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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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Homogeneous, standard-plutonium soil samples were prepared and analyzed by the fusion procedure to determine the precision of the entire procedure, which was found to be $\pm 5.50\%$. Leached soil residues analyzed by the fusion procedure indicated that 92.1% of the ^{239}Pu was actually leached out.

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Inorganic Chemistry

INSTABILITY OF HEPTAVALENT PLUTONIUM IN WATER SOLUTIONS

One of the interesting discoveries in recent times is the heptavalent state of plutonium. If this newly discovered oxidation state can be stabilized in water solutions, many new procedures for processing plutonium and making plutonium compounds may become available. Present prospects for easy stabilization of heptavalent plutonium are not sanguine, however.

Recently a diagram of the $\text{PuO}_5^{3-}/\text{PuO}_2(\text{OH})_2$ couple as a function of acidity was presented.¹ This diagram is misleading, however, and it would be desirable to have more accurate potential-pH diagrams for the heptavalent state of plutonium. Truly accurate potential-pH diagrams for plutonium in highly oxidizing, highly alkaline media will probably not be available for several years because the chemistry of hexavalent plutonium in alkaline solution is so poorly understood. The previously presented diagram¹ is misleading for several reasons: 1) there was no correction for the possible amphoterism of hexavalent plutonium; 2) the potential of the couple $\text{PuO}_5^{3-}/\text{PuO}_2(\text{OH})_2$ has no useful meaning in highly acid solutions (such as near pH 0), because the form of hexavalent plutonium at pH 0 is PuO_2^{2+} , not $\text{PuO}_2(\text{OH})_2$, and it seems doubtful that heptavalent plutonium would exist as unprotonated PuO_5^{3-} near pH 0; 3) the calculated potential of the $\text{PuO}_5^{3-}/\text{PuO}_2(\text{OH})_2$ near pH 0 is shown to be lower in the previous diagram than its predicted value at this acidity due to a computational error. These reasons are sufficient for a closer examination of plutonium in highly oxidizing media in order to try to summarize what may occur in such media. Several reactions are of interest in the region where PuO_5^{3-} may exist.

1. Water decomposes:

$$E = 1.229 - 0.05916 \text{ pH} \quad (1\text{b})$$

2. Hexavalent plutonium dissolves:²

3. Heptavalent plutonium is reduced:

$$E = E^* + 0.05916 \log \frac{[\text{PuO}_5^{3-}]}{[\text{OH}^-]^4} \quad (3b)$$

4. Heptavalent plutonium is reduced:

$$E = E^* + 0.05916 \log \frac{[\text{PuO}_5^{3-}]}{[\text{PuO}_2(\text{OH})_3^-][\text{OH}^-]^3} \quad (4b)$$

The value of the formal potential of the $\text{PuO}_5^{3-}/(\text{reduced form})$ was taken from Reference 3. Unfortunately, the reduced form of heptavalent plutonium, a species of hexavalent plutonium, is not well understood.⁴ It may be solid or colloidal $\text{PuO}_2(\text{OH})_2$, or a soluble species such as $\text{PuO}_2(\text{OH})_3^-$, or $[\text{PuO}_2(\text{OH})_2]_2\text{OH}^-$, or $\text{Pu}_2\text{O}_7^{2-}$. Hence, both reactions 3 and 4 are written with the same formal potential of 0.85 V.

In Figure 1 are plotted Equations 1-4 assuming that the formal potential of 0.85 V for the reduction of heptavalent plutonium corresponds to reaction 3. In Figure 2 are plotted Equations 1-4 assuming that the formal potential for the reduction of heptavalent plutonium refers to reaction 4. In both of these diagrams line 1 represents the upper limit of the thermodynamic stability of water, and in both diagrams the soluble plutonium species concentrations are taken as 0.01M. Line 2 corresponds to the alkaline dissolution of hexavalent plutonium without a change in oxidation state. Line 3 represents Equation 3. From this equation it can be seen that a very high potential would prevail for the system $\text{PuO}_5^{3-}/\text{PuO}_2(\text{OH})_2$ at pH 0. Line 4 represents Equation 4. If the solubilized species of hexavalent plutonium $\text{PuO}_2(\text{OH})_3^-$ is nonexistent, and if hexavalent plutonium is not amphoteric at all, then lines 2 and 4 should be removed from Figure 1, and the potential-pH diagram should contain only line 1 and line 3 and its dotted extension. This dotted extension shows that PuO_5^{3-} could exist in water only in solutions of alkalinity of about 100M. Since the concept of pH may have limited significance at such high alkaline strengths, the abscissas in both Figure 1 and Figure 2 are labeled 14 - pOH. Plotted in Figure 2 are some experimental points representing observed solution-alkalinity behavior for some solutions of heptavalent plutonium.³ These points suggest that the heptavalent plutonium system does not behave exactly as predicted for the $\text{PuO}_5^{3-}/\text{PuO}_2(\text{OH})_3^-$ couple. The rapid drop in observed solution potentials with increasing alkalinity suggests a new phenomenon, perhaps stabilization of PuO_5^{3-} through association with sodium:

FIGURE 1 - Formal potential for the reaction $\text{PuO}_5^{3-} + 3\text{H}_2\text{O} + e = \text{PuO}_2(\text{OH})_2 + 4\text{OH}^-$ is 0.850 V.

FIGURE 2 - Formal potential for the reaction $\text{PuO}_6^{3-} + 3\text{H}_2\text{O} + e = \text{PuO}_2(\text{OH})_3^- + 3\text{OH}^-$ is 0.850 V.

or through further coordination with oxygen:

Both Figure 1 and Figure 2 indicate that heptavalent plutonium (PuO_6^{3-}) should be unstable in water solutions of usual alkalinity values.

(G. L. Silver)

REACTION OF PLUTONIUM WITH HYDROGEN PEROXIDE

One of the interesting unresolved problems in plutonium chemistry is the reaction of plutonium in the trivalent or tetravalent state with hydrogen peroxide. While this reaction has been the subject of much study, a satisfactory explanation of the properties of this reaction has never been presented. Some unexplained properties include: the steady-state ratio $\text{Pu(IV)}/\text{Pu(III)}$ in acid solutions of plutonium containing hydrogen peroxide, the effect of acidity upon this ratio, and the effect of the absolute plutonium concentration upon this ratio. While only a little quantitative information about the effect of acidity upon the $\text{Pu(IV)}/\text{Pu(III)}$ ratio seems to be available, it may be possible to obtain from this limited information something more than qualitative observations.

For example, the $\text{Pu(IV)}/\text{Pu(III)}$ ratio may serve as an indicator of the potential-controlling reaction:

$$E_{\text{Iv,III}}^* + 0.06 \log \frac{[\text{Pu(IV)}]}{[\text{Pu(III)}]} = E_{\text{H}_2\text{O}_2}^* + \frac{0.06}{n} \log [\text{H}^p \text{X}] \quad (5)$$

In Equation 5, the subscript $\text{H}_2\text{O}_2?$ indicates the formal potential of the unknown potential-controlling peroxide reaction, and the letters "n" and "p" represent, respectively, the number of electrons in the unknown potential-controlling reaction and the hydrogen ion dependence of this reaction. No doubt the right-hand member of Equation 5 should contain terms representing the concentrations of the unknown peroxide species. All of these terms are brought together in the symbol "X".

Table 1 indicates some $\text{Pu(IV)}/\text{Pu(III)}$ ratios in perchloric acid solution for a total plutonium concentration of 0.01M.

Equation 5 may be rearranged:

$$\log \frac{[\text{Pu(IV)}]}{[\text{Pu(III)}]} = \frac{E_{\text{H}_2\text{O}_2}^* - E_{\text{Iv,III}}^*}{0.06} + \frac{1}{n} \log (\text{X}) + \frac{p}{n} \log (\text{H}) \quad (6)$$

Table 1

RATIOS OF Pu(IV)/Pu(III) IN PER-
CHLORIC ACID CONTAINING
HYDROGEN PEROXIDE
(Pu = 0.01M)⁶

Acidity (M)	Ratio Pu(IV)/Pu(III)
8	0.24
6	0.18
5	0.15
4	0.12
2	0.06

Since it may be assumed that the active peroxide agent concentration is unchanging during the time interval at which the ratios shown in Table 1 prevailed, the term $(1/n)\log(X)$ will be assumed to be constant. In Figure 3 is plotted $[Pu(IV)]/[Pu(III)]$ on a log scale against (H) (also on a log scale) as for Equation 6. The slope of this line is close to unity. Hence p/n , the ratio of the acidity dependence to the number of electrons in the potential-controlling reaction, is unity. The intercept at $H = 1$ is 0.03. Hence, were the number "X" also near unity, the formal potential of the peroxide potential-controlling reaction would be (since $E^*_{IV, III} = 0.9819$ if no complexation of plutonium

FIGURE 3 - Plot of the ratio Pu(IV)/Pu(III) as a function of acidity.

by hydrogen peroxide is assumed) about 0.89 V. This number is close enough to that observed for the peroxide electrode⁶ to suggest that the same reaction which controls the potential of the peroxide electrode might also control the Pu(IV)/Pu(III) ratio. If the term "X" cannot be assumed to be near unity, then assume that the unknown formal potential is that of the peroxide electrode (i.e., about 0.84 V). Then the term "X" obtains the approximate value 10, which may correspond to the degree to which the concentration of the active oxidizing agent from peroxide (probably a free radical or a free radical ion) is increased beyond its concentration in the presence of pure platinum or gold (i.e., a measure of the catalytic power of plutonium to decompose hydrogen peroxide relative to platinum or gold).

Exactly what agent might be responsible for the observed ratios of plutonium species in acid solution has never been elucidated. However, Evans, Hush and Uri⁷ have proposed some interesting candidates such as HO_2 , HO_2^- , OH , and O_2^- . With these candidates, several schemes might be proposed which may be made to fit the form of acidity dependence provided the rate-determining step is acid-dependent. All of the schemes suffer shortcomings; for example, the steady-state concentration of the OH radical is probably too small to be a rate-controlling agent, as is the concentration of the HO_2^- ion in strongly acid solutions. Complex formation with Pu^{4+} (such as PuOOH^{3+}), however, might nevertheless allow this latter species an important role.

Scheme (1):

If reaction 10 were rate-controlling, a linear dependence of acidity and potential might be expected.

Scheme (2):

In Scheme (1), the active oxidizing agent is the OH radical for which

Hence, for the reaction

which compares with the value of about -21 kcal for the apparent equilibrium reaction leading to the steady-state ratios in Table 5.

(G. L. Silver)

Radiochemistry

^{231}Pa DETERMINATION IN AIRPORT CAKE SAMPLES BY GAMMA-RAY ANALYSIS

Preliminary measurements were undertaken to obtain quantitative analysis of the ^{231}Pa content of Airport Cake residues² using a Ge(Li) gamma-ray spectrometer system. Eight samples were analyzed; six were obtained from the Cotter process and two are liquid standard samples. Table 2 shows the results of the initial analysis and further describes the sample types. Counting time for the samples ranged from about 4 hr for the concentrated samples to 24 hr for the more dilute samples.

The solid material had high activities of ^{214}Pb and other daughters of ^{238}U and ^{230}Th . Analysis of these samples was performed using the 284, 300, 303, 354, and 357-keV gamma rays of ^{231}Pa after the contributions to these peaks from the 295 and 352-keV gamma rays of ^{214}Pb were subtracted. The samples were treated as point sources located at the face of the detector housing, and no corrections were made for attenuation of the gamma rays in the sample.

Analysis of the liquid samples was performed using only the 284-keV gamma-ray transition assuming a point source of ^{231}Pa located at the center of the liquid sample. As for the solid samples, no corrections were made for source self-absorption. A different geometry correction was used for these sources on the assumption that the self-absorption would be quite small in the liquid.

Agreement between measured and reported values is good for all samples except COT-2. These measured values are somewhat low because no corrections were made for the self-absorption of the gamma rays in the source and the finite size of the source.

For future samples, more detailed work could be performed to determine the self-absorption in the source to obtain more accurate results. Or, if some uniform sample size and composition could be maintained, relative measurements with respect to a "standard source" could be made to a high degree of accuracy.

Since the calculation of the amount of ^{214}Pb is a by-product of the calculation of the amount of ^{231}Pa for the residue sources, the amount

of ^{230}Th present in the sample could be estimated if the date of separation of the residue from the uranium ore were known.

Table 2

GAMMA-RAY ANALYSIS OF AIRPORT CAKE SAMPLES

<u>Sample</u>	<u>Type</u>	<u>Measured Weight of ^{231}Pa</u>	<u>Weight as Determined by Other Methods</u>
COT-1	15 g feed residue	19.6 ppb	24 ppb
COT-2	15 g leached residue	15.9 ppb	5.2 ppb
COT-21	15 g feed residue	10.5 ppb	12 ppb
COT-24	20 ml pregnant organic	3.9 $\mu\text{g/l}$	6 $\mu\text{g/l}$ $<W < 12 \mu\text{g/l}$
COT-31	20 ml pregnant organic	4.3 $\mu\text{g/l}$	Same as COT-24
COT-33	20 ml filtered carbonate	0.9 $\mu\text{g/l}$	Less than COT-24
Pa Std. Soln.	20 ml liquid standard	8.0 μg	7.4 μg
297914B	Liquid standard	9.48 μg	10.99 μg

(F. X. Haas, Jr. and A. R. Campbell)

Analytical Chemistry

DETERMINATION OF IMPURITIES IN PLUTONIUM OXIDE BY CARRIER DISTILLATION

A study was made of possible matrix compositions applicable for the analysis of impurities in plutonium oxide to develop a procedure which would require minimum amounts of material for analysis, yield low limits of detection, and be sufficiently simple for rapid routine analysis. The need for such a procedure arose from the purity requirements of the plutonium programs and from a commitment to provide improved methods of analysis.

The investigation into the development of an improved optical procedure for the analysis of impurities in plutonium oxide consisted of three parts. One part of the study was involved in comparing the merits of various carrier-buffer materials. Another part concerned the effects of matrix composition on limits of detection, and the third phase was concerned with attaining optimum operating parameters for the procedure.

The substances selected for study as suitable carrier materials were silver chloride, lithium fluoride, gallium oxide, and varying mixtures of these substances. The selected buffer materials were added to stock matrices of 1:1 uranium-thorium containing 500 and 100 ppm Spex-mix of common elements. In general, it was found that the addition of silver chloride and lithium fluoride tends to hasten the appearance of elemental lines, while gallium oxide tends to retard the volatilization of elements from the sample cup.

Due to the more vigorous burn conditions induced by the silver chloride-lithium fluoride buffers, refractory-type elements such as molybdenum, vanadium, or titanium appear more strongly in the silver chloride-lithium fluoride-buffered spectra than in the gallium oxide-buffered spectra. On the other hand, more volatile elements such as tin, lead or cadmium have better detectability limits in gallium oxide-buffered samples due to the slower volatilization rates and suppressed background spectra.

Because it was easier to overcome the effects of the slow volatilization rates of gallium oxide than the problems associated with silver chloride-lithium fluoride carrier buffer, gallium oxide was selected as the carrier buffer. To improve the detectability of refractory-type elements, gallium oxide-buffered samples were mixed with carbon and exposed for

longer periods and at higher currents. In addition to improving the burn conditions for refractory-type elements, the carbon was also useful as a diluent and blending agent for introducing the internal standard and gallium oxide carrier to the sample.

From past experience, it has been observed that detectability of impurities by the carrier procedure was best in uranium matrix samples. A test was therefore made to see whether detectability of impurities in plutonium is improved by the use of mixed composition matrix. Both thorium and uranium additions have a beneficial effect on analysis. The use of equal amounts of uranium and plutonium had a greater effect on detection limits than did the use of thorium. The increase in detectability is due mainly to the increased volatilization of the sample as evidenced by the heavier spectra of the uranium-plutonium mix.

Several advantages accrue from the use of the uranium-plutonium matrix. One advantage is that the increased sensitivity of the mix requires half as much plutonium per analysis and provides the same limits of detection as does a plutonium matrix. This also means that the use of standard plutonium material is reduced in half. Another advantage of the mixed matrix is that effects on burn conditions of variations in particle size and density of the plutonium material are reduced by the addition of uranium.

The operating conditions used to excite the samples are given in Table 3. In Table 4 the elements of special interest and the limits of detection for selected analytical lines are shown. Concentrations of the impurities

Table 3

OPERATING PARAMETERS FOR SAMPLE EXCITATION

Spectrograph:	3.4 M Ebert
Photographic Plates:	SA #1 plates
Electrode Cathode:	National SPK L 4236
Anode:	Ultra Carbon 1990
Sample Charge:	80-mg charge consisting of 36% PuO ₂ 36% U ₃ O ₈ 20% Ga ₂ O ₃ 8% graphite 100% charge
Exposure Time:	3-sec preburn, 80-sec burn
Excitation:	dc arc, 15 A, shorted
Wavelength Region:	1st order 2250-4550 Å

Table 4
DETECTION LIMITS OF
SELECTED ELEMENTS

<u>Element</u>	<u>Spectral Line (Å)</u>	<u>Limit of Detection (ppm)</u>
Mg	2779.8	<25
Al	3961.5	<25
Si	2506.9	<25
Ca	4226.7	<25
Cr	4254.3	<25
Fe	2483.2	N.D. ^a
Ni	3492.9	<25
Cu	3247.5	<25
Co	3405.1	<25
Na	3302.3	100

^a Not determined. Base material contains iron at 50-100 ppm.

are determined by visual comparison of sample and standard spectra. The precision and accuracy of the comparisons are ~0.5-2 times the stated value. For elements (such as iron) which are present in the samples at or above the specified maximum limits of concentration, an intensity ratio technique is used to determine the concentration. The intensity ratio of Fe 2483.27 Å to Eu 2727.78 Å, the internal standard, is correlated to percent concentration of iron. The relative standard deviation of the measure is 10%, while the accuracy is estimated to range from 15 to 50% depending on how closely the samples match the standards. (Y. G. Ishida)

DETERMINATION OF PLUTONIUM IN SOIL

A complete procedure was established for the determination of plutonium in soil by a fusion technique, and results were reported previously for blank determinations and soil samples.^{9,10}

In the present study, two homogeneous standard-plutonium soil samples, spiked with ²³⁸Pu, were prepared to determine the precision of the entire fusion procedure. The soil was dried for 24 hr at 140°C, broken up, and sieved through a 200-mesh screen. Small pieces of rock and sand were not ground up.

The material passing through the screen was moistened with enough water to give a smooth paste in a platinum dish. A standard-²³⁸Pu aliquot was added and mixed thoroughly. The slurry was evaporated on a hot plate with continuous stirring until the mass became immobile. After thorough drying, the sample was ignited for 4 hr at 1000°C in a muffle furnace. After cooling, the sample was ground until all of the sample passed through a 200-mesh screen. This soil was then mixed with unspiked soil that had also passed through a 200-mesh screen, and was blended for 2 days. The samples were analyzed using the fusion technique.¹⁰

The results of the fusion technique analysis are given in Table 5. The error limit given for the individual determinations is based solely on counting statistics, while the error limit given for the average value is the experimental standard deviation. The average relative standard deviation obtained for these two standards was ±5.50%. Standard A-7 was a 20-g sample, while all others were 1-g samples.

Table 5

PLUTONIUM DISINTEGRATION RATES FOR STANDARD SOIL SAMPLES

<u>Sample Number</u>	<u>^{238}Pu in Sample (dis/min/g)</u>	<u>Sample Number</u>	<u>^{238}Pu in Sample (dis/min/g)</u>
A-1	35.99 $\pm$ 1.61	B-1	55.89 $\pm$ 2.91
A-2	34.92 $\pm$ 1.72	B-2	54.27 $\pm$ 2.88
A-3	41.22 $\pm$ 3.29	B-3	49.34 $\pm$ 2.23
A-4	35.24 $\pm$ 1.59	B-4	53.40 $\pm$ 2.21
A-5	35.43 $\pm$ 1.44	B-5	55.48 $\pm$ 2.64
A-6	38.02 $\pm$ 1.35	B-6	51.34 $\pm$ 2.36
A-7	35.27 $\pm$ 2.28		
Av	36.58 $\pm$ 2.29	Av	53.29 $\pm$ 2.53
Rel. Std. Dev.	$\pm 6.27\%$	Rel. Std. Dev.	$\pm 4.74\%$

The residues from 20-g leached soil samples were analyzed by the fusion procedure to determine what percentage of the plutonium had been leached out of the sample. The samples were leached and prepared on slides for alpha pulse height analysis. The slides, along with the slides obtained by the fusion analysis of the residue, were analyzed by counting.

The results from eight samples are shown in Table 6. The average amount of ^{238}Pu leached was 92.1%. The disintegration rates are given on a

Table 6

PLUTONIUM DISINTEGRATION RATES FOR LEACHED SOIL SAMPLES

<u>Sample Number</u>	<u>^{238}Pu in Leached Soil Residue (rel dis/min/g)</u>	<u>^{238}Pu in Leach Solution (rel dis/min/g)</u>	<u>Total ^{238}Pu in Soil Sample (rel dis/min/g)</u>	<u>^{238}Pu Leached (%)</u>
A-1	8.30	53.8	62.1	86.6
A-2	7.60	89.0	96.6	92.1
A-3	5.60	156.1	161.7	96.5
A-4	8.52	73.3	81.8	89.6
A-5	8.73	93.1	101.9	91.4
A-6	5.14	69.3	74.5	93.1
A-7	4.67	65.0	69.7	93.3
A-8	8.93	142.9	151.8	94.1
Av	7.19	92.8	100.0	92.1
Std. Dev.	1.76	37.3	37.5	
Rel. Std. Dev.	$\pm 25\%$	$\pm 40\%$	$\pm 38\%$	

relative basis. (The average total ^{239}Pu disintegration rate was arbitrarily set at 100 dis/min/g and all other rates are reported relative to this value.) The relative standard deviation for these samples ($\pm 37.5\%$) is much larger than the relative standard deviation for the standard samples ($\pm 5.50\%$), indicating a nonuniform distribution of plutonium in the samples. (R. K. Gillette, E. B. Nunn, M. L. Curtis and C. T. Bishop)

DETERMINATION OF THORIUM IN PLUTONIA BY X-RAY FLUORESCENCE

The present spectrophotometric method for determining small concentrations of thorium in plutonia necessitates ion exchange separation of the plutonium in an HCl medium. The extensive corrosion of alpha-box internal surfaces and equipment makes this procedure quite undesirable. Alternate solvent extraction techniques for separating plutonium and thorium cannot be utilized because limited alpha-box air flow results in the possibility of fire from flammable solvent vapors.

A literature search indicated that thorium in the concentration range of interest (500-15,000 ppm) could not be determined without prior separation of the plutonium. Efforts were therefore made to separate (and eventually determine) thorium after separation from plutonium in a non-chloride medium. Palei and Milyukova stated that, with a zirconium carrier, small quantities of thorium could be quantitatively precipitated from plutonium with sodium benzenesulfinate after reduction of the plutonium to the trivalent state with sulfur dioxide.¹¹ Subsequent thorium determinations were then made by emission spectroscopy. Because larger quantities of thorium were involved in the required procedure as compared to the literature procedure (1500 μg compared to a literature maximum of 300 μg), experimentation was conducted to determine whether the same thorium precipitation conditions would be quantitative.

It was believed that x-ray fluorescence would be a better means of determining thorium content than would emission spectroscopy, after precipitation was accomplished. With the x-ray technique, it was felt that the zirconium would not only serve as the carrier but could also serve as an internal standard. The thorium L_{α_1} emitted x-ray could be utilized with the zirconium K_{α_1} , both of which could be measured without interference from small quantities of plutonium. The x-ray spectrum (without plutonium) is shown in Figure 4. Five triplicate thorium standards (50 μg , 250 μg , 500 μg , 1000 μg , and 1500 μg) were prepared in 0.2N HNO_3 , 2 mg of zirconium (as the oxychloride) was added, sulfur dioxide was bubbled through the solutions for 10 min, and the thorium (and zirconium) were precipitated with a 15% aqueous solution of sodium benzenesulfinate. The precipitates were collected on Whatman No. 42 filter paper, which was taped to a 1-1/2-in. (3.8-cm) diameter metal cap for instrument mounting. (For radioactively contaminated samples, the cap was double-bagged in plastic.) Results of peak height ratio calculations (thorium/zirconium) for the thorium standards after background correction are shown in Table 7.

FIGURE 4 - X-ray spectrum showing relationship of concentrations of thorium and zirconium peaks.

Scintillation detection was used for count measurement, and net thorium and zirconium counts were calculated as follows:

$$\text{Net Th counts} = \text{gross Th counts} - \text{background}$$

or

$$\text{Th}_n = \text{Th}_g - \left[A - \frac{\text{Th}_\lambda - A_\lambda}{B_\lambda - A_\lambda} (A - B) \right]$$

$$\text{and net Zr counts} = \text{gross Zr counts} - \text{background}$$

Table 7

PEAK HEIGHT RATIOS (THORIUM/ZIRCONIUM) BY X-RAY FLUORESCENCE FOR THORIUM STANDARDS AFTER BACKGROUND CORRECTION

Thorium Concentration in Standard (%) ^a	Thorium/ Zirconium Ratio
0.05	0.022
	0.022 Av
	0.020 0.021
0.25	0.059
	0.059 Av
	0.059 0.059
0.50	0.104
	0.106 Av
	0.102 0.104
1.0	0.199
	0.201 Av
	0.199 0.200
1.5	0.292
	0.289 Av
	0.295 0.292

^aWith respect to a 100-mg plutonium sample.

or

$$Zr_n = Zr_g - \left[C - \frac{Zr\lambda - C\lambda}{D\lambda - C\lambda} (C - D) \right]$$

where: A, B, C, D = counts at baseline points

$A\lambda, B\lambda, C\lambda, D\lambda$ = wavelength or 2θ values at chosen baseline points

$Th\lambda, Zr\lambda$ = wavelength or 2θ values at Th or Zr peaks

Th_g, Zr_g = gross counts at peak height

The baseline was considered to be a linear function between the two chosen baseline points for a given peak. From data in Table 7, peak height ratios (thorium/zirconium) were plotted versus thorium content, as shown in Figure 5. A least-squares statistical evaluation showed an uncertainty factor of 0.4% for the slope.

Because plutonium hydrolysis was expected below 0.3N HNO_3 and the technique specified 0.2N HNO_3 , studies were conducted to determine whether thorium would precipitate quantitatively in higher acid concentrations. As shown in Table 8, some thorium losses occur at the higher acidities, indicating the need for compromising acid concentration to a level to maintain complete thorium recovery while minimizing plutonium hydrolysis.

The reduction of plutonium to the trivalent state prior to thorium precipitation was also evaluated. Absorption spectra showed that plutonium was quantitatively reduced to the trivalent state and remained as Pu(III)

for at least 8 hr after reduction with sulfur dioxide. However, because of the inconvenience of working with gases inside the alpha-boxes and the time required for reduction (10 min/sample), an alternate plutonium reductant was sought which was compatible with the thorium precipitation. Quantitative thorium data were possible with both mercaptoacetic acid and hydroxylamine hydrochloride as the plutonium reductants, indicating either of these could be used as an alternate to the sulfur dioxide.

(S. A. Tomes)

Table 8

INDICATION OF DECREASING THORIUM RECOVERY WITH INCREASING ACIDITY	
HNO_3 Concentration (N)	Thorium Recovery (1000- μ g Standard) (%)
0.2	100
0.5	92
0.8	90
1.0	90
>1.0	low

DETERMINATION OF TRITIATED WATER IN STACK EFFLUENT SAMPLES

Stack effluent at Mound Laboratory is presently monitored for tritium by means of Kanne chambers. These chambers are basically ionization chambers, and their readings correspond to total activity. Since,

FIGURE 5 - Plot of peak height ratios (Th/Zr) as a function of the thorium content of standards.

however, the Radiation Concentration Guide (RCG) for tritium depends upon whether this isotope is in the form of the pure element (T_2 or HT) or in the form of tritiated water (T_2O or HTO), it is advisable to know what percentage of the total tritium in the effluent is present as tritiated water.

The RCG value for tritiated water in air for a 168-hr week is $2 \times 10^{-7} \mu\text{Ci}/\text{cm}^3$, while the same value for tritiated hydrogen is $4 \times 10^{-5} \mu\text{Ci}/\text{cm}^3$. The purpose of the present work was to develop a method of determining the maximum percent tritium as tritiated water in the effluent air from certain stacks at Mound Laboratory. The present effort was directed toward grab samples only; no attempt was made to develop a system for constant monitoring of tritiated water.

The determination of tritiated water in samples has been reported by other laboratories.¹²⁻¹⁵ Valentine reported the use of a "bubbler tritium sampler" to determine the amount of tritiated water in air samples. This system consisted simply of a dry gas wash bottle with a fritted glass tip on the inlet, and distilled water as the collecting medium. The observed collection efficiency for tritiated water was reported to be 95% for flow rates of 5 liters/min, while the collection efficiency for tritium gas was $<0.1\%$.¹²

Another method of determining tritiated water in samples is to freeze-out the tritiated water by means of a dry-ice/acetone cold trap. Two laboratories of the Environmental Protection Agency have used this method to determine tritiated water in air samples.^{14,15} This was also the method used in the present investigation to determine the percent tritium as tritiated water in stack effluent.

Gas samples for analysis were taken using a vacuum pump to draw the stack air through a 2-liter flask with stopcocks at both ends. A 0.5-in. (1.3-cm)-diameter copper tube was placed into the stack ductwork and approximately centered in the air stream to assure a representative sample. The air was drawn through the flask for ~20 min at a rate of about 14 liters/min, after which the stopcocks were closed and the gas was brought to the radiocounting laboratory for analysis.

Portions of this sample gas were expanded into a 2-liter gas proportional counting tube, methane was added and the specific activity of the gas was determined. The remainder of the air in the sample flask was then flushed through a dry-ice/acetone bath to freeze-out the tritiated water. The flask was flushed with dry helium at a rate of about 350 cm³/min for 20 min. The trap consisted of a 25-cm³ Packard liquid scintillation counting vial, half full of 5-mm-diameter glass beads. The beads were added to increase the contact surface area for greater efficiency in freezing the tritiated water. The activity of this water was then determined by adding liquid scintillation solution to the vial and counting.

In order to determine the effectiveness of the trap in removing tritiated water and allowing tritium gas to pass through, a number of "standards" were subjected to the flushing procedure. Samples of tritiated water (25 λ) containing 3.18×10^5 dis/min of tritium were placed in the 2-liter flask and flushed with dry helium as previously described. Recoveries of two separate samples were 3.27×10^5 dis/min and 3.20×10^5 dis/min, essentially 100%.

Three samples of dry tritium of known activity were also flushed through the trap to determine whether any of this activity would be stopped by the dry-ice/acetone bath. The results are summarized in Table 9, and indicate that practically all of the dry tritium goes through the trap.

Table 9
DRY TRITIUM GAS TRAPPED BY DRY-ICE/ACETONE BATH

Sample ^a	Tritium Activity in Flask (dis/min)	Activity Trapped (dis/min)	Activity Trapped (%)
Dry tritium gas only	2.39×10^5	7.10×10^2	0.3
Dry tritium gas, 25 λ of H ₂ O in trap	1.07×10^5	2.05×10^2	0.2
Dry tritium gas diluted with room air (relative humidity ~50%)	2.02×10^5	4.10×10^2	0.2

^aAll samples were tritium in argon diluted with helium.

Several 2-liter samples were taken for analysis from ducts leading to two different stacks, to be designated as stack "A" and stack "B". The air in the ducts from which samples were taken was believed to be contaminated with tritium only, and measured specific activities were assumed to be due only to this isotope. Data are summarized in Tables 10 and 11. Column three in these tables lists the Kanne chamber reading at the time the samples were taken. The Kanne systems were calibrated and background was subtracted. Percent HTO, listed in column six, represents the maximum percent tritium as tritiated water in the sample. It is obvious from the data in Table 10 that the Kanne values are much higher (by a factor of 6.4 on the average) than the proportional readings. The reason for this is not known, but one feasible explanation is that a small amount of alpha activity may be present in the air. Small amounts of high-energy alpha emitters would greatly increase the reading of the Kanne meter since this instrument is an ionization chamber. On the other hand, the proportional count would be affected only slightly since any ionizing particle, whether a weak beta or a strong alpha, would produce only one count.

The data in Table 11, however, indicate agreement between the Kanne values and the proportional counting values obtained at the duct to stack B. An application of the "t"-test to the data confirms this. The calculated "t" was 1.5 as compared to the critical value of "t" = 2.0 at the 90% confidence level. Since the critical value of "t" is not exceeded, it can be concluded that there is no difference between the sets of data obtained by the two methods on samples taken at the duct of stack B.

Concerning the values for the maximum percent tritium as tritiated water in the effluent air samples, it is clear that the stack A data indicate a quite variable composition ranging from 9 to 47%. Values for samples taken from the duct to stack B, however, indicated a relatively constant maximum percent tritium as tritiated water, the average being 12.0% with an absolute standard deviation of only 0.6%. This value is in fairly good agreement with results obtained at stack B in April 1970. Five determinations were made using 24-hr sampling periods with a bubbler tritium sampler described previously,^{1,2} and an average of about 10% HTO was obtained.

Finally, it is worthy of note that a particulate filter installed in the air stream during the 2-liter grab sample collections resulted in negligible pickup of radioactive particulates, as measured by liquid scintillation counting. At the duct leading to stack A, an average of only $0.01 \mu\text{Ci}/\text{m}^3$ of air passed through the filter was measured on the filter paper, while at the stack B location the average was $0.03 \mu\text{Ci}/\text{m}^3$. (R. L. Ryan, M. M. Bolton, M. L. Curtis, D. R. Bohl and C. T. Bishop)

Table 10

TRITIUM CONCENTRATIONS^a IN AIR GRAB-SAMPLES FROM DUCT LEADING TO STACK A

<u>Date</u>	<u>Time Sample Taken</u>	<u>Tritium Concentration ($\mu\text{Ci}/\text{m}^3$)</u>			<u>HTO^b (%)</u>	<u>Ratio of Total Kanne to Total Proportional</u>
		<u>Total (Kanne System)</u>	<u>Total (Proportional Counting)</u>	<u>HTO^b (Liquid Scintil- lation Counting)</u>		
3/23/71	--	53	11.0	3.4	32.5	4.8
3/25/71	--	--	13.4	1.5	11.0	--
3/25/71	--	58	11.3	1.1	9.3	5.1
3/29/71	3:00 pm	43	9.4	4.4	46.6	4.6
3/30/71	9:00 am	61	9.7	2.0	20.7	6.3
3/30/71	2:00 am	70	11.7	2.5	20.9	5.8
3/30/71	5:30 pm	61	12.7	2.2	17.5	4.8
3/31/71	1:50 pm	61	4.4	1.6	36.6	13.9
4/1/71	10:00 am	61	9.8	3.1	31.9	6.2
				Av	25.2	6.4
				Std. Dev.	12.4	3.1

^aAll activity measured was assumed to be tritium.^bAll cold-trap activity was assumed to be tritiated water.

Table 11

TRITIUM CONCENTRATIONS^a IN AIR GRAB-SAMPLES FROM DUCT TO STACK B

<u>Date</u>	<u>Time Sample Taken</u>	<u>Tritium Concentration ($\mu\text{Ci}/\text{m}^3$)</u>			<u>HTO^b (%)</u>	<u>Ratio of Total Kanne to Total Proportional</u>
		<u>Total (Kanne System)</u>	<u>Total (Proportional Counting)</u>	<u>HTO^b (Liquid Scintil- lation Counting)</u>		
4/2/71	10:35 am	52	55.3	6.8	12.3	0.94
4/3/71	8:15 am	45	44.1	5.1	11.6	1.02
4/3/71	11:11 am	45	42.7	5.2	12.2	1.05
4/5/71	9:46 am	49	49.2	5.5	11.1	0.99
4/5/71	1:39 pm	72	82.7	9.9	12.0	0.87
4/5/71	3:53 pm	72	80.3	10.3	12.8	0.90
				Av	12.0	0.96
				Std. Dev.	0.6	0.07

^aAll activity measured was assumed to be tritium.

^bAll cold-trap activity was assumed to be tritiated water.

EVALUATION OF EXPLOSIVES COMPONENTS

The component materials found in PBX-9007 were analyzed to determine the identity and concentration of plasticizer to verify the manufacturing specifications. The plastic plasticizer was a mixture of $91 \pm 1\%$ polystyrene unmodified, $5 \pm 1\%$ gum rosin and $4 \pm 1\%$ di-n-octyl phthalate (DOP).

Several standard solutions of di-n-octyl phthalate (DOP) plasticizer in carbon tetrachloride were prepared to determine what gas chromatographic conditions would be used to analyze the dioctyl phthalate content of the PBX (plastic-bonded explosive). Two stainless steel columns [1.5-m x 1/8-in. (0.32-cm) and 4.0-m x 1/8-in. (0.32-cm)] were packed with 10% OV-3 on Chromosorb WHP 100/120-mesh. The gas chromatograph (G.C.) was run in the single-column mode with temperature programming and isothermal conditions. Separation of the solvent and the DOP was very poor on the 1.5-m column. The 4-m column retained the DOP so it was not adequate for the intended application. Baseline was very noisy, and with both columns there was considerable baseline drift.

At this time it was decided to run the instrument in the dual differential mode to help stabilize the baseline. Two matched 60-in. (152-cm) x 1/8-in. (0.32-cm) stainless steel columns, packed with 3% SE-30 on Varaport 30 100/120-mesh, were found to give an excellent baseline, poor separation during isothermal operation, and very good separation with temperature programming. The solvent was retained for 15 sec while the di-n-octyl phthalate was retained for 252 sec.

A 1-g sample of the PBX-9007 used in manufacturing was extracted with carbon tetrachloride and the extract was run on the gas chromatograph. The solvent peak at 15 sec and a second major peak at 210 sec were observed. There were minor impurities found in the extract at 110 and 185 sec.

In order to determine what the PBX-9007 extraction and analysis meant, seven samples were prepared to check the extraction technique and the analysis method. Table 12 is a summary of the results. The seven samples were (1) pure di-n-octyl phthalate (DOP) in carbon tetrachloride, (2) pure bis(2-ethylhexyl)phthalate (DEHP) in carbon tetrachloride, (3) a mixture of pure DOP and DEHP in carbon tetrachloride, (4) a 1-g sample of PBX-9007 extracted with carbon tetrachloride in a Soxhlet extractor, (5) a 1-g sample of PBX-9007 doped with DOP in carbon tetrachloride and extracted with hot acetone followed by the addition of carbon tetrachloride and boiling to remove the acetone, (6) the extract from (4) mixed with DOP from (1), and (7) the solid remaining after the Soxhlet extract from (4) was further extracted with hot acetone followed by the addition of carbon tetrachloride and boiled to remove the acetone.

Slight impurities were found in the extracts of the PBX. Sample (1), DOP, had only two peaks: solvent and plasticizer. Sample (4), the Soxhlet extract of PBX, had three peaks: solvent, impurity and plasticizer. Sample (5), the doped PBX sample, had all four materials. Sample (6), the Soxhlet extract mixed with DOP, had all four peaks. Sample (7), the

Table 12

SUMMARY OF PBX-9007 ANALYSIS

<u>Sample Number</u>	<u>Title</u>	<u>17 sec (CCl₄)</u>	<u>110 and 185 sec (impurity)</u>	<u>210 sec (di-n-octyl phthalate)</u>	<u>252 sec [bis-(2-ethylhexyl) phthalate]</u>
1	Di-n-octyl phthalate (DOP)	Yes	No	Yes	No
2	Bis-(2-ethylhexyl) phthalate (DEHP)	Yes	No	No	Yes
3	DOP + DEHP	Yes	No	Yes	Yes
4	Soxhlet extract of PBX	Yes	Yes	No	Yes
5	PBX sample doped with DOP prior to Soxhelt extraction	Yes	Yes	Yes	Yes
6	Soxhlet extract (4) mixed with DOP (1)	Yes	No	Yes	Yes
7	Extract of solid remaining after Soxhlet extract (4)	Yes	Yes	No	No

solid remaining after Soxhlet extraction, had only one peak, carbon tetrachloride. After these samples were analyzed, the DEHP was obtained and analyzed in carbon tetrachloride solution (2) and mixed with DOP in carbon tetrachloride solution (3). The results clearly show that the material found in the PBX extract (4) was identical to that of the DEHP analysis except for the slight impurity.

Since the manufacturing specifications call for DOP, it is not surprising to find DEHP in the PBX because the designation "DOP" does not distinguish among the various isomers of octyl phthalate esters. DEHP is one of the many isomers of octyl phthalate esters.

The quantitative analysis of the DEHP content of the PBX-9007 powder was as follows: Three samples of PBX-9007 (1.0008, 1.0007 and 1.0027 g, respectively) were each extracted with 30 ml of carbon tetrachloride using a Soxhlet extractor for 4 hr. The resulting extract was diluted to 100 ml with carbon tetrachloride and compared with gas chromatography to standards containing 0.01, 0.02 and 0.03% DEHP in carbon tetrachloride. The gas chromatograph was operated according to the conditions in Table 13.

Table 13

GAS CHROMATOGRAPH OPERATING CONDITIONS

<u>Location</u>	<u>Temp. (°C)</u>	<u>Component</u>	<u>Flow Rate (ml/min)</u>	<u>Detector: FID</u>
Injection Port A	345	He	30	Range 10
Injection Port B	343	H ₂	30	Attenuator - As noted
Detector	349	Air	300	

Temperature programming parameters are shown in Table 14.

Table 14

GAS CHROMATOGRAPH TEMPERATURE PROGRAMMING PARAMETERS

<u>Parameter</u>	<u>Value</u>
Initial Temperature	240°C
Final Temperature	300°C
Heating Rate	40°C/min in 0.5-min intervals
Post Injection	2-min hold at 240°C
Program Length	5.5 min with automatic reset at end

The instrument was operated in the dual differential mode (A-B) where A was the analytical column and B was used to blank out column bleed-off. Sample size was 3 μ l for standards and extracts, and each solution was injected five times.

Peak height, taken from the leading edge of the peak, was used as a measure of instrument response to the various solutions. Table 19 contains all of the data for the analysis of the standards and extracts. The data indicate that the method is reproducible, and Figure 6 shows that a linear relationship between amount of DEHP and peak height (instrument response) exists within the range of concentrations being analyzed.

Table 15

RESULTS OF GAS CHROMATOGRAPH ANALYSIS OF DEHP EXTRACTED FROM PBX-9007

	Sample Results					
	0.01% Standard	0.02% Standard	0.03% Standard	PBX #1	PBX #2	PBX #3
Attenuation	32	64	128	32	32	32
Peak height 1	2.36	2.34	1.83	1.31	1.39	1.70
Peak height 2	2.39	2.67	1.95	1.39	1.52	1.50
Peak height 3	2.47	2.64	1.98	1.39	1.52	1.52
Peak height 4	2.59	2.52	2.03	1.28	1.45	1.56
Peak height 5	<u>2.50</u>	<u>2.64</u>	<u>2.05</u>	<u>1.36</u>	<u>1.48</u>	<u>1.52</u>
Av. peak height	2.46	2.56	1.97	1.35	1.47	1.56
Std. Dev.	± 0.09	± 0.14	± 0.09	± 0.05	± 0.06	± 0.08
Attenuation X Av.	78.72	163.84	252.16	43.20	47.04	49.92

The amounts of DEHP found in the three PBX extracts were 0.54, 0.59, and 0.62 wt %, respectively.

The PBX is manufactured with $0.5 \pm 0.1\%$ DEHP. The material appears to be within the manufacturing specification.

FIGURE 6 - Relationship of DEHP concentration to instrument response.

(C. S. Friedman)

Instrumentation and Methods

INFRARED THERMOGRAPHY

An investigation was made of the usefulness of infrared thermography in the nondestructive evaluation of materials and assemblies at Mound Laboratory. The purpose of the investigation was to determine if useful data could be obtained from the thermal images of objects as they radiated infrared energy.

The instrument used was a Barnes Engineering T-101 Infrared Camera. This camera had a temperature range of -20 to $+150^{\circ}\text{C}$, and with range extenders up to 300°C . The image was formed on a modified oscilloscope which framed at a rate of four frames per second. The camera used a liquid nitrogen-cooled indium antimonide detector capable of detecting 0.2°C temperature differences at 30°C . A Polaroid camera was used to record the thermal images on the cathode ray tube.

The objects studied with the camera were:

1. 10-W calorimeter source
2. Nuclear battery
3. Plutonium-238 alpha source
4. Four cans of trash used as standards in the gamma-ray assay of trash.
5. SNAP-27 capsule
6. Plutonia-molybdenum cermet
7. Graphite material used for hot pressing dies

The study of some of the material required the installation of a 6-in. (15-cm)-diameter, 0.5-in. (1.3-cm)-thick NaCl window in a glovebox to transmit the infrared radiation to the camera outside the box. Conventional Plexiglas hood fronts absorbed the radiation.

The object in most cases was to observe the thermal patterns in the object as it passed through thermal changes. These changes involved either

heating the object and watching it cool or, in the case of radioisotopes, cooling the object and watching it heat.

Neither system was successful. Due to reflections and stray radiation from other objects, no single object was successfully observed in a true manner with the exception of the plutonium-238 alpha source. This was a thin cellophane disc with a few milligrams of plutonium-238 deposited. The concentrations of the isotope could readily be observed.

The other objects could not be observed due to reflections of stray radiation from other sources (walls, the camera itself, the operator) and variations in emissivity across the surface of an object. This particularly caused a problem in the SNAP-27 capsule which had a discolored oxidized area at the middle joint that appeared to be at a much different temperature than did the rest of the capsule.

The problems of reflections and emissivity could be solved, given adequate time for development. However, the results may not justify the expense involved, and no further work is planned in this area. (P. L. Blue)

Separation Chemistry

RESIDUE ADSORPTION

Indium-113m is a useful scanning agent in biological and medical research¹⁶ because of its short half-life (99.8 min) and energetic gamma emission (393 keV). It is produced by the decay of its long-lived parent, ^{113}Sn ($T_{1/2} = 115$ days), from which it is usually separated by ion exchange.^{17,18} It has now been found that $^{113\text{m}}\text{In}$ can be separated from ^{113}Sn , with satisfactory yield and radiochemical purity, by the method of residue adsorption.

The material used in this study was purchased from International Chemical and Nuclear Corporation and, according to data supplied by the vendor, contained 14.7 mCi of ^{113}Sn per gram of inert tin as SnCl_2 in 6N HCl. On the basis of this information, a stock solution suitable for gamma-counting was prepared by dilution with 6N HCl which contained, after correction for decay, approximately 0.1 μCi of ^{113}Sn and 25 μg of inert tin per drop (50 μl).

The method of residue adsorption is based on the principle that any inorganic compound which is insoluble in a given solvent at the macroscopic level can be made to adsorb on a nonreactive surface at the trace level if the microcrystals can be brought into contact with that surface during the process of formation. Once adsorbed, the compound or compounds can be selectively desorbed by the same reagents in which they would normally be soluble at macroscopic levels.¹⁹⁻²²

The $^{113}\text{Sn}/^{113\text{m}}\text{In}$ system appears to be an excellent candidate for separation by the method of residue adsorption. Sn(II) is very unstable in the presence of air and is easily oxidized to Sn(IV) unless all oxidizing agents are excluded. Sn(IV) , in turn, hydrolyzes readily to form products of uncertain composition, which are difficult to redissolve in dilute mineral acids ($<0.7\text{M}$ HCl, for example).²³ On the other hand, the hydrolysis of In(III) , which begins at ca. pH 3.4, is readily reversible at lower pH values.²⁴

To test the feasibility of the method, one drop (50 μl) of the ^{113}Sn stock solution was transferred to a glass vial, diluted to 6 ml with water and heated at 95°C for 1 hr. While still hot, the solution was filtered through glass wool which was packed so as to yield a gravity flow rate of

ca. 0.7 ml/min. Upon analysis by gamma-counting, the radionuclides were found to be distributed as follows:

	<u>Tin-113</u> <u>(%)</u>	<u>Indium-113m</u> <u>(%)</u>
Original Vial	76.9	32.4
Glass Wool Filter	6.3	8.7
Filtrate	<u>16.9</u>	<u>54.2</u>
Material Balance	100.1	95.3

An attempt to desorb the ingrown ^{113m}In selectively by leaching the original vial with hot 0.1N HCl was unsuccessful. Nevertheless, the partial separation effected by the hydrolytic experiment indicated that, if it were adsorbed under appropriate conditions, ^{113}Sn could be made to act as a "cow", or generator, for periodic "milking" of ^{113m}In .

In the usual residue adsorption procedure,¹⁹ the solution containing the cation which is to be adsorbed is evaporated to dryness and the residue is converted in situ to a suitable insoluble species by the addition of a precipitating reagent. This was not possible with SnCl_2 because of the volatility of SnCl_4 , which boils at 114.1°C .²⁵ For example, when a drop of the ^{113}Sn stock solution was evaporated to dryness at $95\text{--}100^\circ\text{C}$, the loss of ^{113}Sn ranged from 23.5% to 66.5%. It was found, however, that the volatilization of SnCl_4 could be suppressed by the prior addition of a suitable anion. Phosphate ion, in the proper concentration, proved to be an effective suppressant when added either as $(\text{NH}_4)_2\text{HPO}_4$ or Na_3PO_4 (Table 16).

To determine the optimum conditions for separating ^{113m}In from ^{113}Sn , sources were prepared by the following procedure:

Three 2-dram vials (50 mm high x 17 mm i.d.) were rinsed with water and drained, but not dried. To each was added one drop of ^{113}Sn stock solution (6N HCl) and one drop of 0.01M $(\text{NH}_4)_2\text{HPO}_4$. The vials were dried in a heating block at 100°C and gamma-counted. To insure complete oxidation of Sn(II) and to redistribute the residual phosphate around the sides of the vials, 5 drops of 0.1N HNO_3 were added to each vial and the solutions were evaporated to dryness at 100°C . The vials were again gamma-counted.

Counting was performed with a 3 x 3-in. (7.5 x 7.5-cm) NaI(Tl) well crystal and a single-channel pulse-height analyzer operated in the integral mode. The lower discriminator was set to reject all pulses representing energies below 315 keV, approximately, and the upper discriminator was disabled. Thus, all counting was based essentially on the 393-keV photopeak of ^{113m}In . The yield of ^{113}Sn was determined by counting the samples after the ^{113m}In was again in equilibrium (i.e., after at least 16 hr).

Table 16

SUPPRESSION OF THE VOLATILIZATION
OF TIN(IV)

Reagent	Drops Added	Residual ^{113}Sn (%)
None	-	33.5
H_2O	1	76.5
0.01N H_2SO_4	1	71.0
0.1N H_2SO_4	1	94.1
0.001M Na_3PO_4	1	85.2
0.001M Na_3PO_4	1	78.3
0.001M Na_3PO_4	5	100.0
0.01M $(\text{NH}_4)_2\text{HPO}_4$	1	99.4
0.01M $(\text{NH}_4)_2\text{HPO}_4$	2	100.0
0.01M $(\text{NH}_4)_2\text{HPO}_4$	3	100.5
0.1M $(\text{NH}_4)_2\text{HPO}_4$	1	99.4
0.001M Na_2EDTA	1	84.3
0.001M Na_2EDTA	2	88.9
0.001M Na_2EDTA	3	94.0
0.001M Na_2EDTA	5	97.2
0.01M Na_2EDTA	1	97.0
0.01M Na_2EDTA	1	100.6

The three vials were leached with HCl , HNO_3 and H_2SO_4 , respectively, the same source being leached successively with different concentrations of the same acid. Thus, the percentages reported in Table 17 are based, in each case, on the amount of ^{113}Sn and ^{113}In remaining in the vial after the previous desorption. At each concentration, the vial was leached twice with 5 drops of the same reagent, which was heated for 2 min at 95°C before being transferred to a receiving vial.

The results of the three series of desorptions are given in Table 17, expressed as the percentages of ^{113}Sn and ^{113}In desorbed and the separation factor (ratio of indium to tin in the desorbate). It will be noted that the initial desorption with water, in each case, removed between 12 and 15% of the ^{113}In and approximately 5% of the ^{113}Sn ; this behavior is attributed to physical, as distinguished from chemical, action. The small amount of hydrolyzed tin(IV) which was deposited on the surface of the

dried phosphate rather than on the glass was mechanically removed from the vial when the phosphate was dissolved. After the vial had been washed free of excess phosphate, only 1% or less of either tin or indium was desorbed at the lower acid concentrations. The desorption of ^{113}In increased sharply in 0.1N HCl and significantly, but less sharply, in 1N HNO_3 and 1N H_2SO_4 , demonstrating that the effect was due not only to the acidity but to the nature of the anion as well. This behavior is typical of residue adsorption, reflecting its similarity to macroscopic precipitation and dissolution.

In all cases thus far tested, desorption with acid yielded separation factors equal to or significantly greater than unity; that is, more ^{113}In than ^{113}Sn was desorbed. Since tin(IV) is known to form a stannate ion in alkaline solution,²⁶ it was of interest to determine whether the relative desorption could be reversed. One drop of ^{113}Sn stock solution and one drop of 0.01M $(\text{NH}_4)_2\text{HPO}_4$ were evaporated to dryness at 100°C in a 2-dram glass vial. Five drops of 0.1N NaOH were added to the vial and

Table 17

DESORPTION OF TIN AND INDIUM FROM GLASS BY MINERAL ACIDS

Acid Normality	HCl			HNO ₃			H ₂ SO ₄		
	^{113m} In (%)	¹¹³ Sn (%)	Separation Factor ^a	^{113m} In (%)	¹¹³ Sn (%)	Separation Factor ^a	^{113m} In (%)	¹¹³ Sn (%)	Separation Factor ^a
0.0000 ^b	14.4	7.2	2.0	11.9	4.5	2.6	12.8	5.1	2.5
0.0001	1.4	1.3	1.1	0.7	0.9	0.8	-	-	-
0.001	0.6	0.6	1.0	0.3	0.4	0.8	0.5	0.6	0.8
0.01	0.6	0.4	1.5	0.3	0.4	0.8	0.7	0.6	1.2
0.1	44.6	2.6	17.2	7.0	0.9	7.8	10.4	1.2	8.7
1	96.5	80.3	1.2	44.7	10.1	4.4	55.2	19.5	2.8
3	-	-	-	59.3	30.0	2.0	-	-	-
6	-	-	-	70.0	41.0	1.7	-	-	-

^a Separation Factor = Ratio of ^{113m}In desorbed to ¹¹³Sn desorbed.

^b H₂O.

the evaporation was repeated. The dried residue was leached twice with 5 drops of water and heated for 2 min at 95°C, and the two leach solutions were combined in a second vial. The desorbate was found to contain 33.1% of the ^{113}mIn and 91.9% of the ^{113}Sn , for a separation factor of 0.36.

The solution was evaporated to dryness and the vial was stoppered and allowed to stand for 24 hr. The residue was then leached as before, with two portions of hot water. Again, significantly more ^{113}Sn than ^{113}mIn was desorbed; the desorbate contained 77.0% of the ^{113}Sn and 38.5% of the ^{113}mIn (separation factor: 0.50). The fact that the second desorption yielded less of the ^{113}Sn while removing approximately the same fraction of the ^{113}mIn suggests that, on aging in the dry state, the stannate ion, $[\text{Sn}(\text{OH})_6]^{-2}$, is converted to the intractable β form of stannic oxide.

The results in Table 17 were applied to the preparation of a ^{113}Sn "cow", or generator, for periodic "milking" of ^{113}mIn . A sample of ^{113}Sn was adsorbed on the walls of a 2-dram glass vial as described above and the residue was washed several times with water to remove excess phosphate. After the vial was allowed to stand overnight to permit equilibration of ^{113}mIn , it was leached periodically with various amounts of hot 0.1N HCl. After desorption, the generator was stoppered without being dried and allowed to stand for one or more days (except in one case) when it was again leached with 0.1N HCl. The results of nine such "milkings" are given in Table 18.

Table 18
DESORPTION OF INDIUM-113m FROM A TIN-113 "COW"

Time Since Last Desorption (hr)	Yield of ^{113}mIn (%)	Contaminated by ^{113}Sn (%)	Separation Factor	Desorption Conditions
24	32.1	0.6	53.5	A
24	46.9	0.6	78.2	A
72	36.3	0.3	121.0	A
24	47.4	1.0	47.4	B
24	49.7	1.3	38.3	B
0.4	21.6	1.5	14.4	C
22	47.9	1.8	26.6	C
25	48.7	1.8	29.7	C
72	60.3	1.2	51.0	D,A

A - Desorbed twice with 5 drops of 0.1N HCl heated for 2 min at 95°C.

B - Desorbed once with 1 ml of 0.1N HCl heated for 5 min at 95°C.

C - Desorbed once with 2 ml of 0.1N HCl heated for 5 min at 95°C.

D - Dried at 100°C just before desorption.

The data of Table 18 suggested that there was an irreducible residual amount of ^{113}mIn which remained incorporated in the SnO_2 crystal lattice. To determine to what extent it was possible to desorb the ^{113}mIn , a fresh ^{113}Sn cow was prepared and leached at frequent intervals with 5 drops of 0.1N HCl heated for 5 min at 95°C . The results (Table 19) showed that approximately the same absolute amount of tin(IV) was desorbed by each leaching but the fraction of indium(III) which was desorbed depended upon the time elapsed since the last desorption (i.e., the degree to which fresh ^{113}mIn had been regenerated by the decay of ^{113}Sn).

It is important to note that in the desorptions in which the ^{113}Sn was left undisturbed for an hour or more, there was an increase in both the absolute and the relative amounts of ^{113}mIn desorbed. In no case, however, did the amount of ^{113}mIn desorbed exceed 50% of the theoretical total amount regenerated. It appears likely, therefore, that the only indium atoms available for desorption without rupture and dissolution of the SnO_2 crystals are those which lie at or near the unattached surfaces of the crystals. If this is so, it should be possible to improve both the yield and the purity of the desorbed ^{113}mIn by controlling the thickness and the distribution of the adsorbed layer.

Table 19
INDIUM-113m DESORPTION SHOWING YIELD
DEPENDENCE ON TIME SINCE LAST DESORPTION

Time Since Last Desorption (min)	^{113}Sn Desorbed (γ counts/sec)	^{113}mIn Desorbed (γ counts/sec)	^{113}mIn Yield (%)	Separation Factor
0 ^a	78.37	557.40	41.9	7.1
8.2	33.57	304.76	38.0	9.1
8.3	30.40	131.10	24.5	4.3
8.2	37.98	95.58	21.2	2.5
8.2	38.67	81.03	20.2	2.1
8.8	41.08	78.38	21.1	1.9
57.7	38.72	233.09	43.1	6.0
8.4	38.48	75.00	21.2	1.9
118.9	41.13	353.08	52.5	8.6
8.4	39.39	84.08	23.7	2.1
8.3	40.47	63.65	20.7	1.6
~1100 ^b	23.82	399.05	47.1	16.8
~3000 ^b	25.10	380.00	46.8	15.1
~7200 ^b	27.23	331.57	43.0	12.2
~1440 ^b	22.86	324.01	44.4	14.2

^a Contained residual phosphate from preliminary adsorption.

^b Desorbed by adding 5 drops of 0.1N HCl and leaving at 25°C for the time shown.

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