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# REPORT OF THE CHEMISTRY DIVISION FOR THE MONTH

# DECEMBER 15, 1946 - JANUARY 15, 1947

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J. R. Coe and E. H. Taylor

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## I. RADIOCHEMISTRY

### Chemistry and Radioisotopes of Element 43 (G. E. Boyd, Q. V. Larson)

Attention is called to the proposal of C. Perrier and E. Segre, Nature 159, 24 (1947), for naming element 43 as "Technetium", symbol Tc.

Studies on the volatility of the oxides of Tc have been concluded for the time being. In the most recent experiment dry $Cl_2$ gas was bubbled through concentrated $H_2SO_4$ heated to 250-270°C and containing tracer Tc activity. Approximately 54% of the Tc was found to have been volatilized after collection of the $Cl_2$ for sixty minutes in 6 N NaOH. This figure may be compared with the 20-25% volatilization observed under the same conditions when dry HCl gas was employed.

Preliminary adsorption experiments with the cation and anion exchange adsorbents, Amberlite IR-1 and IR-4, were completed. As might be expected, the Tc was extensively removed (94% by 1 gm adsorbent in 100 ml of tracer containing 0.1 N HCl) by IR-4, presumably as the anion $TcO_4^-$. However, when 10 gms of the cation exchange adsorbent IR-1 were used with 100 ml of solution, 56% of the Tc activity was removed. The unexpected adsorption by the cation exchanger may be explained tentatively by a reducing action on the acid $TcO_4^-$ solution to give lower valent, cationic forms of Tc (i.e., possibly $Tc^{+4}$, $TcO^{++}$, or $Tc^{3+4}$) which will be appreciably adsorbed by a base exchange mechanism. Using a very dilute solution of $MnO_4^-$ under the same conditions, reduction took place quickly.

### Activities Induced in Nickel by Neutron Bombardment (A. R. Brosi)

Two nickel samples, one with predominantly $Ni^{59}$ activity and the other with predominantly $Ni^{63}$ activity, have been prepared. Borkowski has measured argon absorption curves of these samples and found two soft components in the $Ni^{63}$. Samples of other activities which emit known soft radiations have been prepared and measured by Borkowski as an aid in the interpretation of these results.

### Activities Induced in Palladium by Neutron Bombardment (A. R. Brosi)

Both 17 d $Pd^{103}$ and 42 d $Ru^{103}$ appear to decay almost exclusively to the excited 56 min isomer of $Rh^{103}$. Since 17 d $Pd^{103}$ decays by orbital electron capture, calculation of the disintegration rate from the counting rate is uncertain. Samples have been prepared for comparison of 17 d $Pd^{103}$ with 42 d $Ru^{103}$ through the common daughter $Rh^{103}$. From these measurements it is hoped to get better values for the cross-section of the $Pd^{102}(n,\gamma)Pd^{103}$ reaction and for the conversion coefficients of the $Rh^{103}$ gamma radiation.

Abundance Ratio of Copper Isotopes (A. R. Brosi, J. A. Swartout)

No further work was done on the determination of the natural abundance ratio of the copper isotopes by the simultaneous activation of accurately known amounts of natural copper and isotopically enriched copper. It is planned to resume work on this during the next month.

Radiochemical Measurements and Standardization (R. T. Overman, W. C. Peacock, L. R. Zumwalt, H. M. Clark, J. W. Jones)

Decay Schemes. The machine work on the beta ray spectrometer is being done at X-12. The tentative completion date is February 24. A new coincidence amplifier-recorder has been completed and is being installed and tested.

Standardization. Work is being continued on the three-way gold calibration for absolute disintegration rate. The methods being checked are the standard beta counting with RaD-E-F standards, coincidence and calorimetry measurements. The growth curves for the RaD-E-F calibration have been finished and the geometry of the top shelf of several counters has been determined. The methods are not yet in complete agreement. It is planned to continue the checking with $UX_{II}$ standards and other activities which can be measured by the various methods. A micro technique for preparing samples involving volumes of the order of 10 lambda has been worked out. Results are obtained which are reproducible to $\frac{1}{2}\%$.

Calibrated absorbers of various thicknesses of Zr, Cb, Ta, Mo, Sn, Au, and Be have been prepared to be used in the study of low energy gamma rays and X-rays.

Yield Measurements. Preliminary work on the flux monitoring of individual samples is being continued. Calculations have been made by K. Way of the Physics Division which seem to indicate that the disagreement between the flux measurements that have been made are not so large as was thought.

Experimental work is continuing on the detection of impurities in ultra pure chemicals. The work on the impurities in various samples of carbon is finished and will be reported. Work is also continuing on the determination of the yield and half-life of $Ca^{41}$. The existence of the activity has been confirmed in the separated stable isotope of bombarded $Ca^{40}$, but contaminants have prevented us from obtaining a good half-life value.

Radiochemical Studies with Tin (W. H. Sullivan, J. A. Swartout, H. E. Wyatt)

Experiments were conducted to determine the beta and gamma ray energies of a 10-11 minute activity which appears in pile-irradiated tin samples. The activity is probably identical with the 9 minute Sn activity, reported by Livingood and Seaborg and assigned to $Sn^{125}$, although none of its characteristics, other than half-life, are known.

The technique employed for the observations on this short-lived activity consisted of making simultaneous decay and absorption measurements on fractions of a given irradiated sample and extrapolating the absorption curve data for the initial cycle of measurements to the mid-time of that cycle. In this way, errors from interfering radiations of the longer-lived activities are minimized.

From two sets of lead absorption data (different bombardments) half-value thicknesses of 0.72 and 0.75 gm/cm$^2$ Pb were obtained. These values correspond to an average energy value of 0.7$_4$ Mev.

Analyses of the beta ray absorption curve data by the Feather Comparison Method gave discordant results, but a minimum energy value of 2.2 Mev was indicated.

A 6.7 mg sample of $Sn^{112}O_2$ was received from Y-12. It will be encapsulated for a pile irradiation of about six months.

The study of the radioisotopes of Sn with the object of determining characteristics of radiations and mass-assignment by use of the enriched stable isotopes is being continued. Distillation and electrolytic procedures for purifying and isolating Sn are being investigated.

Radiochemical Studies with Iron (J. A. Swartout)

Analysis of the data for the specific beta and gamma activities of $Fe^{59}$ produced in simultaneous bombardments in the pneumatic tube of compounds of iron including Fe metal, $Fe_2O_3$, $Fe_3O_4$, and $K_3Fe(CN)_6$ indicated no variation with compound of the cross-section for the reaction, $Fe^{58}(n, \gamma)Fe^{59}$. Gamma activities followed over at least two half-lives on the high pressure ionization chamber and extrapolated to time of removal from the pile agreed within $\pm$ 1.5%; specific beta activities measured with a mica end-window tube agreed within $\pm$ 6%. The average of twenty independent measurements for the half-life of $Fe^{59}$ was 46.3 $\pm$ 1 d.

Radiochemical Studies (H. A. Levy, M. H. Feldman) - P.A. CK4-3

Search for (t, p) Reactions. The work on the search for (t, p) reactions continues. Some irradiations of various combinations of Cb and Li (including controls) seem to give a soft radiation whose range is close to range of $\beta$ radiation from $Cb^{95}$. However, the half life of the radiations has not yet been determined, due to its magnitude. Similar tests are being carried out with Li and Br; the 2.4 hr Br, if formed, will decay to 113 m Kr which is susceptible of measurement under the experimental conditions.

Cross Sections of Chromium Isotopes. The measurement of cross sections of Cr isotopes awaits repair of instruments at the pile. Gold monitors were prepared after a micro balance became available.

Short Lived Hard Gamma Emitters. Measurement and identification of hard gamma emitters of short life (from fission) proved impossible, due to high activities encountered in irradiated uranium. Therefore, a mechanically

controlled chemical apparatus is being designed and constructed. In addition, a mechanical hand-like machine is being designed to assist in this work.

## II. APPLICATIONS OF RADIOISOTOPES

Diffusion in Electrolytes (G. E. Boyd, R. F. Newton)

Further preliminary studies have been pursued on the radioactivity of the tracers to be used. The radioactive sodium prepared by neutron bombardment of reagent grade sodium nitrate was found to have a long-lived activity in small, but appreciable amounts. To determine the most convenient way of minimizing this activity, bombardments of the following were made:

(1) Reagent grade sodium nitrate
(2) Reagent grade sodium carbonate
(3) Sodium nitrate prepared by adding concentrated C.P. nitric acid to (2) until crystals precipitate, and collecting the crystals
(4) Sodium nitrate prepared by evaporating the mother liquor from (3).

After further decay of the $Na^{24}$ activity, the residual activity will be determined to judge the best method of preparing samples of $Na^{24}$.

Use of Radioisotopes in Organic Chemistry - P.A. CX4-4

The Radioactive Assay of $C^{14}$ (G. E. Boyd, W. B. Leslie). Time has been divided between counting studies on $C^{14}$ and the development of a method for the synthesis of methanol from carbon dioxide. Measurements are being made on a series of samples of $BaCO_3$ in order to compare the ionization chamber - dynamic condenser electrometer method of measurement with G. M. Counters.

The isolation and estimation of small amounts of methanol, employing 3,5-dinitrobenzoyl chloride as a reagent, has not been very encouraging up to the present. An alternate method employing a tracer technique is being studied.

Synthesis of $C^{14}$-Containing Mandelic Acid (G. E. Boyd, O. K. Neville). The details of the preparation of mandelic acid from phenylglyoxal and its recovery from the reaction mixture have been worked out after some difficulty. The phenylglyoxal in ether solution is allowed to react with a 10% NaOH water solution. The presence of two separate phases allows the reaction to proceed at a rate which precludes the tar formation that has caused trouble previously. The ether layer is separated, washed with water, and discarded. The basic water layer is brought to a pH of 5-6 with HCl and filtered. To the filtrate is added cadmium nitrate; cadmium mandelate is precipitated. Mandelic acid may then be ether extracted from an acidic water solution of cadmium mandelate. The preparation of $C^{14}$ labeled mandelic acid is now in progress.

Preparation of Lithium Aluminum Hydride and the Reduction of $CO_2$ (G. E. Boyd, W. H. Yanko). Lithium aluminum hydride was prepared from lithium hydride and

aluminum chloride in di-n-butyl ether. Yields of 16.7% and 5.7% were obtained. The poor yields were attributed to the relative insolubilities of the lithium aluminum hydride and lithium chloride in di-n-butyl ether. The solubility of lithium aluminum hydride in di-n-butyl ether was shown to be much less than 1%.

Lithium aluminum hydride was synthesized in diethyl ether in 80.4% yield from lithium hydride and aluminum chloride. A total of 0.5 mole was prepared. The lithium aluminum hydride solutions in ether were assayed by decomposing the hydride with water. The evolved hydrogen was then measured by a water displacement method.

Carbon dioxide was reduced with lithium aluminum hydride both in di-n-butyl solution and in diethyl ether solution. Work is in progress with respect to the identification of the reduction products.

The Synthesis of $S^{35}$-Containing Compounds (G. E. Boyd, D. J. Crowley). A self-absorption curve for $BaS^{35}O_4$ in $BaSO_4$ has been prepared. Twelve duplicate determinations were made with varying amounts of carrier and constant $S^{35}$ activity.

Experiments designed to effect an exchange between $H_2S^{35}O_4$ and $\alpha$-naphthalene sulfonic acid, and also $Na_2S^{35}O_4$ and $\alpha$-naphthalene sodium sulfonate have been initiated.

Surface Studies (S. Ross)

Slow attainment of equilibrium in the low pressure portion of the ethane adsorption isotherm for NaCl at 91° K has been verified both for powdered samples and for crystals having only cube (100) faces. It was found that if mercury vapor condenses on the sample the characteristic first order transitions are not observed. Different mercury vapor traps were tried out.

## III. PHYSICAL CHEMISTRY

Effects of Heavy Particles on Water and Aqueous Solutions (A. O. Allen, T. W. Davis, J. A. Ghormley, C. J. Hochanadel) - P.A. CX5-20

Experiments were performed with ampoules so designed that the pressure of gas over water inside can be determined without opening the ampoule by measurement of the boiling point of the water. Some of these ampoules were placed in the pile; they were removed at intervals, the pressures were determined, and the ampoules then replaced in the pile. The pressures rose but after some days reached steady values, which were different for the different ampoules. The differences presumably arise from differences in the concentration or nature of traces of impurity in the various samples of water. After a steady state was attained, one ampoule was replaced in the pile surrounded with 11/16 in. of lead. The pressure rose. Another ampoule was replaced surrounded with 11/16 in. of paraffin. The pressure fell. This shows that, as expected, the steady-state pressure of gas produced by irradiation of water

with fast neutrons is higher than that given by gamma rays, while the normal pile steady state lies between the two.

Considerable data were obtained on the amount and composition of products of water irradiated in the pile for various times with various ratios of the volume of the liquid to the available vapor volume. The results showed discouragingly poor reproducibility and poor material balance for small amounts of decomposition. Apparently, our water is not yet sufficiently pure. Frequently $CO_2$ was noted in the gaseous products, indicating organic impurity. Results obtained with water refluxed over acid and alkaline permanganate and distilled through a silica tube containing nickel pellets at 1000°C were no better than those obtained from untreated ordinary distilled water. Further efforts will be made to prepare water free of all organic matter.

Assembly and Operation of the Van de Graaff Generator (A. O. Allen, D. M. Richardson) - P.A. CX11-8

Plans for construction of the building for the generator are now essentially complete. The time was occupied in working with the Project Engineering Division on these plans.

Chemistry of Gas and Peroxide Formation Induced by Radiation in Water Solutions (E. Shapiro, J. W. Boyle) - P.A. CX5-7

An experiment to determine the rate of thermal recombination of $H_2$ and $O_2$ in 4 mm I.D. silica tubing was repeated. Twelve tubes were irradiated until $H_2$ pressures of 50 atmospheres (at 250°C) were reached. Two tubes were used as blanks and nine were heated for three different periods (20 hr, 70 hr, and 140 hr) at 250° ± 5°C. Although the results varied considerably, the recombination half time was about 50 hours. This result shows that the rate of recombination as measured by the change in pressure per unit time per unit surface area is less in 4 mm I.D. silica tubing than in 0.8 mm I.D. silica capillary tubing by a factor of three. It remains now to determine steady-state pressures in 4 mm I.D. tubing in order to get a measure of the radiation induced recombination rate.

The initial rate of gas production for depleted $UO_2SO_4$ in 1 N $H_2SO_4$ was found to be greater than the initial rate in 1 N $H_2SO_4$ alone. After three days in the pile, however, the gas production in depleted $UO_2SO_4$ was considerably less than in $H_2SO_4$.

The background effect, i.e., that of 1 N $H_2SO_4$, was investigated for longer irradiation times, and the steady-state pressure of about 20 atmospheres of $H_2$ indicated in the last report was found to be in error. At present, the pressure of $H_2$ is above 40 atmospheres and continues to rise.

Chemistry of Solutions (C. H. Secoy)

An effort to check transition points in the system uranyl sulfate - water by observing the variation of density of the crystals with temperature failed to yield conclusive evidence. Furthermore, solubility measurements made with a new salt preparation, supposedly identical with the first, did not check

those made with the first preparation. Consistent data were obtained for each preparation with points lying on smooth curves, but the curves failed to coincide, somewhat higher solubilities being obtained with the second preparation.

The older literature displays a wide variation in values reported for the solubility of uranyl sulfate trihydrate. Bucholz reports the saturated solution at "ordinary temperature" as being 3.95 molal; Ebelman gives 5.07 molal at 21°C; and de Coninck reports 0.461 molal at 16°C. The value 3.72 molal at 20° was obtained with the first preparation and 4.55 molal at the same temperature with the second. These variations are far too great to attribute to experimental error in the solubility measurement. It seems evident that they must be due to variations, either chemical or physical or both, in the salt crystals with which the determinations are made. One is impressed, when reading the literature of the 1900's concerning uranyl sulfate, with the wide variations in compositions reported for crystals obtained under slightly different conditions of crystallization.

Therefore, present efforts are devoted to attempting to prepare uranyl sulfate under conditions which, if duplicated, will give consistent preparations displaying not only the correct chemical analysis, but also appearing identical under microscopic examination and proving identical in x-ray measurements. If the crystal size is uniform, such preparations should give reliable solubility data.

The preparation involves two general factors, (1) purification of the material and (2) conditions of crystallization. Chemical methods of purification are well known and standard procedures are being followed. However, the second factor will require investigation. A study of the effects of acidity, temperature of crystallization, and the use of precipitating agents, such as acetone, is being made. No conclusions have been reached to report at this time.

## IV. CHEMICAL PHYSICS

Electron Microscopy (L. T. Newman, T. E. Willmarth)

The electron microscope has been transferred from K-25, and the pumps and power wiring installed. The polishing table has been designed and has now been built and installed.

X-Ray Diffraction (M. A. Bredig)

A small, simple model of an "x-ray microspectrograph" was made, which will be tested soon in the x-ray laboratory of the K-25 plant. Its resolution is expected to be sufficient for identification of elements up to Z = 40.

Calorimetric Studies (C. V. Cannon, G. Jenks)

The liquid nitrogen calorimeter has been used successfully to measure the total energy emitted by $Au^{198}$ decay. Several curies of $Au^{198}$ contained in

1 gram of activated gold were placed in the calorimeter and the decay (2.7 day half life) followed over a period of a week. The accuracy of the energy measurements is probably ± 2%, though this will not be claimed before further analysis of the data.

After calorimetric measurements were completed, the gold was dissolved and aliquots given to W. C. Peacock and L. R. Zumwalt for absolute disintegration determination by coincidence methods and absolute $\beta$ standard methods, respectively.

Cloud Chamber Studies (R. Livingston) - P.A. CX4-1

Cloud chamber work is continuing.

Experiments with Molecular Beams of Radioactive Isotopes (E. H. Taylor) - P.A. CX10-21

The apparatus for preliminary experiments is being assembled and tested for leaks.

Neutron Energy Dependence of Cross Section (S. Freed, A. R. Brosi, G. W. Parker, with S. Bernstein, J. Dial, and M. M. Shapiro of the Physics Division)

Apparatus is being assembled and exploratory experiments are under way to measure the total cross section of xenon$^{135}$ for neutrons as a function of their energy. This is being done by a group comprising physicists and chemists.

Spectroscopy of Heavy Elements in Crystals and Solutions (S. Freed, F. J. Leitz)

A series of experiments is being undertaken to measure the spectra of heavy elements in crystals and solutions.

Theoretical Chemistry (O. K. Rice)

Two papers have been prepared, abstracts of which follow:

On the Behavior of Pure Substances Near the Critical Point. It has been suggested several times that the phenomena of condensation could be understood by considering the vapor as a system in which molecules are associating into clusters, these obeying the ordinary laws of equilibrium. One can also consider the liquid as a system in which bubbles of vapor are forming. The present paper attempts to apply these ideas to phenomena occurring in the neighborhood of the critical point. Only thermodynamic methods are used, in conjunction with some general assumptions concerning the properties of the molecules involved. Some aspects of the surface tension of the liquid near the critical point have been considered in some detail. The highest temperature $T_m$ at which a meniscus can exist is assumed to be the temperature at which the surface tension vanishes at the same time that the condition for equilibrium between liquid and vapor phases is fulfilled. It is concluded that the pressure-volume isotherm at $T_m$ has a finite horizontal region, corresponding to the squeezing out of surface when the surface tension is zero.

The slope of the isotherm at $T_m$ in the vapor region outside the flat portion is closely related to the slope in the liquid region just to the other side of the flat part; these slopes approach zero as the flat part is approached. Above $T_m$ there is still a process which may be called condensation, but no horizontal part to the isotherms. This is in contradiction to conclusions reached by Mayer and Harrison on the basis of their statistical theory of condensation, but is apparently not in real contradiction to the theory.

The Effect of Pressure on Surface Tension. The thermodynamic formula for the change of surface tension with pressure is interpreted for a one-component system and for a two-component system consisting of an inert gas over a liquid. In the latter case the effect of pressure on surface tension can be due in part to absorption of gas at the surface of the liquid and in part to an intrinsic decrease in density of the liquid at the surface. The equations are interpreted in terms of the Gibbs adsorption isotherm. The adsorption of gas at the liquid surface has been estimated in several cases from data in the literature.

## V. ANALYTICAL CHEMISTRY

### Research

Development of Radiochemical Procedures (R. W. Stoughton with M. J. Cook of the Health-Physics Department) - P.A. CX3-4

In the method for analysis of $U^{233}$ in urine now being considered the uranium is carried with cupric ferrocyanide; the ferrocyanide precipitate is then destroyed with fuming $H_2SO_4$ and the $U^{233}$ extracted into cellosolve. After the $H_2SO_4$ fuming sometimes some difficulty is experienced in dissolving the residue and extracting the $U^{233}$. Alternative methods to the $H_2SO_4$ treatment are now being investigated.

Developmental Studies on Radiochemical Methods (J. E. Hudgens, G. C. Bell, O. M. Bizzell, F. L. Moore) - P.A. CX7-2

Preliminary experiments directed toward the determination by pile activation of small concentrations of impurities in beryllium have been completed. With the beryllium sample used the decay scheme is too complex to make the method accurate. A refined experiment is now being conducted in order to eliminate variables known to be present in the first experiment. It is believed that chemical separations after activation will be necessary if accurate results are to be obtained. The accuracy of the method is limited by knowledge of activation cross sections, by pile flux determinations, by knowledge of the specific activities of each element, and by inherent errors in counting samples of mixed activities for decay measurements.

The separation of scandium ($Sc^{46}$) activity from calcium ($Ca^{45}$) activity using T. T. A. (thiophene-trifluoro-acetoacetone) complex to facilitate the extraction of scandium activity into a benzene phase has been tested. While insufficient amounts of $Ca^{45}$ tracer are available to make the results conclusive,

the efficiency of the separation of the two activities is sufficient to make the extraction worthwhile as part of an analytical method for scandium or for calcium in the presence of scandium.

Purification of BeO (L. B. Rogers, F. H. Sweeton) - P.A. CX7-2

Further experiments were carried out to test the possibility of removing boron by methyl alcohol at elevated temperatures. Limited success was attained only by the use of sealed tubes at elevated temperatures.

Polarography (F. H. Sweeton) - P.A. CX7-2

Extensive tests of the new Sargent Model XX polarograph have been made. Its operating characteristics have been studied and a circuit diagram has been prepared which will be distributed to possible future users of the instrument.

Polarographic Determination of Hydrogen Peroxide in Uranyl Carbonate Solutions (R. B. Scott) - P.A. CX7-2

From polarographic data obtained at 50°C under a variety of conditions, it now appears that it will be possible to determine the concentration of moderate amounts of hydrogen peroxide in a solution of uranyl carbonate. The effects of oxygen and palladium (recombination catalyst) have been found to be constant and hence do not interfere. Future runs will include some solutions having higher concentrations of peroxide as well as solutions at temperatures other than 50°C.

Polarography with Stationary Platinum Electrodes (H. H. Miller) - P.A. CX7-2

A report summarizing 8 months' work on the use of stationary platinum electrodes is near completion. Introductory experiments using stationary mercury electrodes were started in order to compare their behavior with the dropping mercury electrode and the stationary platinum electrode.

Polarography of Rhenium and Technitium (L. B. Rogers) - P.A. CX7-2

Preparations have been made for continuing the work begun last October in which the behavior of these elements was compared. Attempts will be made to obtain quantitative information concerning valence changes in various media.

New Analytical Instruments (L. B. Rogers) - P.A. CX7-2

In collaboration with the Instrument Development Group, plans have been drawn up for an extremely versatile fluorimeter which employs the high sensitivity circuit now employed in the instrument used for routine uranium analysis. The same group has just completed the high frequency analyzer whose sensitivity and stability will be tested to determine the suitability of this method as a substitute for conductivity methods. The high frequency instrument should be particularly advantageous in analyzing active solutions or those containing suspensions because direct contact with the solution (via dipping electrodes) is unnecessary. Tests of the electroplating control run in collaboration with Pickel and Ehrlinger are nearing completion.

Electrolytic Studies (D. B. Ehrlinger) - P.A. CX7-2

An investigation of the electrolytic behavior of dilute ($10^{-9}$ M) silver solutions has been begun. Under the conditions of the experiments, less than a monclayer of silver will be formed on the cathode when the deposition has been completed.

## Service

Analytical Service (W. M. Byerly, J. E. Hudgens, L. B. Rogers, G. C. Bell, O. M. Bizzell, A. D. Bogard, R. A. Brown, C. L. Burros, L. T. Corbin, J. H. Edgerton, C. Feldman, E. J. Frederick, J. D. Gile, E. K. Hanig, F. E. Harrington, H. L. Hemphill, C. F. Knesel, U. Koskela, E. W. Milam, F. J. Miller, F. L. Moore, M. Murray, H. A. Parker, G. S. Sadowski, P. F. Thomason, B. Warren, J. N. Weeks, D. Weinberger, G. R. Wilson) - P.A. CX7-1

The following analyses were requested during this period:

| | Gross Activity | Radio-Chemical | Ionic | Control | Spectro-graphic |
|---|---|---|---|---|---|
| Chemistry | 3 | 4 | 31 | 88 | 111 |
| Technical | 27 | 67 | 582 | 1104 | 8 |
| $H_2O$ Activity (Operations) | 635 | | | | |
| Health Physics | 14 | 37 | | | |
| Medical | | | 4 | | |
| Metallurgy | | | 7 | | 1 |
| Power Pile | | | | | 1 |
| Others | | | 2 | | |

The spectrographic laboratory was moved to Room 65 and the instruments readjusted.

Assistance was given to F. Leitz in obtaining visible and ultra-violet absorption spectra of plutonyl perchlorate solutions.

## VI. INSTRUMENTS AND PHYSICAL MEASUREMENTS

Geiger Tube Development (R. L. Butenhoff, C. J. Borkowski) - CX11-1

The geometry of the new low absorption counter has been determined using a $UX_2$ source and an alpha source whose disintegration rate was determined with a standard alpha chamber.

Drawings were submitted to the shop for equipment to make a known-solid-angle Geiger-Muller counter which is to be used for obtaining absolute disintegration rates of beta emitters of various energies. The effects of scattering of the $\beta$ particles in this counter are to be studied.

Development and Construction of Alpha-Counting Equipment (J. H. Parsons, J. K. East) - CX11-4

An all metal vacuum low-geometry alpha chamber has been assembled and is ready for testing with a fast proportional counter amplifier. With this chamber and the "50%" geometry methane proportional counter it will be possible to measure alpha disintegration rates from 1 dis/min. to 5 x $10^6$ dis/min. with the use of only two sample holders.

Development and Construction of Special Instruments (C. J. Borkowski, E. Fairstein, J. V. Francis) - P.A. CX11-5

Preliminary experiments indicate that a non-self-quenching Geiger-Müller counter operating in the discharge voltage region is satisfactory as a voltage regulator in portable high voltage supplies which deliver only 100 microamperes current.

Work is continuing on time stampers and pulse integrators.

## VII. SEPARATION PROCESSES

### Research

Basic Chemistry of Solvent Extraction (F. J. Leitz, J. P. McBride)

Investigation of the absorption spectrum of Pu(VI) in dilute perchloric acid solution has been continued with the Dietert spectrograph. This extension of previous spectrophotometric observations into the ultraviolet revealed high absorption with no detailed structure apparent down to 230 millimicrons. Continuation of this study in organic solvents and at lower temperatures is planned.

The final spectral and chemical data on the photo-decomposition of dilute $UO_2(NO_3)_2$ - dibutyl carbitol solutions which have been allowed to stand in the laboratory under various conditions is being collected. A summary of the work done on the various aspects of the solvent extraction problem is in preparation.

Thermodynamics of Coprecipitation (G. E. Boyd, F. Vaslow) - P.A. CX3-5

The distribution coefficients for traces of $Cl^-$ ion ($10^6$ y $Cl^{36}$ used) in AgBr in equilibrium with 0.7 N $NH_4OH$ were measured at 30, 40, 50, and 66°C, giving values of 3.6, 3.7, 3.8, and 4.9 x $10^{-3}$, respectively. Measurements of the solubility of AgBr at 30°C gave 2.1 and 4.1 x $10^{-7}$ moles $Ag^+$ $liter^{-1}$ when ceresin coated and glyptal coated glass bottles, respectively, were used. Both values still appear to be low. A rate of recrystallization experiment using $Br^-$ (34 h $Br^{82}$) with AgBr at 46°C was completed. A progress report is being written.

Radiochemistry of the Heavy Rare Earths (G. E. Boyd, B. H. Ketelle) - P.A. CX3-5

The study of the half-lives of activated erbium has continued. Samples of activity were taken from various points on the desorption band of erbium as it was removed from an IR-1 column. The decay of these samples is being followed to establish the ratios of the several activities in each sample. Thus, it should be possible to establish whether each activity is that of an erbium isotope or whether one of the activities may be a thulium daughter. The samples have not decayed sufficiently to permit their analysis.

Another column separation was made in which Ho and Y activities were adsorbed initially. It was shown that the last peak obtained in each of the previously reported erbium separations (MonN-229, p.14) is due to yttrium impurity. This experiment also indicates yttrium is desorbed from an IR-1 column at about the same time as dysprosium and terbium.

Finally, a sample of ytterbium was adsorbed and a rare earth separation was made on the column. The activity desorbed is being studied to assist in the interpretation of data which have been collected during the past six months using "spectrographic standard" ytterbium.

It can be reported at this time that, in addition to the 2½ hr activity of $Yb^{177}$ and the activity of somewhat over 100 hour half-life assigned to $Yb^{175}$ by Inghram and studied simultaneously in this laboratory, there is a third Yb activity of about 33 day half-life. There is associated with this latter period a $\gamma$ ray of about 0.3 Mev, a beta ray of about 0.3 Mev, X-rays, and conversion electrons. On the basis of the Bohr-Wheeler estimate of the energy of $Yb^{175}$ it is believed that the 35 day activity belongs to this isotope. Coincidence counting is under way, and it is expected that it will be possible definitely to establish whether this assignment is correct.

Isolation of $C^{14}$ from Beryllium Nitride (D. S. Anthony, A. J. Weinberger) - P.A. CX1-10

All work to date has been directed toward determining the total amount of $C^{14}$ in a sample of $Be_3N_2$ since any distribution figures must be based on a knowledge of the total. In 2 runs with and 2 runs without added carrier, values for total $C^{14}$ were obtained which show a total spread of less than 5%. Furthermore, these values show reasonable agreement with a yield figure calculated from the cross-section and assuming a Hanford:Clinton flux ratio of 10. For the sample and amount employed in the above determinations, the calculated yield was 6-7 μc; the determined values ranged from 7.7 to 8 μc.

The procedure which gave the consistent total $C^{14}$ yields from $Be_3N_2$ starts with dissolving in hot 6 N NaOH with stirring. Aeration during this process removes some 65% of the total $C^{14}$ (CO and hydrocarbons would appear here). Upon acidification of the residue with continued aeration variable amounts of $C^{14}$ have been released, but it appears that this fraction is of the order of 5% of the total ($CO_2$ and HCN would appear here). The remaining 30% is recovered by aeration of the acid solution following the addition of $CrO_3$ (alcohols and acids would appear here). In all cases the active gas was led through an ionization chamber, through a furnace containing CuO at 800°C

and into alkali traps. Aliquots of the alkali traps were precipitated as $BaCO_3$ and counted.

The coming month will be spent in preliminary studies of the distribution of $C^{14}$ among types of compounds and in studies of the specific activity of the above three major fractions.

Rare Earth Separations (E. R. Tompkins, P. C. Tompkins, A. Broido, D. H. Harris, S. W. Mayer) - P.A. CX1-24

Fractionations of Rare Earth by Precipitation. Several one hundred gram lots of impure Y compounds from various sources have been fractionated by precipitation procedures. Most of the Ce is removed as the $Ce(NH_4)_2(NO_3)_6$, the remainder being precipitated as $Ce(OH)_4$. By carefully adjusting the basicity of the resulting filtrate it was possible to precipitate most of the rare earths away from La, leaving the latter in solution. The precipitates resulting from these fractionations were then dissolved for later column separation into constituent elements.

Column Separation. Seven ion-exchange column runs mostly on rare earths have been completed during the past month: (a) two on a mixture of terbium earths; (b) two on mixtures of Lu, Yb, Tm, and Er, the latter with $Sc^{46}$ and $Y^{91}$ tracers; (c) one run on a mixture of Gd and Sm; (d) one run on a sample of $Y^{91}$ prepared over a year ago from a mixture of fission products; (e) one run on Hf - Zr separation. The spectrographic and counting analyses are not complete for several of these runs, but complete separation of the rare earths of these groups does not appear to have been obtained in any of the runs. It seems now that the quantities of rare earths were several times too large for good separations. New runs will be made using larger column area/rare earth ratios. One of the runs indicated that Sc can be completely separated from rare earths by eluting it at a pH below 2.4. This investigation is being continued using a sample of Sc which contains small amounts of Y and Yb.

Additional work on separation of yttrium group rare earths has been started. The results of the last run for separating the Y group fission products were inconclusive so it will be repeated later with several rare earths in carrier concentration to aid in identification of the unknown radioisotopes. The run to test the separation of $Y^{88}$ and $Y^{91}$ is under way but no activity has been eluted as yet.

Batch Equilibrium Experiments. These experiments are being continued. The various factors which affect the distribution coefficients of the rare earth between citrate and resin are under investigation. Sufficient data have not yet been obtained to determine the inter-relationships.

It was shown that there is no appreciable exchange between the dry resin and a rare earth complex dissolved in a non-polar solvent. This is what was expected since exchange is an ionic reaction.

A few equilibrium experiments on deuterium and protium separation are being carried out. Solutions of various composition and varying concentrations of deuterium are shaken with resin and a radioactive alkali element. The distribution coefficients are determined by determining the level of radioactivity in the solutions.

Reports. The first report on rare earth separations and the second report, which is a theoretical analysis of the separations column process, have been completed and submitted for declassification.

Separations Chemistry. Scandium may be extracted from an aqueous solution of pH $>1.5$ by T.T.A. in benzene. Calcium does not extract appreciably below pH 6. The final pH of the scandium solution may be predetermined by controlling the initial concentration of Sc, since 3 $H^+$ are released for each Sc extracted.

These facts form the basis for a simple method of preparing carrier-free Ca from irradiated Sc, or for the analysis of Sc in Ca solutions. The Sc is extracted into the benzene phase at a pH $<6$, leaving the carrier-free Ca in the aqueous phase. The feasibility of adapting the method to the determination of Sc in Ca has been demonstrated. An apparatus to do the separation on a semi-hot scale was devised, and the feasibility of the method for the preparation of carrier-free Ca from Sc was demonstrated. Present indications are that the separation was quantitative for the recovery of both Ca and Sc at a purity greater than 99%. Final analyses are not yet complete.

## Process Development

Isolation of $U^{233}$ from Thorium by Solvent Extraction (E. G. Bohlmann, E. H. Bonner, C. F. Booth, G. E. Creek, J. W. Gost, D. N. Hess, C. E. Higgins, K. K. Kennedy, R. E. Wacker) - P.A. CX9-1

The column in the pilot plant has been re-packed and further tests have been made. In the first of these tests, C-5, the results were somewhat encouraging in that the losses in the raffinate decreased from approximately fifteen percent before re-packing, run C-4, to about four and one-half percent in C-5 after re-packing. This, however, still does not come up to performance anticipated on the basis of experience with the one-inch laboratory column. Unfortunately the poor results could not definitely be allocated to the column since the solvent flow rate during the run was very irregular because of deterioration of the packing in the Proportioneer pump. This finally made it necessary to discontinue the run without the attainment of any really satisfactory operating period.

In planning the next run an attempt was made to set up as clear cut a study as possible. This was done by making up sufficient quantities of the solutions involved to allow for duplicate runs with identical solutions in both the one-inch laboratory column and the three-inch pilot plant column. The results with the laboratory column were quite satisfactory. Uranium losses ranged between one and two percent with the factor of separation from thorium around $10^5$. In the first part of the operation of the pilot plant column the results were at least as good as this, but about the middle of the run the loss suddenly went up to six to seven percent and stayed there. This change in efficiency coincided with the addition of about one hundred cc of approximately one normal nitric acid containing 30.4 mg of $U^{233}$. This "spike" was added in an attempt to get better loss data since the thiocyanate-acridine procedure is not very reliable at low levels. We have been unable to find

an explanation for the sudden increase in the loss. Although the thiocyanate-acridine procedure has given a good deal of trouble with process solutions, it is unlikely that discrepancies of the order of a factor of six would be involved. We are now investigating the possibility of the difficulty lying in the added $U^{233}$ solution, but it would seem that no undesirable substances should have been present with this $U^{233}$, since it was taken to dryness with nitric acid twice and the final nitric acid solution titrated with permanganate before addition to the process feed solution.

The Recovery of Uranium from Enriched Piles (F. T. Miles, J. B. Chrisney, G. R. B. Elliott, E. H. Turk) - P.A. CX5-9

The job of adjusting the concentrations of fuel solutions for the critical experiments (cf. A. H. Snell and M. M. Mann to J. R. Coe, January 7, 1947) has required about one-half man month during the last period and will require about one additional man month for completion.

As part of the work on physical properties of the process solutions, measurements of viscosity and interfacial tension have been extended over a wider range of compositions. The distribution of nitric acid between hexone and aqueous solutions has been remeasured. The distribution ratio has a negative temperature coefficient of $4 \times 10^{-3}$ per °C.

Some work has been started with ruthenium tracer to investigate the observed large changes in the distribution ratio.

In a conference with Messrs. Wigner, Coe, and Stoughton, it was decided that the process should be arranged to facilitate the recovery of Np and Pu, if this is feasible. The present process with an oxidizing first cycle and a reducing second cycle satisfies these conditions. Np and Pu would be separated as a hydroxide precipitate from the IIAW stream (cf. CL-RWS-27 and E. P. Wigner to M. C. Leverett, January 2, 1947).

The projected "Data Book for 25 Recovery" is still being assembled. Since it will not be complete until the chemical work is finished, many of the data have been distributed by W. K. Eister for use in the Technical Division before the final Data Book is available.

Preparation of Radioisotopes (G. W. Parker, G. M. Hebert, P. M. Lantz, A. C. Meredith, J. Reed, J. W. Ruch, P. O. Schallert) - P.A. CX1-9

All-Column Fission Products Separations Apparatus. Two of the ion chambers are finally finished and installed; the other two are promised soon. Tests will start when they have been installed and their operation checked.

Mass Identity of 5.3 d and 49 h Isotopes of Element 61. In a private communication, M. G. Inghram has confirmed the 149 mass number for the 49 h 61 by direct measurement. It was also possible to make certain of the element by comparing ratios of the emitted ions $M^+$ and $MO^+$ of the 49 h activity at 149 and 165 and those of the accompanying 4 y 61 at 147 and 163. The possibility of confusing the 49 h activity with 47 h $Nd^{(149)}$ was thus eliminated.

A 5 day activity arising from (n, $\gamma$) on $61^{147}$ was prepared and submitted for mass investigation and was confirmed as 148. A 5 day activity tentatively classified as an isotope of 61 was originally described by Pool as resulting from cyclotron investigations of the rare earths at Ohio State University.

Attempted Mass Assignment of $10^6$ y 43. A sample of the long-lived 43 has also been submitted to Chicago for mass assignment. In preparation, some experimental work has been conducted on the choice of a favorable chemical form of the 43 for ionization in the mass spectrograph. Preliminary trials by Inghram have indicated that the conventional hot-wire ionization technique was not suitable when used with rhenium oxide which is comparable but somewhat less volatile than the oxides of 43.

Absorption Spectra of 61 and 43. An initial experiment to determine the absorption of 61 on the Beckman Quartz Spectrophotometer using a special light collimator and a quartz microcell furnished by Dr. Cunningham and about one milligram of material gave essentially the absorption bands characteristic of neodymium, although spectroscopically the sample is almost free of any rare earth contaminant. The most important bands gave about 35% absorption which at the same concentration is considerably more than that known for neodymium. Visibly the 61 was somewhat similar in color to neodymium and more intense.

Absorption experiments have been run on the pink and the yellow states of 43 which give gradual absorption near the violet.

Shipments (12/16/46 to 1/15/47)

Off Area: 0.3 mc $61^{148}$ to Chicago
5.0 mc Rare Earths to Chicago
1.0 mg Element 43 to Chicago

On Area: 1300 mc $Sr^{89-90}$

## VIII. BASIC CHEMISTRY OF HEAVY ELEMENTS

Basic Chemistry of Plutonium (K. A. Kraus, A. Garen, R. W. Holmberg, F. Nelson, G. W. Smith) - P.A. CX3-2

No new results can be reported. Work is being initiated on the chemistry of neptunium, the first objective being the elucidation of its hydrolytic behavior.

Recovery of Plutonium (K. A. Kraus, F. J. Fitch, G. E. Moore, G. W. Smith) - P.A. CX3-3. No recovery work was carried out, all time being spent in making a plutonium inventory.

Chemical, Physical, and Nuclear Properties of Heavy Isotopes (R. W. Stoughton, J. E. Barney, F. T. Bonner, A. J. Fry) - P.A. CX10-22

The building of a fission counter to be inserted into the pile at a flux of about $5 \times 10^{10}$ is contemplated for the determination of fission cross-sections with very small amounts of material.

The work on the determination of the capture cross-section of $Ra^{226}$ and the half-life of $Ra^{227}$, which was begun by S. Peterson at Chicago and continued for a while by J. P. Hunt at Clinton Laboratories, will now be continued here.

The negative iodate complex with thorium seems to be rather weak since, under the conditions used, it seems to take about 16 moles of iodate ions to dissolve one mole of thorium iodate. Work in the future will involve maintaining a pH of about 3 and probably maintaining the ionic strength constant by the addition of $LiClO_4$, $LiIO_3$ being added to vary the iodate concentration. By maintaining the pH as high as 3, the $(IO_3^-)/(HIO_3)$ ratio will be about 160; by keeping the pH as low as 3, no hydrolysis (or metathesis) of thorium (or thorium iodate) should occur.

## REPORTS ISSUED

MonC-174 - "Experimental Use of $C^{14}$: Synthesis of Acetic Acid from Radioactive Carbon Dioxide" by L. B. Spector and G. E. Boyd. P.A. CX4-4.

MonN-231 - "Radiation Effects in Solvent Extraction Processes" by J. P. McBride, C. J. Hochanadel, A. O. Allen.

MonC-59 - "Studies in the Preparation of Organic Radio-Halides" by J. W. Richter and G. E. Boyd. P.A. CX4-4.

## Distribution of Technical Personnel

| P.A. No. | Description | No. of Men Past Month | No. of Men Next Month |
|---|---|---|---|
| | **Radiochemistry** | | |
| | Chemistry and Radioisotopes of Element 43 | 1 | 1 |
| | Activities Induced in Nickel by Neutron Bombardment | 1/2 | 1/4 |
| | Activities Induced in Palladium by Neutron Bombardment | 1/2 | 1/2 |
| | Abundance Ratio of Copper Isotopes | 0 | 1/4 |
| | Radiochemical Measurements and Standardization | 3-3/4 | 4-1/2 |
| | Radiochemical Studies with Tin | 1-1/4 | 1-1/4 |
| | General Radiochemistry | 1/2 | 1/4 |
| | Radiochemical Studies with Iron | 1/4 | 0 |
| CX4-3 | Radiochemical Studies | 1-1/2 | 1-1/2 |
| | **Applications of Radioisotopes** | | |
| | Diffusion in Electrolytes | 1/2 | 1/2 |
| CX4-4 | Use of Radioisotopes in Organic Chemicals | 3-1/2 | 4 |
| | Surface Studies | 1 | 1 |
| | **Physical Chemistry** | | |
| CX5-20 | Effects of Heavy Particles on Water and Aqueous Solutions | 3-1/4 | 3-1/4 |
| CX11-8 | Assembly and Operation of the Van de Graaff Generator | 1-1/2 | 1-1/2 |
| CX5-7 | Chemistry of Gas and Peroxide Formation Induced by Radiation in Water Solutions | 2 | 1-1/2 |
| | Chemistry of Solutions | 1 | 1 |
| | **Chemical Physics** | | |
| | Electron Microscopy | 2 | 2 |
| | X-Ray Diffraction | 1 | 1 |
| | Calorimetric Studies | 2 | 2 |
| CX4-1 | Cloud Chamber Studies | 1 | 1 |
| CX10-21 | Experiments with Molecular Beams of Radioactive Isotopes | 1/2 | 1 |
| | Neutron Energy Dependence of Cross Section | 1/2 | 1/2 |
| | Spectroscopy of Heavy Elements in Crystals and Solutions | 3/4 | 3/4 |
| | Theoretical Chemistry | 1 | 1 |
| | **Analytical Chemistry** | | |
| CX3-4 | Development of Radiochemical Procedures | 1/2 | 1/2 |
| CX7-2 | Research and Development Studies on Analytical Procedures | 11-1/2 | 10-1/2 |
| CX7-1 | Analytical Service | 23 | 23-3/4 |
| | **Instruments and Physical Measurements** | | |
| CX11-1 | Geiger Tube Development | 1-1/2 | 1-1/2 |
| CX11-4 | Development and Construction of Alpha-Counting Equipment | 2 | 2 |
| CX11-5 | Development and Construction of Special Instruments | 2-1/2 | 2-1/2 |

Distribution of Technical Personnel (Continued)

| P.A. No. | Description | No. of Men Past Month | No. of Men Next Month |
|---|---|---|---|
| | **Separation Processes** | | |
| | Basic Chemistry of Solvent Extraction | 1-3/4 | 1-3/4 |
| CX3-5 | Basic Studies of Separations Processes | 2 | 2 |
| CX1-10 | Isolation of $C^{14}$ from Beryllium Nitride | 3 | 3 |
| CX1-24 | Rare Earth Separations | 4 | 4 |
| CX9-1 | Isolation of $U^{233}$ from Thorium by Solvent Extraction | 9 | 9 |
| CX5-9 | The Recovery of Uranium from Enriched Piles | 4 | 4 |
| CX1-9 | Preparation of Radioisotopes | 6-3/4 | 7 |
| | **Basic Chemistry of the Heavy Elements** | | |
| CX3-2 | Basic Chemistry of Plutonium | 2-1/2 | 3-1/4 |
| CX3-3 | Recovery of Plutonium | 2-1/2 | 1-1/2 |
| CX10-22 | Chemical, Physical, and Nuclear Properties of Heavy Isotopes | 3-1/2 | 3-1/2 |
| | Plutonium Project Record | 1-1/2 | 1-1/2 |
| | Supervision | 2-1/2 | 2-1/2 |
| | Design Engineering | 2-3/4 | 2-3/4 |
| | On Loan to Technical Division | 1/2 | 0 |
| | On Loan to Atomic Energy Commission | 1/4 | 3/4 |
| | On Leave | 2 | 2 |
| | Unassigned | 1 | 1/2 |
| | Total Number of Technical Personnel in the Division | 121-1/4 | 121-1/4 |

Technical Personnel Added: 4
Technical Personnel Terminated: 1
Non-Technical Personnel: 39
Training Program Members Assigned to Chemistry: 5