u>Energy (MeV)</u>	<u>Fraction of Total Plutonium (wt %)</u>	<u>Method of Analysis</u>
^{238}Pu	87.8	α	5.495 (72%)	81.24 $\pm$ 0.23 ^a	Mass Spectrometry
		α	5.452 (28%)		
^{239}Pu	2.436×10^4	α	5.147 (72.5%)	15.91 $\pm$ 0.18 ^a	Mass Spectrometry
		α	5.134 (16.8%)		
		α	5.096 (10.7%)		
^{240}Pu	6.580×10^3	α	5.162 (76%)	2.49 $\pm$ 0.039 ^a	Mass Spectrometry
		α	5.118 (24%)		
^{241}Pu	13	β	0.021	0.275 $\pm$ 0.007 ^a	Mass Spectrometry
^{242}Pu	3.79×10^5	α	4.898 (76%)	0.075 $\pm$ 0.009 ^a	Mass Spectrometry
		α	4.858 (24%)		
^{241}Am	458	α	5.477 (85%)	0.045 $\pm$ 2%	Gamma Counting
		α	5.435 (12.6%)		
		α	(Others)		

^aLimit of error.

Table 3

CALORIMETER MEASUREMENTS

<u>Sample Number</u>	<u>Power (μW)</u>
1	1986.4
2	1998.4
3	1986.3
4	1983.3
Average	1988.7

Subtracting 0.108% for other isotopes yields 1986.7 μ W from ^{238}Pu . Using the conversion factor 30.20 $\mu\text{Ci}/\mu\text{W}$ yields 59.99 mCi or 1.332×10^{11} dis/min/ml. Error in wattage measurements (95% confidence level) is $\pm 0.35\%$.

Table 4

LOGAC MEASUREMENTS

<u>Dilution Number</u>	<u>Slide Number</u>	<u>Rate (dis/min/10 μl)</u>	<u>Average (dis/min/ml)</u>
1	1	1.341×10^5	1.329×10^{11}
	2	1.317×10^5	
	3	1.330×10^5	
2	1	1.366×10^5	1.351×10^{11}
	2	1.347×10^5	
	3	1.341×10^5	
3	1	1.312×10^5	1.316×10^{11}
	2	1.316×10^5	
	3	1.320×10^5	
Average total alpha			1.332×10^{11}
Less 0.1% for other alpha emitters			1.331×10^{11}

Limits of error in geometry factor $\pm 0.25\%$.

Standard counting statistical error per sample $\pm 0.51\%$.

Table 5

LIQUID SCINTILLATION MEASUREMENTS

<u>10⁴ Dilution Number</u>	<u>Sample Number</u>	<u>Rate (dis/min/10 μl)</u>	<u>Average (dis/min/ml)</u>
1	1	1.316×10^5	1.333×10^{11}
	2	1.343×10^5	
	3	1.341×10^5	
2	1	1.345×10^5	1.356×10^{11}
	2	1.335×10^5	
	3	1.387×10^5	
3	1	1.337×10^5	1.344×10^{11}
	2	1.339×10^5	
	3	1.357×10^5	
Average total alpha			1.344×10^{11}
Less 0.1% for other alpha emitters			1.343×10^{11} due to ^{238}Pu

Standard counting statistical error per sample $\pm 0.11\%$.

Table 6

SUMMARY OF MEASUREMENTS

<u>Method</u>	<u>Rate (dis/min/ml)</u>	<u>Deviation from Calorimeter (%)</u>
Calorimeter	1.332×10^{11}	
Logac	1.331×10^{11}	0.0
Liquid Scintillation	1.343×10^{11}	+0.8

Table 7

TIME REQUIRED FOR ANALYSIS

<u>Counting Method</u>	<u>Number of Samples</u>	<u>Sample Preparation Time (hr)</u>	<u>Instrument Time (hr)</u>	<u>Operator Time (hr)</u>
Logac	9	1	24 ^a	2
Liquid Scintillation	9	$\frac{1}{2}$	1	$\frac{1}{4}$

^a Not typical.

Where large numbers of samples are involved, since they are easier to prepare, and can be counted automatically with no one in attendance, the time savings using liquid scintillation counting can be tremendous. Calculations of disintegration rates involve simply dividing the total count by the time and subtracting the background. It is important that the alpha emitter be dissolved and that it stay in solution to yield 100% counting efficiency. It is obvious that alpha radiation which dissipates its energy before it can emerge from an undissolved particle cannot result in a scintillation.

For samples which contain both alpha and beta emitters, difficulties arise in distinguishing between the two. Each application must be considered separately. In the case of the plutonium used in the cross check, it was possible to discriminate against the 20-keV betas from ^{241}Pu and count only the alphas from the other isotopes. A ^{210}Po source was used to determine the discriminator settings since it emits no betas. The lower discriminator was moved upward to the point where the counting rate started to drop, and then lowered slightly from this point. This discriminator setting was considerably higher than was required to discriminate against the 18.6-keV maximum-energy beta from tritium. This result indicated that the ^{241}Pu beta would not be counted at these discriminator settings.

In conclusion, it can be stated that liquid scintillation counting is the ideal counting method for routine analysis of alpha emitters. The measurements are accurate when counting samples having disintegration rates as high as 2×10^8 dis/min/ml (using 10- μ l aliquots) or 2×10^9 dis/min/ml (using 1- μ l aliquots). The measurements are rapid, and results are available quickly. While the instrumentation is more expensive compared to that for other counting techniques, and the vials and solutions are more costly than slides, the manpower time saved more than compensates for these costs. Sample preparation and counting can be performed by technicians. (M. L. Curtis and M. M. Bolton)

PREPARATION OF TRITIATED-HYDROGEN GAS STANDARDS

Low-level, dry tritiated-hydrogen gas standards are being prepared from standard tritiated water for checking the efficiency and the absolute accuracy of tritium gas proportional counting. The preparation of the gas standards was attempted by the reduction of water with zinc and nickelic oxide,⁸ and by the reduction of water with amalgamated magnesium.⁹

Reaction tubes approximately 17 cm long with break-tips made from 1.1-cm o.d. Pyrex 1720 glass tubing were used for the reduction of water with zinc and nickelic oxide; ordinary Pyrex is not sufficiently heat-resistant. One gram of 20-mesh zinc and 100 mg of nickelic oxide powder were added to the reaction tubes along with approximately 12 mg of water that was sealed in a capillary tube with a break tip. The filling was accomplished by placing the open tip of a heated capillary in the water and allowing the water to be drawn into the capillary as the tube cooled. The capillary was then sealed. The reaction tubes were constricted, evacuated to a pressure of approximately 50 μ m Hg, and sealed. The reaction tube was shaken to break the capillary containing the water, then heated at 640°C for 3 hr. The temperature was gradually increased to this value so that no great temperature change would break the tube. After the reaction tube had cooled, the gas was released and collected on a gas rack where pressure and volume measurements were made. The pressure obtained from these samples was approximately 17% of what it was expected to be. A sample was prepared using zinc that had been freshly cleaned with dilute HCl. This improved the yield, but quantitative reduction apparently had not occurred.

Ordinary Pyrex tubing was used to prepare reaction tubes of the same dimensions for the reduction of water with amalgamated magnesium. Approximately 16-18 mg of water sealed in a capillary with a break-tip were added to the reaction tube with 0.4 g of magnesium ribbon and 0.8 g of mercury. The amalgamation was done in an argon atmosphere, after a fresh surface for the magnesium ribbon was prepared with sandpaper, since amalgamation did not always occur in an air atmosphere. The reaction tube was evacuated to a pressure of approximately 50 μ m Hg and sealed. The capillary was broken and the reaction tube was heated at 400°C for 2 hr. Pressures of several atmospheres build up inside the reaction tube so that careful handling is necessary. The gas was collected and the pressure and volume measurements were made.

The results from three regular water samples and two blanks are given in Table 8. The gas produced from the amalgam blank represents less than 0.5% of the expected total gas. The reaction seems to be fairly complete. In the preparation of the tritiated hydrogen standards, the percent reaction is not important as long as no isotopic effect occurs. The expected specific activity of the gas can be calculated from the specific activity of the water and the pressure measurement obtained. Since it is important to prepare a dry gas, the reaction tube was placed in liquid nitrogen for several minutes before the tube was broken so that any moisture would be frozen out. Three samples of tritiated-hydrogen

Table 8

GAS PRODUCED FROM WATER AND BLANKS

<u>H₂O Taken (mmole)</u>	<u>Gas Found (mmole)</u>	<u>Recovery (%)</u>
1.0167	0.8840	86.9
0.9444	0.8726	92.4
1.0556	0.9063	85.9
None	0.0062	--
None	0.0019	--

gas were produced from standard tritiated water and have been counted to evaluate the counting efficiency of proportional counting tubes.

The specific activity of the tritiated-hydrogen standards will be determined and compared to a calculated value to determine if any isotope effect was observed. More standards will be prepared to determine a better value for the efficiency and the absolute accuracy of tritium gas proportional counting. (R. K. Gillette)

X-RAY FLUORESCENCE OF THORIUM OXIDE-URANIUM OXIDE MIXTURES

Samples of ThO₂-U₃O₈ have been prepared for x-ray fluorescence analysis by mechanical blending of the oxides. To ensure homogeneity of the oxide mixtures, samples are now being prepared by coprecipitation of the hydroxides of thorium and uranium from their nitrate solution by ammonium hydroxide, evaporating to dryness, sintering in a furnace at 700°C for 2 hr and, when cool, grinding to a fine powder with an agate mortar and pestle.

Instead of preparing disks by combining the oxides with gum arabic binder and pressing in an aluminum pan, the oxide is now weighed on the outside surface of the pan after being placed there as a single pile with a stainless steel spatula and gently patted down with the flat surface of the spatula to form a uniformly thick spot of sample. After weighing, the sample is secured in position by covering with a strip of cellophane tape. Finally, the aluminum pan and sample are enclosed in two layers of plastic.

It was found that 5-15 mg of pure oxide sample is sufficient to give a relative standard deviation ranging from 0.04 to 0.75% for five successive 24-sec counting periods of the selected characteristic x-ray fluorescence lines ($L\alpha_1$) of thorium and uranium. Since the standard deviation of counting the emitted x-ray fluorescence energy quanta is equal to the square root¹⁰ of the counts themselves, it was found adequate to count for

two 2-min periods and still maintain a relative standard deviation of less than 0.75% in all of the standards studied.

Data for coprecipitated standard oxide mixtures containing 8, 9, 10, and 11 wt % ThO_2 are plotted in Figure 3. A linear regression analysis and statistical evaluation of the standards gave the following least-squares equation:

$$y = 0.0111x - 0.0124 \quad (2)$$

The average relative standard deviation for the y deviations from the line is 0.30%.

Coprecipitated ThO_2 - PuO_2 mixtures will be handled in the same fashion as the U_3O_8 - ThO_2 standards. They must be tested for complete containment of the radioactive sample before being subjected to x-ray fluorescence analysis. (A. Attalla)

FIGURE 3 - Plot of the average corrected counting rate (2-min) ratios of $\text{L}\alpha_1$ characteristic radiation (x-ray) as a function of ThO_2 concentration in U_3O_8 mixtures.

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