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**CHEMISTRY--RADIATION
AND RADIOCHEMISTRY**

DATE: July 23, 1956

SUBJECT: Development of Radioanalytical
Methods for HRT.

TO: B. B. Briggs

FROM: T. H. Handley and S. A. Reynolds

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For The Atomic Energy Commission

H. F. Canale
Chief, Declassification Branch TC

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TO: R. B. Briggs

DATE: July 23, 1956

COPIES TO: Distribution Shown SUBJECT: Development of Radioanalytical Methods for HRT

The Chemistry and Chemical Technology Divisions have requested many radiochemical analyses in connection with the operation of the HRT and the associated chemical plant. (ORNL CF-55-3-111, 55-7-83, 56-4-101). The status of methods for most of these analyses was given in an earlier memo (CF-56-1-79). A meeting of those concerned with the program was held on January 31, 1956, in which several items were agreed upon. It was decided that the Radiochemistry Group of the Analytical Chemistry Division would undertake the development of methods of separation and measurement for those radionuclides for which adequate methods were not available (as indicated in Table I of 56-1-79). Three man-months of effort were authorized (H. F. McDuffie, memo, March 8, 1956).

At present, 496 man-hours have been expended in this effort, and most of the separation problems have been solved. The above time is almost exactly three man-months; therefore, the authorized time has been used up. It appears that two or three additional man-months of development may be required, principally in the development of measurement techniques, and -- immediately before "start-up" -- calibration of instruments. It is not anticipated that the chemical plant needs (CF-56-4-101) will require much development effort.

It appears that a rigid sample schedule cannot be set up, since the exact "start-up" program is unpredictable. Samples will be taken at intervals which correspond, in integrated power, to full-power operation for 0.5, 1, 2, 4, 8, etc. hours. It seems that no interval between samples will be shorter than about two hours. Analyses for certain nuclides must be done immediately because of short half-life, or rapid growth of an interfering nuclide. Others may be delayed for days or weeks (months in the case of Tc-99). During the early part of HRT operation, the sample load may be such that a large fraction of the radiochemically-trained personnel of the Analytical Chemistry Division will be required to analyze the samples. Some analyses may have to be "sacrificed." It is essential that the persons in the Chemistry and Chemical Technology Divisions, who will correlate and interpret the analytical data, be prepared to make prompt decisions as to "reruns," elimination of non-essential analyses, etc.

The radiochemical methods which have been developed for HRT analyses are given in detail in the latter part of this memo. These may yet require minor modifications.

Table I summarizes calculated concentrations of various fission-product and induced activities, while Table II furnishes similar information of heavy-element activities. The writers are indebted to J. Halperin of the Chemistry Division for most of these data.

Further "progress reports" will be issued when justified by accumulation of data.

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Table I

Fission-Product and Induced Activities -- dpm/ml -- in "Soup"

Nuclide	T _{1/2}	Time at Full Power				
		33m 2x10 ³	2.78 hr. 10 ⁴	27.8 hr. 10 ⁵	11.6 d 10 ⁶	58 d 5x10 ⁶ sec.
P-32	$\sigma = .01 \text{ b}$ 14.3d	1.2x10 ⁶	6x10 ⁶	6x10 ⁷	4.4x10 ⁸	10 ⁹
S-35	$\sigma = .26 \text{ b}$ 87d	2.2x10 ⁵	1.08x10 ⁶	1.08x10 ⁷	1.0x10 ⁸	4.4x10 ⁸
Cu-64	$\sigma = 4.3 \text{ b}$ 12.8 hr.	10 ⁸	3x10 ⁹	2.5x10 ¹⁰	3.2x10 ¹⁰	3.2x10 ¹⁰
Sr-89	54d	3.6x10 ⁸	1.8x10 ⁹	1.8x10 ¹⁰	1.5x10 ¹¹	6x10 ¹¹
Y-91	58d	4.2x10 ⁸	2.1x10 ⁹	2.1x10 ¹⁰	2.0x10 ¹¹	7.5x10 ¹¹
Zr-95	63d	4.2x10 ⁸	2.1x10 ⁹	2.1x10 ¹⁰	2x10 ¹¹	8x10 ¹¹
Nb-95	35d	2x10 ⁵	5x10 ⁶	3x10 ⁸	2x10 ¹⁰	3x10 ¹¹
Nb-96	23.4 hr.	2.4x10 ⁶	1.2x10 ⁷	8.2x10 ⁷	1.4x10 ⁸	1.46x10 ⁸
Tc-99	2.12x10 ⁵ yr.	3.2x10 ²	1.6x10 ³	1.6x10 ⁴	1.6x10 ⁵	8x10 ⁵
Ru-106	1.0y	4.2x10 ⁶	2.1x10 ⁷	2.1x10 ⁸	2.1x10 ⁹	10 ¹⁰
Cs-136	13d	1.9x10 ⁶	9.5x10 ⁶	9.5x10 ⁷	8.3x10 ⁸	1.5x10 ⁹
Cs-137	26 yr.	2.6x10 ⁶	1.3x10 ⁷	1.3x10 ⁸	1.3x10 ⁹	6.5x10 ⁹
Ba-140	12.8d	2x10 ⁹	1.0x10 ¹⁰	10 ¹¹	8x10 ¹¹	1.6x10 ¹²
La-140	40.2 hr.	2x10 ⁹	1.0x10 ¹⁰	10 ¹¹	8x10 ¹¹	1.6x10 ¹²
Ce-144	290d	8.6x10 ⁷	4.3x10 ⁸	4.3x10 ⁹	4.3x10 ¹⁰	2.1x10 ¹¹
Pr-144	17.5m	8.6x10 ⁷	4.3x10 ⁸	4.3x10 ⁹	4.3x10 ¹⁰	2.1x10 ¹¹

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Table II
Heavy-Element Activities¹

Nuclide	Operating Time	Activity dpm/ml
U-237	0.0ld	2.3×10^4
	0.1d	3.7×10^5
	1.0d	1.6×10^7
	10d	1.0×10^9
	100d	2.4×10^{10}
U-239	0.1d ²	6×10^{10}
	1.0d ²	6×10^{10}
U-240	0.1d	5×10^3
	1d	4×10^4
	"saturation"	6×10^4
Np-237	4 mo.	1.7×10^3
	1y	1.5×10^4
Np-238	30d	3×10^7
	100d	4×10^8
	1y	6×10^9
Np-239	2d ²	2.5×10^{10}
	10d ²	6×10^{10}
Pu-239	1 mo.	$\sim 10^8$
		Ratio
Pu-238/Pu-239	30d	0.1
	100d	1
	1y	20
Pu-240/Pu-239	>~1 mo.	~0.025 (wt.)

¹ U and Np assumed to stay in solution; Pu assumed continuously removed.

² Essentially "saturated".

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CESIUMI. Introduction

To separate radiocesium from other fission-product activity, a preliminary precipitation as the silicotungstate is performed. This step is a specific separation of cesium from rubidium and other alkali metals. The silicotungstate is dissolved in sodium hydroxide and scavenged with Fe, Ba and Sr as the hydroxide and carbonates. Cesium is finally precipitated as cesium tetraphenylboron in the presence of disodium versenate as a chelating agent for contaminating activities. The chemical yield is 70 to 80% and the time required for analysis in quadruplicate is about three hours. A decontamination factor $>10^3$ is obtained by repeating several of the steps.

II. Reagents, Special

Dissolve 4g. of sodium tetraphenylboron and 1g. of aluminum chloride hexhydrate in 100 ml of water. Add a few drops of phenylphthelain and then add 6N sodium hydroxide dropwise until the solution just turns red. Allow to stand several hours. Filter and dilute to 200 ml, and store in a cool place (ice box).

Other reagents are those one expects to find in a radiochemical laboratory.

III. Equipment

No special equipment other than that found in standard radiochemical laboratories.

IV. Preparation and Standardization of Carrier

Dissolve 6.4g. of CsCl in H_2O and dilute to one liter with water.

Pipet 5 ml of the above carrier solution into a 250 ml beaker and dilute to 100 ml with distilled water, cool in an ice bath to ice temperature. Add 10 ml of sodium tetraphenylboron dropwise while stirring and allow to stand for about ten minutes. Filter onto a scintered glass filter and wash with several small portions of water. Dry at $110^\circ C$. for 15 minutes, cool and weigh. Four standardizations should agree within 0.5%.

V. Procedure

1. To an aliquot of the sample, add 1 ml of cesium carrier (5 mg), and 2 mg each of Rb and K holdback carriers. Add 15 ml of 6N HCl and 2 ml of silicotungstic acid (1g/ml), digest 10 minutes. Centrifuge and discard the supernate. Wash the precipitate with 5 ml of 6N HCl.

2. Dissolve the precipitate of $Cs_3SiW_{12}O_{42}$ in 1-2 ml of 6N NaOH, add 20 ml 6N HCl centrifuge and discard the yellow precipitate. Add 2 ml of silicotungstic acid, digest 10 min., centrifuge and discard supernate. Wash the precipitate with 5 ml of 6N HCl.

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V. Procedure (Continued)

3. Dissolve the precipitate of $\text{Cs}_8\text{SiW}_{12}\text{O}_{42}$ in 1-2 ml of 6N NaOH (warm if necessary to dissolve). Dilute to 15 ml and make slightly acid with 1N HCl. Add Fe, Ba and Sr carrier (2 mg each), make just basic with 1N NaOH and add 1 ml 3M Na_2CO_3 . Warm to coagulate precipitate. Centrifuge and discard the precipitate.

4. Make supernate slightly acid with 1N HCl, add 2 mg each of Fe, Ba and Sr carriers. Repeat precipitation with NaOH and Na_2CO_3 .

5. Make supernate slightly acid with 1N HCl, Add 4 ml of sodium tetraphenylboron dropwise while stirring (2% solution) and let stand for 10 minutes. Centrifuge and discard supernate.

6. Dissolve the precipitate in 2 ml of acetone, and add 10 ml of 0.1N HCl. Add 4 ml of sodium tetraphenylboron dropwise and let stand for ten minutes. Centrifuge and discard supernate.

7. Dissolve the precipitate in 1-2 ml acetone, and add 10 ml of absolute alcohol containing 0.5% sodium tetraphenyl boron. Let stand in an ice bath for 15 minutes and filter onto a tared No. 42 Whatman filter circle. Wash with alcohol and dry for 15 minutes at 110°C and weigh as $\text{CsB}(\text{C}_6\text{H}_5)_4$.

COPPER

Decontamination: From mixed fission products, a factor of $>10^7$ was obtained.

Yield: 60-80%

Time: Four hours for group of 4 determinations

Equipment: Standard radiochemical equipment

Solution, Special:

1. Standardized Cu carrier
2. SO_2 gas cylinder.

Procedure:

1. To an aliquot of HNO_3 or HCl solution of the activity, add 10 mg Cu, add Fe, Ba and Sr scavenging carriers, make basic with NH_3 and add 1 ml of 3N K_2CO_3 . Warm to coagulate precipitate. Centrifuge and discard precipitate.

2. Make supernate slightly acid, add Fe, Ba and Sr, add NH_3 and K_2CO_3 and warm to coagulate precipitate. Centrifuge and discard precipitate.

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3. Make supernate 0.5N in HCl. Warm and bubble in SO₂, add KCNS until CuCNS precipitates. Let settle several minutes, centrifuge and discard supernate. Wash precipitate with small amount of water.

4. Dissolve CuCNS in small amount of HNO₃ and boil just to dryness. Dissolve in 15 ml of 3N HCl, add Sr, Ta, Y holdback carriers. Bubble in H₂S and precipitate CuS. Centrifuge and discard supernate, wash precipitate with 10 ml of H₂O.

5. Dissolve CuS in a minimum of HNO₃. Dilute to 0.5N H⁺ and scavenge twice with AgCl.

6. Add Fe, Ba and Sr carriers and make basic with NH₃, add 1 ml 3N H₂CO₃ and warm to coagulate precipitate. Centrifuge and discard precipitate.

7. Make supernate slightly acid with HCl and add Fe, Ba and Sr carriers, make basic with NH₃, add 1 ml 3N K₂CO₃ and warm to coagulate precipitate. Centrifuge and discard precipitate.

8. Make supernate 0.5N in HCl. Bubble in SO₂, add KCNS until CuCNS precipitate and add slight excess, filter wash with H₂O and EtOH, dry 15 minutes at 110°C., weigh as CuCNS.

NIOBIUM

Decontamination: $> 10^6$

Yield: 60%

Time: Four hours for group of four determinations

Equipment, special:

50 ml polyethylene centrifuge cones.
Laboratory stirrer, Model 7605 with polyethylene stirring rod.

Solution, special:

Solution 6M in H₂SO₄ and 9M in HF.
Di-isopropyl ketone.
Standardized Nb carrier.

Procedure:

1. An aliquot is transferred to a 50 ml polyethylene centrifuge cone, add 1 ml of Nb carrier and a drop of hydrofluoric acid. Make 6M in hydrochloric acid, and extract three times with half volumes of di-isopropyl ketone. Discard organic layer.

2. Add concentrated hydrochloric acid and hydrofluoric acid to make 6M in hydrochloric acid and 9M in hydrofluoric acid.

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3. Extract three times with half volumes of di-isopropyl ketone, combine ketone layers.

4. Wash combined organic layers three times with a solution 6M in sulfuric acid and 9M in hydrofluoric acid.

5. Extract niobium from ketone three times with half volumes of water. Water layers are collected in a tube containing saturated boric acid solution.

6. Make just basic with ammonium hydroxide and digest. Centrifuge and discard supernate. Wash Nb precipitate twice with slightly basic 1M ammonium nitrate solution, then twice with concentrated nitric acid.

7. Dissolve the precipitate in a solution 6M in sulfuric acid and 9M in hydrofluoric acid (polyethylene tube).

8. Repeat steps 3 through 6 twice more.

9. Transfer precipitate to platinum crucible, ignite and weigh as Nb₂O₅, mount for counting.

PHOSPHORUS

Decontamination: $>10^6$ from mixed fission products

Yield: 80%

Time: Five to seven hours for group of 4 determinations

Equipment: Standard radiochemical equipment

Solutions, Special:

P Carrier: 5 mg P/ml (added as (NH₄)₂ HPO₄ in H₂O) -- standardized.

Ammonium molybdate reagent (200 gm (NH₄)₆Mo₇O₂₄·4 H₂O, 800 ml H₂O, 160 ml conc. NH₄OH).

Magnesia mixture (50 gm MgCl₂·6 H₂O, 100 gm NH₄Cl, 3 to 5 drops conc. HCl, 500 ml H₂O).

Tiron: 5% solution.

Procedure:

1. To the sample in a 40 ml lusteroid centrifuge tube, add 20 ml of 6M HNO₃ and 1.0 ml of (NH₄)₂ HPO₄ carrier solution. Heat the solution on a steam bath and add 2 ml of Zr carrier to precipitate zirconium phosphate. Continue heating for 5 min. Centrifuge and discard the supernate. Wash the precipitate with H₂O and discard the washings.

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2. Dissolve the precipitate in 0.1 ml of conc. HF and add 5 ml of H₂O, 10 ml of 6N HNO₃, 5 drops of 0.1% aerosol solution, and 5 ml of ammonium molybdate reagent. Heat the mixture on a steam bath for 5 min. Centrifuge and discard the supernate. Wash the ammonium phosphomolybdate precipitate with 10 ml of H₂O containing a few drops of aerosol.

3. Dissolve the precipitate in 0.5 ml of conc. NH₄OH, and 10 ml of H₂O and 6 to 8 drops of 30% H₂O₂ and stir thoroughly (add reagents in this order). Add 10 ml of conc. HCl and 2 ml of Zr carrier, and heat on a steam bath for 5 min. Centrifuge and discard the supernate. Wash the precipitate with H₂O and discard the washings.

4. Repeat steps 2 and 3 twice more.

5. Dissolve the ammonium phosphomolybdate precipitate in 1 ml of conc. NH₄OH and 2 ml of citric acid solution (0.5 gm/ml). Add 2 ml of 5% Tiron, 10 ml of magnesia mixture and conc. NH₄OH (dropwise) until the solution is just alkaline, then add 10 drops more. Stir the solution for 1 minute. After precipitation begins, stir the mixture 1 min. more and add 4 additional ml of conc. NH₄OH. Allow the mixture to stand with occasional stirring for at least 10 min. Centrifuge strongly and discard the supernate. Dissolve the precipitate in a few drops of conc. HCl and a few milliliters of H₂O.

6. Add 10 ml of magnesia mixture and just enough conc. NH₄OH to neutralize the HCl in the mixture. (One drop of NH₄OH in excess should cause the precipitate of MgNH₄PO₄·6 H₂O to start forming.) Stir for 1 min. and then add 3 ml of conc. NH₄OH. Allow the mixture to stand for at least 10 min. Filter onto a weighed No. 42 Whatman filter circle. Wash the precipitate with small portions of 1:20 NH₄OH, 50% ethanol and 95% ethanol. Pull air through the filter for 5 min., allow the precipitate to stand near the balance case for 30 min., weigh, mount and count.

Preparation and Standardization of Carrier

Make up a liter of an aqueous solution containing 21.3 gm of (NH₄)₂ HPO₄.

Pipet exactly 5 ml of the solution into a 100-ml beaker and add 20 ml of magnesia mixture. Make the solution slightly basic by dropwise addition of conc. NH₄OH and permit to stand 5 min. with occasional stirring. Then, add 10 ml of conc. NH₄OH and allow the mixture to stand for 4 hours, again stirring occasionally. Filter the precipitate onto a weighed 15 ml coarse sintered glass crucible. Wash the precipitate with 1:20 NH₄OH, 50% ethanol, and finally 95% ethanol. Pull air through the precipitate for 10 min. and then allow it to stand near the balance for 30 min. Weigh as Mg NH₄PO₄·6 H₂O. Four standardizations should agree within 0.5%.

SULFUR

Decontamination: From mixed fission products, a factor $>10^7$ was obtained. This procedure applies to HRT soup solutions that are acid with H_2SO_4 .

Yield: 80%

Time: Three hours for group of 4 determinations.

Equipment required: Standard radiochemical equipment.

Solutions, special: Dissolve 10.0g benzidine hydrochloride in 50 ml water and 2 ml conc. HCl, dilute to 500 ml.

Procedure:

1. An aliquot of the active solution is diluted to 10 ml. Add sulfur carrier as SO_4 and 5 mg Fe scavenger. Precipitate $Fe(OH)_3$ with 6M NH_4OH , avoid an excess, warm to coagulate precipitate. Centrifuge and discard precipitate.
2. Make the supernate acid with 2-3 drops of conc. HCl and add 5 mg Fe carrier. Precipitate $Fe(OH)_3$ with 6M NH_4OH , warm to coagulate precipitate. Centrifuge and discard precipitate.
3. Make the supernate acid with 1M HCl and add 2 ml in excess. Add 2 drops of HF, add 5 ml of benzidine chloride slowly while stirring, add an equivalent volume of ethyl alcohol. Let stand for 5 to 10 minutes and centrifuge. Discard supernate and wash precipitate with a mixture (50%) of distilled water and alcohol.
4. The precipitate is dissolved by suspension in 10 ml water containing 0.5 ml of 6N NaOH and subjected to 3 extractions with 10 ml portions of isopropyl ether. This is done in the centrifuge tube by agitation with a stirring rod, removing the ether layer each time by suction.
5. To the aqueous layer, add 5 mg Fe carrier and heat to remove ether (caution) and coagulate the precipitate. Centrifuge and discard the precipitate.
6. Make the supernate acid with 1N HCl and add 2 ml in excess. Add 5 ml of benzidine chloride (slowly) and an equal volume of ethyl alcohol. Let stand 5-10 minutes and centrifuge. Discard supernate and wash the precipitate with 10 ml of 50% alcohol-water mixture.
7. Dissolve the precipitate by heating in 10 ml distilled water made acid with 2 ml of 1N HCl. Cool to room temperature and add 2 drops HF. Add 5 ml benzidine slowly and an equivalent volume of ethyl alcohol. Let stand 5-10 minutes, centrifuge and discard supernate. Wash precipitate with 10 ml of 50% alcohol-water mixture.
8. Repeat Step 7.

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