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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:

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The separation and purification of a batch of uranium-234 was improved by collecting the product in several fractions instead of a single large fraction. In addition, the flow rate of the hydrochloric acid/iodide wash was increased by a factor of 10. The plutonium-238 levels of the eluate were less than 1 ppm (by weight). The purified product, containing 5.34 g of uranium-234, was sent to the Heavy Elements Isotope Pool at ORNL.

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The effect of the first hydrolysis of Pu(IV) upon the ratio Pu(VI)/Pu(V) in plutonium solutions is proposed.

The acidity for which the ratio Pu(VI)/Pu(V) is most affected by the hydrolysis depends upon the average oxidation number of the plutonium in the solution.

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A rapid technique for monitoring Mound Laboratory effluent for tritium gas and tritiated water vapor is being developed. The system collects the tritiated water vapor in a dry-ice/acetone trap and converts the tritium gas to tritiated water, for similar collection, by oxidation on hot palladium sponge catalyst. Both fractions of the sample are analyzed for tritium by liquid scintillation. The system is being designed for grab sample monitoring but could conceivably be engineered for continual monitoring to complement the present total tritium Kanne monitoring system.

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The procedure for the determination of impurities in Li_2SO_4 was modified to compensate for a loss in speed and sensitivity of the Ebert spectrograph. By the use of a wider

entrance slit, a two-step filter system, and a larger electrode cup, the limits of detection of the procedure have been maintained and in some cases improved. The improvements have resulted from selection of more sensitive analytical lines which were previously unusable due to cyanogen band interferences. The application of the larger electrode cup has reduced the formation of cyanogen bands and has provided more consistent burn characteristics.

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Separation Chemistry

RESIDUE ADSORPTION - SEPARATION OF PLUTONIUM AND URANIUM

A radiometric method is being developed for the analytical determination of trace quantities of uranium-234 in plutonium-238 and of the isotopic ratio of uranium-232 to uranium-234 in the same matrix. The method is based on the strong tendency of plutonium in all its oxidation states to hydrolyze in neutral or weakly acid aqueous solutions.¹ Under the same conditions the uranyl ion, UO_2^{2+} , does not hydrolyze and uranyl salts of all the common mineral acids are, in fact, quite soluble in water.²

Preliminary work was performed with a source, obtained from Mound Laboratory stocks, which contained uranium-234, uranium-232 and plutonium-238 in 1N HCl solution containing a trace of HF. Alpha spectrum analysis showed that the relative alpha activity of the three nuclides was 1.000:0.088:0.791 (see Figure 1).

A sample of this solution was evaporated to dryness in a glass vial and the residue was converted to the nitrate form by dissolution in 0.1N HNO_3 . This solution was evaporated to dryness and the residue, after being dissolved in water, was again evaporated to dryness. The residue was leached with water and the desorbate was transferred to a second vial, where it was evaporated to dryness. The desorption was repeated, and the desorbate was transferred to a third vial. After five sequential desorptions, the desorbate contained 62.6% of the uranium-234 and 0.5% of the plutonium-238 originally deposited. The spectrum (Figure 2) was suitable for isotopic uranium analysis. The progress of the separation is shown in Table 1.

In another type of separation, the 1N HCl solution was evaporated to dryness in a small circular area (~5 mm in diameter) on the surface of a platinum disk suitable for alpha spectrometry. The residue was first converted to the fluoride form by the addition and evaporation of one drop of 1N HF after which it was hydrolyzed in situ with water. The sample was again dried and the residue was leached with hot water which was transferred to a second platinum disk and dried. The second residue was then leached with hot water and the desorbate was transferred to a third platinum disk. Upon analysis, this disk was found to contain 97.1% of the uranium isotopes and 1.6% of the plutonium-238.

An artificial mixture was prepared in which the uranium-234 represented only 1.75% of the total alpha activity. A sample of this material was evaporated to dryness on a platinum disk, converted to the fluoride form, and hydrolyzed with water. The residue was leached with hot water and the desorbate was transferred successively to a second, a third and a

FIGURE 1 - Alpha spectrum of uranium-plutonium starting material.

6 FIGURE 2 - Alpha spectrum of uranium-234 plus uranium-232 purified by residue adsorption.

Table 1
SEPARATION OF PLUTONIUM-238 AND URANIUM-234
IN GLASS VIALS

<u>Adsorbate Number</u>	<u>^{238}Pu (%)</u>	<u>$^{232}\text{U} + ^{234}\text{U}$ (%)</u>	<u>U/Pu Activity Ratio</u>
1	43.8	1.9	0.05
2	30.5	2.7	0.11
3	15.6	7.3	0.57
4	6.1	13.9	2.79
5	3.5	11.7	4.08
Product	0.5	62.6	141.0

fourth platinum disk. The distribution of the uranium and the plutonium is given in Table 2.

Table 2
SEPARATION OF PLUTONIUM-238 AND URANIUM-234
ON PLATINUM DISKS

<u>Disk Number</u>	<u>^{238}Pu (%)</u>	<u>$^{232}\text{U} + ^{234}\text{U}$ (%)</u>	<u>U/Pu Activity Ratio</u>
1	90.2	5.6	0.001
2	6.6	6.0	0.018
3	1.3	6.8	0.10
4	1.0	75.7	1.41
Material Balance	99.1	94.1	-

It was found that the uranium remaining on the first three disks could be recovered by repeating the metathesis, hydrolysis and desorption. However, this rather tedious procedure is not satisfactory for use as a routine procedure, and work currently in progress is aimed towards reducing the number of steps required and improving the degree of separation at each stage. (H. W. Kirby)

URANIUM-234 RECOVERY

The initial separation and intermediate purification of the uranium-234 batch designated A-12 was described in the last report.³ A portion of this material containing 5.9 g of uranium-234 and 9.0 mg of plutonium-238 was evaporated to dryness to remove excess nitric acid, then taken up in dilute nitric acid and salted with aluminum nitrate. This feed solution was passed through a Dowex 1X4 anion exchange column, and the column was washed with 9M hydrochloric acid, then 9M hydrochloric acid containing iodide to reduce and wash off the quadrivalent plutonium. When the uranium was eluted with dilute hydrochloric acid and analyzed, it was found that more than 20% of the plutonium remained.

The poor removal of plutonium was attributed to the presence of hexavalent plutonium rather than quadrivalent plutonium, so the uranium fraction was treated with hydrazine in hot 6M hydrochloric acid. After adjustment to 9M with hydrochloric acid, the solution was loaded back on the anion exchange column and washed with 9M hydrochloric acid containing iodide ion. Analysis of the uranium eluate showed that only half of the plutonium had been removed.

The uranium fraction was treated by a third cycle of anion exchange, with two modifications: 1) the uranium product was collected in several fractions instead of a single large fraction, and 2) the flow rate of the hydrochloric acid/iodide wash was increased by a factor of 10. In previous work, the plutonium seemed to be eluted before the uranium, so the first elution fractions may contain more plutonium than the later fractions. Also, it seemed that most of the iodide had been absorbing near the top of the column, and perhaps was not contacting plutonium absorbed further down the column. It was thought that the very fast flow rate would sweep part of the iodide on through the column where it could come in contact with all of the plutonium. Analysis of the uranium eluate fractions showed that the plutonium separation had been excellent. Plutonium-238 levels were less than 1 ppm (by weight) and were close to the limits of detection.

Four uranium eluate fractions, containing the bulk of the uranium and the least amount of plutonium-238, were combined and the uranium was precipitated with ammonium hydroxide. The precipitate was collected on ashless filter paper, dried and calcined. The oxide weighed 6.328 g and was calculated to contain 5.34 g of uranium-234. Mass spectrometry showed uranium-234 at 99.86% isotopic purity, and alpha spectroscopy indicated 25.5 ppm (by weight) of uranium-232. This material, designated batch A-12-1, has been sent to the Heavy Elements Isotope Pool at Oak Ridge National Laboratory. (P. E. Figgins)

Inorganic Chemistry

EFFECT OF THE FIRST HYDROLYSIS OF THE PLUTONIUM(IV) CATION ON THE Pu(VI)/Pu(V) RATIO IN SOLUTIONS OF PLUTONIUM WITH DIVERS OXIDATION NUMBERS

One of the interesting unresolved problems in plutonium chemistry is the effect of the hydrolysis of plutonium ions upon ionic plutonium equilibria. The principal hydrolyzing species in plutonium solutions is the Pu^{4+} cation, and until the second and third hydrolysis reactions of this ion have been better elucidated, a quantitative analysis of the effect of hydrolysis upon plutonium ion equilibria is likely to remain an unresolved problem. A qualitative idea of hydrolysis effects, however, may be obtained by studying the effects of only the first hydrolysis of tetravalent plutonium upon plutonium ionic equilibria:

This study is aided by Equation 2:

$$(N-3)(K_2^2\text{H}^4) + (N-4)(K_2\text{H}^4)(M) + (N-5)(K_1M^2) + (N-6)(K_1M^3) = 0 \quad (2)$$

$$\text{where: } K_1 = \text{WYH}^4/\text{X}^2 \quad (3)$$

and

$$K_2 = \text{WZ}/\text{XY} \quad (4)$$

[W = Pu(III), X = Pu(IV), Y = Pu(V), Z = Pu(VI), M = Pu(VI)/Pu(V)].

Equation 2 is a useful equation⁴ for studying plutonium equilibria, and it is rather interesting that it does not seem to have been proposed until recently. For any acidity value and any value for the average oxidation number, N, it yields the Pu(VI)/Pu(V) ratio, denoted as "M". It neglects heptavalent plutonium, but this species is not ordinarily of concern except under rather unusual circumstances. The second term in this equation [the term containing (N-4)] relates to tetravalent plutonium, and by multiplying this term by $(1 + 0.03/\text{H})$, the alpha factor for first hydrolysis, Equation 2 yields the ratio $M = \text{Pu(VI)}/\text{Pu(V)}$ under various conditions of average oxidation number and acidity. A plot of the ratio of M values under conditions of hydrolysis and no hydrolysis is shown in Figure 3. Interestingly, for $N < 4.0$ hydrolysis decreases the predicted M value, whereas for $N > 4.0$ hydrolysis increases the predicted M value. Of course, for $N = 4.0$ (pure tetravalent plutonium) hydrolysis does not affect the M values, but only decreases the extent of disproportionation. Even more interesting, however, is the apparent

FIGURE 3 - Ratio of $M [Pu(VI)/Pu(V)]$ values for hydrolysis of Pu(IV) and for no hydrolysis of Pu(IV) in solutions of five different average oxidation numbers (N).

shift of the acidity of maximum hydrolysis effect to higher pH values with increasing values of the average oxidation number N. (G. L. Silver)

PLUTONIUM IN NATURAL WATERS

In recent times, attention has been drawn to the fate of radioelements released to the environment. Because plutonium is released from time to time to the surroundings, there has been some question as to the form that the plutonium might assume during its dispersal⁵. It is often assumed that the form would be some manifestation of the tetravalent state, because this state is most frequently encountered in plutonium solutions and in plutonium compounds used for reactor fuels; it is often alleged that accidentally released "soluble" plutonium would polymerize and be dispersed in the form of plutonium polymer, or else as solubilized ionic trivalent plutonium. These are reasonable assumptions since, under laboratory conditions, tetravalent plutonium in very dilute acid frequently polymerizes to a rather intractable colloid. Moreover, nature provides an abundance of organic materials which may act as reducing agents toward an oxidizing material such as the Pu^{4+} ion, so that were the Pu(IV) polymer to depolymerize, it might yield trivalent plutonium ions. While these arguments have to their advantage considerable weight of opinion, this is not the only interpretation possible.

Experiments designed to prove the behavior of plutonium are usually performed in a manner as much suited to laboratory conveniences as to what might be expected in nature. Solutions of plutonium are used as starting materials, and the time scale of the experiments is suited to human

designs rather than natural designs. Plutonium might enter the environment in several ways. Consider what might occur to highly refractory plutonium dioxide which falls into ocean waters. In this situation, the plutonium does not begin as a conveniently soluble material, and the time scale may be measured in years rather than a few hours or days. As radioactive decay and natural causes slowly degrade the oxide, plutonium may be released to the ocean water very slowly and at such low concentration that polymer formation may not be possible. Several things may occur to such released soluble plutonium: it may become attached to a bit of sediment or organic material, and remain so attached in the tetravalent state; it may be reduced to Pu(III); it may be oxidized to a higher form.

The pH of seawater depends upon depth and geography, but for the purpose of illustration may be taken as about 8; likewise the oxidation potential of seawater is about 0.43 V.⁶ A computer program for predicting the final form of soluble plutonium in given conditions of acidity, potential and complexation factors has recently been proposed.⁴ What the sequestering ability of seawater toward the various plutonium ions might be is not known, but it is probably high for Pu(IV), lower for Pu(III) and Pu(VI), and still lower for Pu(V). Using the computer program for the above conditions, and alpha factors for Pu(III), Pu(V) and Pu(VI) of 100, 1, and 100, respectively, the final form of the soluble plutonium is predicted to be in significant proportion the pentavalent state for any Pu(IV) alpha factor of less than about 10^{20} . For Pu(IV) alpha factors greater than about 10^{20} , complexed tetravalent plutonium will be the soluble species in overwhelming concentration. Table 3 illustrates some sample calculations for water with potential and pH similar to that of seawater. The alpha factors in Table 3 are guesses, and may bear no relation whatsoever to the values for seawater.

Table 3

DISTRIBUTION OF SOLUBLE PLUTONIUM OXIDATION
STATES IN WATER WHICH MAY BE SIMILAR TO SEA-
WATER (pH = 8, E = +0.43 V)

Assumed Alpha Factors for:				Distribution of Soluble Plutonium Species (%):			
<u>Pu(III)</u>	<u>Pu(IV)</u>	<u>Pu(V)</u>	<u>Pu(VI)</u>	<u>Pu(III)</u>	<u>Pu(IV)</u>	<u>Pu(V)</u>	<u>Pu(VI)</u>
100	10^{20}	1	100	0.17×10^{-6}	76	24	0.14×10^{-4}
100	10^{18}	1	100	0.67×10^{-6}	3.1	96.9	0.58×10^{-4}

(G. L. Silver)

Analytical Chemistry

DETERMINATION OF PLUTONIUM IN SOIL

The residues from leached soil samples continue to be analyzed by the fusion procedure to determine what percentage of plutonium has been leached out of the sample. Since previous work⁷ indicates that plutonium is concentrated in a few small particles such that even multiple riffing of a large sample would not necessarily produce smaller samples of the same plutonium composition, the sample size was increased from 10 g to 50 g.

An attempt to fuse 50 g in a 700-ml graphite crucible proved unsuccessful; however, the fusion was completed in a 500-ml platinum can. To obtain a workable volume (e.g., less than 2 liters), half of the solution from dissolution of the 50-g fusion melt was carried through the analysis, and the remaining half was held for reference.

Two new electrolysis cells were constructed for the electroplating step. They replaced the existing one which was difficult to position and used an excess of water for cooling. Analysis time is reduced by 2.5 hr when the two cells are operated simultaneously.

A rapid electrodeposition technique that will possibly reduce plating time from 75 min to 15 min will be investigated. (R. D. Hamman, E. B. Nunn, M. L. Curtis and J. O. Frye)

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

Results of proportional counting of six air samples⁸ taken in April 1971 from an effluent stream gave a ratio of tritium measured by the Kanne system to tritium measured by proportional counting of 0.96 ± 0.07 . The HTO content of these samples as determined using a dry-ice/acetone cold trap was $12\% \pm 0.6\%$. Similar measurements of air samples from a second effluent stream gave a ratio of tritium measured by Kanne to tritium measured by proportional counting of 6.4 ± 3.1 , and HTO concentrations of $25.2\% \pm 12.4\%$. Further studies were made to determine the reason for the discrepancies sometimes observed between the Kanne monitors and proportional counting.

A series of measurements was made on an effluent stream, through a sample port at the exit of the Kanne chamber monitoring this stream. Duplicate samples were taken in 2-liter flasks connected in series.

Air was flushed through the flasks for 20 to 30 min before closing the stopcocks and retaining a sample in each flask. One of each pair of samples was measured for total tritium by proportional counting, and for HTO by freeze-out in a dry-ice/acetone trap followed by liquid scintillation counting.⁸ The other sample was measured by first separating the HTO using the dry-ice and acetone trap, then oxidizing the HT on palladium catalyst and collecting this HTO in a second dry-ice/acetone trap. Both fractions were measured by liquid scintillation (see p. 19 of this report).

Results of measurements of two such samples are listed in Table 4. The total measured tritium content was higher using the palladium catalyst oxidation technique than with proportional counting. Since both techniques afforded accurate analysis when tested with known amounts of tritium diluted in room air,⁹ the discrepancies are attributed to sorption problems resulting from the high HTO concentration in these samples. The tritium appeared to be adsorbing on the sides of the flasks and Kanne chamber. This resulted in a low total tritium count as determined by proportional counting of the gas in Flask I. The HTO measurement from Flask I would not be affected, since the adsorbed tritium would be flushed out of the flask into the cold trap with helium.⁸ Likewise, the adsorbed tritium in Flask II would be flushed into the cold trap and palladium column with argon and hydrogen, and so would be counted. Sorption on the walls of the Kanne chambers would lead to erratic readings as adsorption and desorption occurred with a constant flow of effluent through the chambers. The background, taken after outside air is flushed through the chamber for about 5 min, is not representative of chamber background when effluent measurements are made. The measured background is usually half or more of the Kanne reading of the effluent.

To test these hypotheses, the interior of Flask I was coated with cellulose acetate, Flask II was left uncoated, and samples of the effluent were taken as described above. After the gas in Flask I was measured by proportional counting, the flask was evacuated (thereby removing part of the adsorbed tritium), and the cellulose acetate was dissolved in scintillator solution and counted. Results given in Table 5 indicate that on these samples (all with a major portion of the tritium in the form of HTO) the adsorption is highly significant. Adsorption was increased by allowing the effluent to flow through the flasks for 20 to 30 min before sampling, resulting in a build-up of adsorbed tritium on the walls of the flasks. Samples 2, 3, and 4 were taken using flushing times of 20, 10, and 1 min, respectively, and decreased adsorption with decreased flushing time was observed. Samples 5, 6, and 7 were taken with flushing times of 30 sec, and samples 8 and 9 were grab samples. The HTO contents of the last four samples were extremely high, and here the adsorption effects were most pronounced. The last two samples were taken by putting a tee in the effluent line and putting the sample flasks in parallel rather than in series, since it is logical that the first flask in the series would adsorb more tritium than the second. No record had been kept of which flask was first in the series.

It was also noted that the gas with high HTO content from the coated flask gave consistent counts when several aliquots were measured by proportional counting. The same gas from the uncoated flask counted higher, but the counting rate dropped on successive measurements. This indicated that initial adsorption was greater on the cellulose acetate than on the glass, but that it quickly reached equilibrium on the cellulose acetate while it continued to build up on the glass.

Table 4

TRITIUM CONCENTRATIONS IN AIR SAMPLES, TOTAL STREAM EFFLUENT

<u>Date</u>	<u>Total T₂</u> <u>(Kanne)</u> <u>($\mu\text{Ci}/\text{m}^3$)</u>	<u>Flask I</u>			<u>Flask II (Palladium)</u>		
		<u>Total T₂</u> <u>by PC^a</u> <u>($\mu\text{Ci}/\text{m}^3$)</u>	<u>HTO</u> <u>by LSC^b</u> <u>($\mu\text{Ci}/\text{m}^3$)</u>	<u>HTO</u> <u>(%)</u>	<u>Total T₂</u> <u>by LSC</u> <u>($\mu\text{Ci}/\text{m}^3$)</u>	<u>HTO</u> <u>by LSC</u> <u>($\mu\text{Ci}/\text{m}^3$)</u>	<u>HTO</u> <u>(%)</u>
9/22/71	<u>36.</u>	<u>39.0</u>	12.8	32.8	<u>47.1</u>	11.1	23.6
9/23/71	<u>45.</u>	<u>45.9</u>	19.7	42.9	<u>58.7</u>	17.0	29.0

^aProportional counting.

^bLiquid scintillation counting.

Table 5
EFFECTS OF ADSORPTION ON TRITIUM MEASUREMENTS

Sample Number	Date	Total T ₂ (Kanne) ($\mu\text{Ci}/\text{m}^3$)	Flask I (Proportional Counting)			Flask II (Palladium Catalyst)		
			Total T ₂ ($\mu\text{Ci}/\text{m}^3$)	T ₂ in Gas by PC ^a ($\mu\text{Ci}/\text{m}^3$)	Adsorbed T ₂ ($\mu\text{Ci}/\text{m}^3$)	Total T ₂ by LSC ^b ($\mu\text{Ci}/\text{m}^3$)	HTO by LSC ($\mu\text{Ci}/\text{m}^3$)	HTO (%)
1	9/27/71	<u>45</u>	<u>83.5</u>	58.0	25.5	<u>77.4</u>	31.0	40.0
2	9/28/71	<u>27</u>	<u>37.8</u>	26.6	11.2	<u>35.0</u>	11.6	33.1
3	9/30/71	Not measured	<u>39.8</u>	32.2	7.6		Not measured	
4	10/5/71	<u>27</u>	<u>38.0</u>	34.9	3.1	<u>43.0</u>	13.3	30.9
5	10/12/71	<u>45</u>	<u>33.8</u>	31.7	2.1	<u>41.4</u>	20.6	49.8
6	10/19/71	<u>30.6</u>	<u>53.07</u>	20.96	32.11	<u>43.9</u>	36.3	82.7
7	10/21/71	<u>9.</u>	<u>31.28</u>	7.56	23.72	<u>28.1</u>	19.9	70.8
8	10/22/71	<u>9.</u>	<u>26.31</u>	4.14	30.45	<u>60.6</u>	42.2	69.6
9	10/25/71	<u>75.6</u>	<u>35.52</u>	28.9	6.62	<u>72.4</u>	59.2	81.8

^aProportional counting.

^bLiquid scintillation counting.

These studies lead to the conclusion that accurate assay is obtained on effluent samples with low HTO concentration by three analytical techniques: Kanne system, proportional counting, and palladium catalyst oxidation. However, tritium sorption effects on high HTO concentration effluent lead to erratic results on both Kanne and proportional counting measurements. A defective valve on a dryer system was discovered on October 26, 1971. This was undoubtedly the source of the extremely high HTO content of the effluent. Nevertheless, it may be necessary in the future to monitor effluent of high HTO concentration. Therefore, methods to overcome the sorption problems must be found.

Effluent samples for proportional counting will be taken in a metal container with a lid and O-ring seal. The interior will be coated with cellulose acetate and, after the gas has been analyzed by proportional counting, the can will be opened and the cellulose acetate will be peeled from the interior and dissolved for liquid scintillation counting. The sample flask which has been used to the present time had to be evacuated before the cellulose acetate was dissolved, thereby losing some of the adsorbed tritium. Proportional counting and palladium catalyst oxidation techniques will again be compared.

Techniques for minimizing adsorption will be tested in an attempt to reduce adsorption on Kanne chamber walls. Gold plating and heating of container walls will be tried. (M. L. Curtis, M. M. Bolton, D. C. Carter, R. L. Ryan and T. M. Flanagan)

SEPARATION AND SIMULTANEOUS COLLECTION OF TRITIUM GAS AND TRITIATED WATER VAPOR FOR TRITIUM DETERMINATION BY LIQUID SCINTILLATION

Tritium gas and tritiated water vapor in gaseous samples have previously been determined by gas proportional counting for determining total tritium and a separation technique for determining the tritiated water vapor. After gas proportional counting, the sample is passed through a dry-ice/acetone trap to collect the tritiated water vapor for liquid scintillation determination of tritium.^{8,9} This procedure is time-consuming, however, and as a result not very acceptable for routine monitoring purposes.

A new system was designed in which a 5% hydrogen-95% argon carrier gas transports a 2-liter sample (at 400 cm³/min) through a dry-ice/acetone trap to collect the tritiated water vapor, through a hot (325°C) copper oxide catalyst, and finally through a second dry-ice/acetone trap to collect the oxidized tritium gas. The tritiated water samples are trapped directly on 4-mm glass beads in 25-ml plastic liquid scintillation vials and are analyzed for tritium by liquid scintillation. Four runs indicate an average of only 15.6% recovery of dry tritium gas standard (~10⁵dis/min) after passage through the copper oxide catalyst (Table 6).

Table 6

OXIDIZATION OF TRITIUM GAS ON HOT COPPER OXIDE CATALYST

Sample Number	Tritium Added (dis/min)	Tritium Recovered (dis/min)	Recovery (%)
2	2.26 x 10 ⁵	2.84 x 10 ⁴	12.5
3	3.63 x 10 ⁵	6.31 x 10 ⁴	17.4
4	3.73 x 10 ⁵	5.42 x 10 ⁴	14.5
5	3.73 x 10 ⁵	6.50 x 10 ⁴	17.4

Ostlund describes a technique for simultaneously oxidizing and collecting tritium gas on palladium-coated molecular sieve at room temperature.¹⁰ This system was modified and incorporated into the copper oxide system described above by substituting palladium metal sponge as the catalyst. On the basis of one run, only 10.1% of a standard tritium gas sample was collected when passed through the palladium catalyst at room temperature. The poor result was attributed to absorption of the tritiated water thus formed into the catalyst. The system's efficiency has been greatly improved, however, by heating the palladium catalyst to 350°C. On the basis of nine runs using the elevated catalyst temperature, 96.3% recovery has been attained with an absolute standard deviation of 5.5% (Table 7). In order to determine water vapor collection efficiency, four of the previous nine samples were run simultaneously with tritiated water standards ($\sim 10^5$ dis/min) placed in the flask with the gas samples. Poor tritiated water recovery was attained on the first two runs and can be attributed to insufficient flushing of the sample (20 min). The last two samples were flushed for 40 min for an average collection efficiency of 97.5% (Table 8).

Table 7

OXIDIZATION OF TRITIUM GAS ON HOT PALLADIUM CATALYST

Sample Number	Tritium Added (dis/min)	Tritium Recovered (dis/min)	Recovery (%)
6	3.78×10^5	3.48×10^5	92.0
7	3.75×10^5	3.35×10^5	89.2
8	3.78×10^5	3.53×10^5	93.4
9	3.78×10^5	3.58×10^5	94.9
10	3.75×10^5	3.52×10^5	93.7
11	3.78×10^5	3.65×10^5	96.8
12	3.45×10^5	3.40×10^5	98.6
13	2.73×10^5	2.74×10^5	100
14	2.74×10^5	2.95×10^5	108
Average			96.3
Standard Deviation			5.5

Table 8

COLLECTION OF TRITIATED WATER VAPOR IN DRY-ICE/ACETONE TRAP

Sample Number	Tritiated Water Added (dis/min)	Tritiated Water Collected (dis/min)	Recovery (%)
11	3.12×10^5	2.20×10^5	70.5
12	3.11×10^5	2.04×10^5	65.7
13	3.11×10^5	3.10×10^5	99.6
14	3.11×10^5	2.97×10^5	95.4

All runs were made for only 20 min to prevent clogging of the delivery tube in the dry-ice/acetone trap. Forty-minute runs were made in two 20-min increments with new traps for each increment. Tentative figures indicate approximately 97% of a tritium gas sample is flushed from a

2-liter flask in the first 20 min and essentially 100% after 40 min with a 400-cm³/min flow. Approximately 91% of a tritiated water vapor sample is collected in the first 20 min and essentially 100% after 40 min with the same flow. The increased time required for flushing the water vapor is attributed to adsorption on the surface of the flask.

Immediate plans are to run more standards for optimizing operating conditions so as to improve collection efficiencies. Once the operating parameters are optimized, grab samples of the effluents will be analyzed routinely. The feasibility of employing the system as a continual monitor will be investigated. (D. C. Carter, M. M. Bolton, M. L. Curtis and R. L. Ryan)

Instrumentation and Methods

SPECTROGRAPHIC ANALYSIS OF IMPURITIES IN Li_2SO_4

Due to a change in the response of the Ebert spectrograph, it became necessary to revise the procedure for the determination of impurities in Li_2SO_4 . The instrument suffered a loss in sensitivity and speed which could not be regained by adjustments in the optical system.

To increase the signal flux reaching the photoplate, a wider entrance slit was employed. Although the wider slit increases the amount of emission reaching the plate it also increases the background continuum. To control the background level, a two-step filter system was introduced.

A SPK-L3700 electrode which has a deeper and wider cup than the electrode used formerly was chosen to contain the sample charge. The larger electrode size was selected to permit burning larger sample charges in order to improve detection limits, to provide easier sample electrode preparation, and to minimize sample "popping" during arcing.

Three separate sets of Li_2SO_4 standard samples were prepared. One set contained 10 noble metals, the second set contained 16 rare earths, and the third set contained 38 common cations of interest. The standards were excited under the conditions listed in Table 9.

Table 9

EXCITATION CONDITIONS FOR Li_2SO_4 ANALYSIS

Spectrograph	JACO 3.4 M Ebert
Current	15 A d.c. (shorted)
Slit	
Width	30 μm
Height	2 mm
Wavelength Range	1st order 2200-4600 $\text{\AA}$
Atmosphere	60:40 Ar: O_2
Flow Rate	5 liter/min
Arc Gap	5 mm
Exposure	Complete burn
Sample Charge	60 mg Li_2SO_4 :graphite (3:1)
Electrode	
Anode	SPK-L3700
Cathode	SPK-L4273
Plate	SA #1
Transmission	Two-step filter 100%:25%

One advantage which accrued from the use of the wide electrode was the decrease in cyanogen band formation. This permitted selection of sensitive analytical lines which had suffered cyanogen band interferences. The improvement in the detection of the rare earths was especially significant. The limits of detection for cerium, praseodymium, samarium, and terbium were improved from about 80 ppm to 8 ppm.

Although the use of more sample per burn has maintained the desired detectability, the cooler burning has resulted in poorer detection limits for some elements. On the other hand, the smoother burn of the wider cup has resulted in a more consistent excitation level and less likelihood of sample loss during arcing. The sample charge is also more easily packed in the wide cup, and sample electrode preparation is less susceptible to variation in operator skill.

By the use of a wider entrance slit, a two-step filter, and a larger electrode cup, the limits of detection have been maintained and, in some cases, improved. The improvements have resulted from selection of more sensitive analytical lines which had been previously unusable due to cyanogen band interferences. The use of the larger electrodes has reduced the formation of cyanogen bands and has provided more consistent exposures. (Y. G. Ishida)

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