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MonN-266

Contract No. W-35-058, Eng. 71

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REPORT OF THE CHEMISTRY DIVISION FOR THE MONTH

JANUARY 15 - FEBRUARY 15, 1947

* * *

J. R. Coe and E. H. Taylor

Date Received: 3/12/47

Date Issued: 3/12/47

[REDACTED]

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I. APPLICATIONS OF RADIOISOTOPES

Diffusion in Electrolytes (R. F. Newton)

The work is somewhat hampered by failure to receive a thermostat which had been ordered. However, preliminary calibrations are being made of diffusion cells at room temperature. These calibrations will need to be repeated when the thermostat is available, but because of the preliminary calibrations at room temperature it should be possible to carry them out more rapidly. Preliminary calibrations are being made with 0.1 N KCl as calibrating solution.

Use of Radioisotopes in Organic Chemistry (G. E. Boyd, General Supervision; W. G. Brown, Special Consultant) - P.A. CX4-4

The Radioactive Assay of C¹⁴ (W. B. Leslie). Work on the gas ionization chamber method of C¹⁴ measurement is being continued. A comparison of three solid sample counting methods has been made, and the efficiency of each method calculated.

Synthesis of C¹⁴-Containing Compounds: Mandelic Acid (O. K. Neville). Carbon¹⁴-labelled mandelic acid has been prepared by the scheme previously worked out on dead material. One gram of acetophenone labelled in the carbonyl group yielded, upon oxidation to phenylglyoxal and treatment with NaOH, 1.31 grams of cadmium mandelate, 76% of theoretical yield.

The mandelic acid was recovered from the cadmium salt by dissolving the salt in the minimum amount of water and HCl, saturating the solution with NaCl, and ether extracting the mandelic acid. The ether was removed and the white solid was recrystallized twice from benzene.

A weighed amount of mandelic acid was oxidized to benzoic acid by alkaline KMnO₄. The solution was acidified and the CO₂ evolved was swept into an ionization chamber for determination of radioactivity. The recovered benzoic acid was oxidized by the previously described wet-oxidation method for a determination of its radioactivity. (See MonN-211, p.9.) The results of these measurements will be described subsequently.

Reduction of CO₂ Using LiAlH₄ (W. H. Yanko). A total of three reductions of ca. 2 g quantities of carbon dioxide with lithium aluminum hydride were made. During the isolation of run #1 an explosion occurred. Runs #2 and #3 are in the process of evaluation. An additional quantity of 1.16 moles lithium aluminum hydride was prepared.

Synthesis of C¹⁴-Containing Compounds (C. J. Collins). The investigation of general synthetic methods for certain organic compounds has been initiated. Model experiments in two series leading to the synthesis of designated compounds

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have been carried out successfully. Work is in progress on the improvement of yields prior to the use of carbon¹⁴ in these reactions.

The Synthesis of S³⁵-Containing Compounds (D. J. Crowley). An unsuccessful attempt was made to effect exchange of radioactive sulfur from dilute aqueous solutions of sulfuric acid and of sodium sulfate with naphthalene sulfonic acid and naphthalene sodium sulfonate, respectively. In view of the fact that it is believed that exchange is more likely to take place in concentrated sulfuric acid medium, it is planned to continue the experiments with this medium. At present sulfonation and analytical procedures are being investigated.

Surface Studies (S. Ross)

Sodium chloride pulverized in a boron carbide mortar has the same transitions as the sample pulverized in a mullite mortar, showing that they are not caused by specific impurities introduced by grinding. Crystals of potassium chloride were prepared in the same way that was used for the preparation of the sodium chloride crystals. A surface phase transition of ethane is found to take place at $p = 3.95 \times 10^{-4}$ mm on these crystals. A new type of hysteresis is found on these crystals, the sorption portion of the isotherm lying above the desorption portion.

II. 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 with solutions of oxygen in water (oxygen pressure = 63 cm) show that the oxygen scarcely affects the decomposition of the water when the system is placed in the pile; the hydrogen pressure at the steady state is of the same order as it would be with no added oxygen. Part of the oxygen is converted to hydrogen peroxide and the total pressure at first falls rather slightly.

Two new batches of synthetic water, made from hydrogen and oxygen, have been bombarded in the pile. The results from the first batch are in accord with two tendencies evident in a number of recent experiments: (1) Steady state concentrations attained in systems where there is a gas phase in contact with the irradiated water are higher than in systems without a gas phase and (2) when ampoules are strung together for filling, the water in the bottom ampoule decomposes more completely than in the ampoules above it. The latter circumstance suggests that foreign matter of some sort is washed down from the upper ampoules into the lower ones, and these materials promote the decomposition of the water when it is placed in the pile. In preparing the

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second batch, provision was, therefore, made for running deaerated water through all the ampoules for 4 to 5 hours before the ampoules were filled. The concentrations of hydrogen built up in these ampoules after exposure in the pile for periods ranging from 7 seconds to an hour were lower than with the first batch, indicating flushing of ampoules to be desirable. Presence of traces of CO_2 in the water, after exposure, indicates that the methods of purification and degassing are still significantly imperfect.

Some calorimetric studies were initiated in an attempt to determine the total rate of energy input for samples of water and other materials exposed in the pile.

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

The fundamental design of the building to house the Van de Graaff generator has been altered, and the month has been spent in cooperating with the Project Engineering Division in preparing the new plans.

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

Studies are continuing on rate of gas evolution from H_2SO_4 solutions in the pile. The initial rate appears to vary when the volume of free space over the solution is changed. The steady state pressure is over 40 atm. for both 1 N and 2 N acid.

Chemistry of Solutions (C. H. Secoy)

Hydrated uranyl sulfate, of sufficient purity to give consistent solubility data, has been prepared. The method consists of adding the equivalent amount of dilute sulfuric acid to either uranyl nitrate or the trioxide; precipitation of the acetone complex; dissolving the complex in an excess of water; boiling to drive off the acetone; and crystallization of $\text{UO}_2\text{SO}_4 \cdot \text{XH}_2\text{O}$ from the resulting solution. Gravimetric analyses, by ignition in air with a gas-oxygen torch, give constant weight residues which, if calculated as $\text{UO}_2.5$, agree very well with volumetric analyses performed by the analytical division. Gravimetric SO_4^- analyses are also in agreement. Furthermore, the pH of solutions of the salt agrees well with values reported by McInnes (CCA-380) and by Helmholtz and Friedlander (LAMS-30).

With this salt, new solubility data have been obtained over the range 40° to 160°C . There is indication of a very flat transition point between 80° and 100° , which was previously reported at 100.2° . Present data indicate that, if a transition does occur in this vicinity, it is at a somewhat lower temperature. Due to the small difference in the slope of the curves below and above the transition, the establishment of the point is somewhat difficult. Efforts to prove its existence are being continued by the following methods: (1) the securing of more accurate points on the solubility curve, (2) by obtaining warming curves, and (3) by crystallographic study with the hope of obtaining distinguishable crystals above and below the transition temperature.

By the third line of attack, the following information has been obtained concerning the room-temperature stable hydrate. The crystals are biaxial positive, probably monoclinic. Only parallel and oblique extinctions have been observed. The crystals are prismatic with prominent faces in the 300, 010, 001, and 101 planes. The refractive indices have not been measured.

Efforts to obtain a high temperature form have, so far, yielded only cigar shaped particles which show only parallel extinction. These may be only poorly formed crystals identical with the low-temperature form. At room temperature and in contact with the liquid phase, they revert in a short time to the well-formed prisms described above. This study is being continued.

III. CHEMICAL PHYSICS

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

The dark room is now complete except for very minor details. There has been a delay in the transfer of the metallograph from K-25. Some time has been spent taking micrographs of sodium and potassium chlorides which S. Ross is using in his surface area work.

Delay in clearance for the RCA Service man has postponed the installation of the electron microscope, and RCA advises that 17 March is now the earliest possible date. In the meantime, a certain amount of time is being spent in cleaning and polishing various parts of the instrument, replacing fluorescent screens, etc.

Some time is being spent on redesigning the silica evaporator so that it will be a more versatile unit.

X-Ray Diffraction (M. A. Bredig)

In testing the first "micro-x-ray-spectrograph" model with an x-ray tube at the x-ray laboratory of the K-25 plant, difficulties were encountered with the quality of the sodium chloride crystal that was available. However, expectations of high speed to be attained with the apparatus were shown to be justified. When exposure times were in the range of a few seconds, the copper K_{α} line was largely overexposed.

To overcome the difficulty of the need for a rather good crystal, which is inherent in the principle applied in this model, another one was built, employing the Seemann method of collimating the x-ray beam by the crystal itself and a metal edge, rather than by a slit. Sodium chloride, quartz, and mica crystals were used, and the results were improved, even though these crystals, too, were far from perfect, or even satisfactory. With the x-ray tube running at 40 Kilovolt and 20 milliamperes, the copper K_{α} line, diffracted on a sodium chloride crystal, appeared overexposed in less than 1 second. With 40 Kilovolt and 1 milliampere, this line, after an exposure of less than

1 second, appeared in sufficient intensity, and traces of the K_α line, of approximately one-fifth of the intensity of the α line, were also visible on the film. Thus, the speed of the instrument may be several hundred times that of the usual x-ray spectrographic equipment and, therefore, may be useful for the investigation of low-intensity x-ray sources, whenever the requirements of resolution are moderate or low. The experiments will soon be extended to radioactive sources of characteristic x-rays and, by using still another model, possibly also into the range of elements with higher atomic numbers.

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

A final report is being prepared on the "gamma calorimeter" which has been built and used. The report will include the detailed calibration data and the total energy measurements made on Au¹⁹⁸.

Preliminary work has been started on the design of a "beta calorimeter" that will be practicable for energy measurements of pure beta emitters including H³ and C¹⁴.

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

A nickel cylinder with plastic windows is being machined to replace the glass cloud chamber cylinder. A new stroboscopic light source has been built and is now ready for use. Work has started on the construction of a camera. The procurement of plastics, fluorine, fluorocarbons, and other materials is still causing considerable difficulty.

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

Leak testing is continuing.

IV. ANALYTICAL CHEMISTRY

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

A complete run was made on the present method of determining U²³³ in urine. Starting with 1616 c/m of U²³³ in 1500 ml of urine, the U²³³ was carried with cupric ferrocyanide, fumed with H₂SO₄ to destroy the ferrocyanide, solvent extracted into cellosolve from a nitrate solution, back extracted and electroplated from (NH₄)₂C₂O₄ solution onto a platinum cathode. The resulting platinum plate counted 1580 c/m, indicating high efficiency for the process. Several repeat runs will be made to check the method further and then attempts will be made to shorten the procedure. It seems reasonably certain, for example, that the H₂SO₄ fuming can be replaced by a shorter and more convenient step.

Research and Development Studies on Analytical Procedures (W. M. Byerly, General Supervision) - P.A. CX7-2

Determination of Beryllium in Urine (U. Koskela). On the basis of an analysis method for beryllium listed in the National Institute of Health Bulletin No. 181, a spectrophotometric method has been worked out for the determination of beryllium in the range of 1 to 10 micrograms. It is believed that this can be developed as a procedure for the analysis of urine for beryllium.

Development of Photofluorimetric Methods and Apparatus for Process Solutions (G. Sadowski). The determination of uranium in "25" Purification Process solutions is complicated by the presence of chromium (0.1 M). At the present radiation level, the chromium is being removed by volatilization as CrO_2Cl_2 , and the samples are analyzed fluorimetrically. However, at higher radiation levels this fuming technique will no longer be feasible due to the radiation from the samples.

Work at the present time is directed toward setting up a procedure whereby samples containing chromium can be analyzed directly using small volumes (0.010 ml). This is possible since the effect of chromium on the fluorescence, and in turn the uranium recovery, in each sample can be determined by "spiking" the sample with a known amount of uranium. This permits a correction of the "apparent" value of uranium. The loss in accuracy is being determined.

Determination of Low Concentrations of Nitric Acid in Radioactive Solutions (P. F. Thomason). The free acid concentration in the alloy solutions of the "25" Purification Process must accurately be known on the level of 0.1 to 0.2 normal. Large amounts of aluminum and approximately 0.02 molar uranium are present. The nitric acid analysis now employed determines 0.1 N of acid in 1 ml of solution in the presence of 3 molar aluminum with an accuracy of $\pm 6\%$ by complexing the aluminum with potassium fluoride and titrating with standard caustic to a phenolphthalein end point. The sample size of the "hot" runs will be limited by the radioactivity to less than 0.1 ml of solution for each titration.

The above method is being adapted to a micro scale employing a Kirk burette titrating 10λ samples. The results to date are approximately 25% low, probably due to the occlusion of the nitric acid by an aluminum potassium fluoride complex. Recent experiments indicate an improvement by delaying the addition of the potassium fluoride until the equivalent caustic is nearly added. A suitable method should result with further refinements.

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

In order to check the results obtained in a determination of small concentrations of germanium by activity measurements, a radiochemical method for this element has been developed and determinations involving chemical separations are being carried out. Preliminary results indicate 10^{-9} concentrations of germanium in Be can be determined with reasonable accuracy.

Since calcium is used in the manufacture of Be metal and is, therefore, a probable contaminant in this material and since Ca^{49} activity must compete with other activities of nearly the same half life (Ca^{41} and Ca^{45} activities are long lived and therefore time consuming in radiometric determinations by decay measurements), a tentative radiochemical method for the determination of Ca activity has been developed. This method has application not only to radiometric analyses for trace impurities in samples of pure chemicals, but also to the analysis for Ca^{46} activity formed by the n,p reaction on Sc^{45} .

Purification of BeO (F. H. Sweeton) - P.A. CX7-2

Studies of direct removal of boron impurity from Clifton BeO by use of CH_3OH have continued using a Clifton sample containing about 4 ppm. High pressure tests in sealed tubes show (1) that there is no observable decrease in boron content after treatment for 5 hours at 200°C ; (2) that treatment at 260° (the critical temperature of CH_3OH is 240°C) for 20 hours removes 2 ppm which is the same amount removed in a 37 hour test at 210° ; (3) that three successive 30 hour treatments at 210° are no more effective than one such treatment.

To date, no experiment has shown removal of greater than 2 ppm (50%) B from this sample. Additional experiments are now in progress. The study will be extended using a sample of Brush BeO containing 7 ppm of B which has just been received.

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

Diffusion current vs. concentration relationships have been established for peroxide at 50°C in sodium carbonate solutions with and without uranyl ion present.

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

Work is continuing on the report summarizing previous work. Additional information has been obtained concerning the advantages and the limitations of different sizes of electrodes.

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

Difficulty was encountered in finding chemicals of sufficient purity for these studies. Calibrations of equipment have been completed. G. E. Boyd and Q. V. Larson have supplied a standard solution of Tc for these studies.

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

The high frequency instrument built according to directions in the literature was found to lack sensitivity when compared with regular conductivity. The Instrument Development Group (under R. L. Quinn) is now working on an improved circuit. The same group is attempting to extend the range of amperage that can be handled by our constant voltage electrolytic instrument.

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

Preliminary data indicate that good material balances can be obtained in electrolytic separations of silver in tracer concentrations. An investigation of the minimum time required for complete deposition is now in progress.

Analytical Service (W. M. Byerly, J. E. Hudgens, L. B. Rogers, G. C. Bell, O. M. Bizzell, A. D. Bogard, C. L. Burros, L. T. Corbin, W. H. Davenport, 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, B. Warren, J. N. Weeks, D. Weinberger, G. R. Wilson, W. Wolkowitz) - P.A. CX7-1

The following analyses were requested during this period:

	<u>Gross Activity</u>	<u>Radio-chemical</u>	<u>Ionic</u>	<u>Control</u>	<u>Spectro-graphic</u>
Chemistry	8	39	59	738	95
Technical	18	85	609	1742	22
H ₂ O Activity* (Operations)	478				
Health Physics					1
Medical					3
Metallurgy					2
Others			6		

*The responsibility for the performance of the samples from the waste area (206-Area) was transferred from the radiochemical analytical group to the 706-D analytical control group in order that shift analyses may be performed. This change became effective at 4:00 PM, February 7, 1947.

The radiochemical group has in this report period expanded the number of analyses for which methods are available to include Fe, Ge, Sn, Ca, and Hg. The analyses requested during the report period increased in complexity and difficulty of the separations involved. The radiochemical group has since 1 January isolated radiochemically pure activities traceable to isotopes of 31 elements.

Conditions and standards were defined for the determination of traces of iron and copper in solutions containing large amounts of uranium and aluminum.

V. INSTRUMENTS AND PHYSICAL MEASUREMENTS

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

Considerable effort has been spent making a very thin window counter to be used in connection with the beta-ray spectrometer to determine the energy

spectra of low energy betas and conversion electrons. Mica split to surface densities of 0.6 mg/cm^2 and up was supported between two metal grills and cemented to the counter using various methods. The majority of the windows broke up on evacuation. A counter with a 1.5 mg/cm^2 window was finally completed.

A counter is being designed to give essentially 100% geometry. Samples of beta emitters will be mounted on 0.1 mg Formvar film and introduced directly into the sensitive volume of the counter. Absolute disintegration rates obtained with this counter will be compared with disintegration rates obtained from coincidence counting and calorimetric measurements.

Development and Construction of Alpha-Counting Equipment (J. H. Parsons) - P.A. CX11-4

The forty-eight channel analyser has been remodeled to provide more stable pulse height selection. This improvement should allow a finer resolution to be obtained.

The self-recording sweep analyser that is being built by the instrument shop is practically completed.

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

An attempt was made to adapt a proportional alpha counter to the counting of low energy beta emitters. It was found necessary to add additional amplification to the unit. This was done by placing the A-1 preamplifier ahead of the proportional amplifier. Promising results were obtained. A C^{14} sample exhibits a 200 volt plateau, while a 17 day Pd sample exhibits two plateaus, indicating two groups of conversion electrons. The results so far indicate that it may be possible to obtain energy distribution curves for low energy beta particles with less difficulty than with beta ray spectrometers.

It was also found that the sharp rise in counting rate at the upper end of the voltage plateau for alpha samples is due to "overshoot" in the proportional amplifier causing the scalar to trigger. This can be eliminated by placing a IN34 crystal rectifier across the output terminals of the amplifier, substantially increasing the length of the plateau.

It appears possible to calculate absolute number of disintegrations in sources emitting X-rays using the spherical Ionization Chamber. The ion currents in this chamber for 20 kev X-rays follow:

He - 2.5×10^{-15} amps
N₂ - 6.3×10^{-15} amps
A - 176×10^{-15} amps
Kr - 1160×10^{-15} amps

The high currents obtained by suitable choice of gas gives one an exceedingly sensitive method for measuring X-rays of different energies.

Work is continuing on vibrating reed electrometers and time stampers.

VI. SEPARATION PROCESSES

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

The Bausch and Lomb quartz prism spectrograph is being adapted for absorption spectroscopy to take advantage of its large continuous wave-length coverage.

A memo on the work carried on in this field to date is being prepared.

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

A draft copy of a progress report for the past six month period has been prepared. One interesting generalization which may be put forth tentatively is that tracer ions causing a contraction of the "host" or "carrier" lattice lead to negative deviations from Raoult's law and hence are better coprecipitated than ions causing a lattice expansion together with positive deviations from an ideal solid solution.

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

In an attempt to shorten the time of separation of the heavy rare earths to facilitate the study of their activities, a steam jacketed Dowex-50 ion exchange column has been used. The separation of ytterbium and thulium was studied. At 25°C a fair separation was made in 38 hours. At 100°C a very good separation was obtained in 36 hours. In another experiment a fair separation of the same pair of elements was accomplished in seven hours. Finally a sample of impure erbium (Hilger-Spectrographic Standard) was bombarded, and a separation was made on the heated column. Whereas the same material had been fairly well separated into its constituents, thulium, erbium, holmium, and yttrium at room temperature on an Amberlite column in 62 hours, a much better separation was obtained on the heated column in 46 hours.

From a preliminary study of the reason for the improved separation, it was shown that the dissociation constant of the rare earth citrate complex increases more rapidly than does the dissociation constant for the rare earth resin complex. It is probable that the improvement in separation is due to the difference in the increase of the rare earth citrate complexes as the temperature is increased. Earlier work (see MonN-2, MonN-6, MonN-15, and MonN-26) on the structure and dissociation constants of the rare earth citrate complexes is being resumed, and their temperature dependence will be measured.

Isolation of C¹⁴ from Beryllium Nitride (D. S. Anthony, A. J. Weinberger) - P.A. CX1-10

Most of the month was spent in constructing an all-glass apparatus for specific activity determinations on Hanford-irradiated Be₃N₂. Collection of data on this problem should begin in a few days.

Experiments on the solubility of Be₃N₂ in alkali are continuing.

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

Fractionation of Rare Earths by Precipitation. The fractionations described previously have been continued. After the Ce and La are separated from the rare earth mixture, the remaining elements are separated into three fractions by fractional crystallizations of the double magnesium nitrates. These contain: (1) Pr (~95% pure); (2) Nd (~90% pure); (3) Sm (plus the heavier rare earths in the original mixture). The Sm fraction contains Eu which is desired by the operations group. In addition, other of the heavy rare earths are present in small amounts. If a 61 isotope does occur naturally, it would be expected in this fraction. For this reason plans are being made for the fractionation of 100 lbs of the crude cerium oxalate with the aid of the technical department. From this it is hoped that we will be able to get 10-30 grams of Eu, 100-300 grams of Gd and Dy, and smaller quantities of other heavy rare earths. If a 61 isotope occurs in a concentration as high as 0.1 part per million, it should be detectable. Also Nd, Pr, Sm, Ce, and La in quantities from one pound to twenty pounds will be available for further purification if they are desired for future work.

Test runs on the separation of Sc_2O_3 from thortveitite have been started. Solution of the mineral seems to be the most difficult step.

Column Separation. A number of column separations have been run or are in progress.

- (a) Purification of Nd from crude $\text{Nd}(\text{NO}_3)_3$.
- (b) Separation of heavy rare earths as a group from 7.5 g of impure Y. The Er group thus obtained is being run on another column to separate the individual members.
- (c) Two runs on separation and identification of long lived, low fission yield fission products of the rare earth group. A gamma activity has been found which follows Y^{91} in column behavior. This was 0.02% of the Y beta activity. Two other betas and another gamma are being studied further.
- (d) Purification of scandium. The first run is nearing completion, but the yield appears to be low.
- (e) Yttrium isotope separation. This will be completed in about a month.

Batch Equilibrium Experiments. The first portion of this study is nearing completion. A report will be written in the near future describing this phase of the work. Some of the results obtained to date are:

- (1) The distribution coefficient of the rare earth between resin and citrate solutions at various pH's seems to indicate the complex is chiefly $\text{M}(\text{H}_2\text{Cit})_3$ in the pH range used for the separations.
- (2) The relative distribution coefficients of a number of rare earths measured at pH 2.4 were: Tm - 0.44; Y - 1.2; Tb - 1.4; 61 - 2.2; Nd - 2.9; Pr - 4.2; Ce - 8.5. Qualitatively this order is the same as the order of elution of these elements from a column. The ratios between these values and those calculated for the column separations runs for Nd, Pr, and Ce are quantitatively nearly identical.
- (3) The effect of the NH_4^+ concentration in the presence of citrate is to cause the distribution coefficient to vary as the reciprocal of the third power of the ammonium ion concentration.

(4) The rare earth concentration does not affect the distribution coefficient when its concentration is below 3×10^{-4} M. No hysteresis effect could be noted when equilibrium was approached from both sides (i.e., by lowering the pH in one case and raising it in the other).

(5) Nalcite was found to be superior to IR-1 in that (a) it had a much higher capacity; (b) it has only one type of exchangeable group; and (c) it shows greater differences in the distribution coefficients between the rare earth citrates.

These studies are being continued, and another series to compare various other organic complexing agents with citrate has been started.

Separations Chemistry. The development of a successful method for the preparation of carrier-free Ca from Sc was reported last month. Although Ca and Sc were quantitatively separated from each other, the Ca fraction contained radioactive impurities. None of the impurities has been identified, but results to date indicate that at least one is an amphoteric substance which is neither tin nor antimony. Purification of Sc by T.T.A. extraction prior to bombardment should eliminate all impurities that will not follow Sc in the irradiated sample.

The use of T.T.A. depends on the reaction $Me^{+n} + n (T.T.A.) \rightarrow Me(T.T.A.)_n + nH^+$. If it is assumed that Me^{+n} and H^+ are solely in the aqueous phase, that T.T.A. and $Me(T.T.A.)_n$ are completely in the benzene phase, and that no other form of Me^{+n} will extract, the following equilibrium equation can be set up:

$$K_{eq} = \frac{(Me)_{benz}}{(Me)_{H_2O}} \times \frac{(H^+)^n}{(T.T.A.)^n}$$

The determination of K_{eq} for a series of cations will prove to be a very useful method for calculating the conditions under which two metals can be separated if the difference between their respective K_{eq} values is much greater than errors inherent in the measurements. A survey of several rare earths is being made to estimate the feasibility of this experimental approach.

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

During the past period two runs have been completed using the entire pilot plant column as an extractor. This was done to give greater packing length in which to measure HETS and also to make it possible to take measurements without the added variable of the rate of mixing of the two aqueous streams. The results obtained in these studies are summarized in the table on page 14.

The results substantiate the semi-works experience with dibutyl cellosolve in that the theoretical plate heights are substantially greater than expected from experience with the laboratory column where heights less than two feet were obtained under similar flow conditions. This run also produced the first occasion, in our experience, of difficulty from the formation of crud in the column. In attempting to drain the column at the end of the runs it was found

that the exit line at the base was plugged with a white, rubbery material whose composition has not yet been determined.

Separation of Uranium and Thorium by Continuous Counter-Current Dibutyl Cellosolve Extraction

Conditions:

Feed: 5 N Th(NO₃)₄, 1 N HNO₃
 Scrub: 6 N Al(NO₃)₃, 2 N Ca(NO₃)₂, adj. to pH 1.6 with Ca(OH)₂

Run No.	Feed, l/hr	Scrub - Feed Ratio	Solv. - Aq. Ratio	No. of Theor. Plates	Height Theor. Plate, ft	U ²³³ Distrib'n Coef.	%U Loss	Th - Decontm'n Factor
C-7	3.0	1.14	1.24	2.3	4.8	6.7	1.0	135
C-8	1.5	1.4	1.15	2.2	5.0	6.2	1.09	117-226

As a result of the several difficulties encountered with the dibutyl cellosolve system, a series of studies under the conditions used by the Chicago group in the isolation of U²³³ from metal bombarded at Hanford are now being contemplated. The process used there employed hexone as the solvent with the following conditions of operation:

Feed: 4 N Th(NO₃)₄, 3 N NH₄NO₃, 0.05 N HNO₃, two volumes.
 Scrub: 6 N NH₄NO₃, one volume.
 Hexone: 3 volumes.

These studies will make it possible to compare operation of the two units and thus give further information on the question of the discrepancies between the small-scale studies and those made in the pilot plant.

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 preparation of solutions for the critical experiments has taken up practically all of two men's time. In the meanwhile the measurement of properties of the solvents and solutions has been continued.

The viscosities of Al(NO₃)₃ - HNO₃ - H₂O solutions at 25°C can be expressed by the formula:

$$\log_{10} \eta = -0.048 + 0.276 M + 0.060 M^2 + 0.013 N$$

where η = viscosity in centipoises
 M = moles Al(NO₃)₃ per liter
 N = moles HNO₃ per liter

Aqueous solutions saturated with hexone have viscosities 2 to 4% higher than given by the above equation.

New equipment is being assembled to test the variation of distribution ratio using single fission products at high activity levels. Cesium activity will be used to check the apparatus for phase separation.

Because of unsatisfactory column results obtained in Semi-Works with dibutyl cellosolve, hexone is again the first choice for the solvent.

Preparation of Radioisotopes (G. W. Parker, W. W. Gillis, 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. The testing has been started using non-radioactive solutions to determine the flow rates under various conditions and check the controls. A number of revisions in the flow sheet have been necessary as well as some minor changes in the apparatus design. The apparatus is now ready for a final dummy run after which the tracer activity runs will be made.

Separation and Purification of 10^6 y Element 43. Continued search for the optimum conditions for the existing sulfide precipitation- H_2SO_4 distillation process for the recovery of element 43 from fission has resulted in obtaining a consistent yield of at least 50% of the theoretical. During the past month six slugs have been processed from which about six milligrams of the element were produced.

Accumulation will be continued for a program involving reduction to metal, physical characterization, separation from rhenium, and general distribution. Search for the n, γ product 43^{100} is still confused by minor rhenium contamination. No results have been reported from attempts at direct mass assignment. An attempt to excite the 10^6 y isotope to the 6 hr meta-stable state by gamma irradiation from La^{140} failed to produce any measurable results.

Attempt to Obtain X-Ray Spectra of Element 61. A sample containing about one milligram of the 4 y 61^{147} was mounted and exposed to high voltage discharge on the Y-12 X-Ray spectrograph in an attempt to obtain the L-lines at the voltage available. Unfortunately, the sample was accidentally flaked off by burning a silicone covering which was used in hope of avoiding vaporization and loss. The material was recovered and is being prepared for a new attempt.

Separation of 61 has been inactive recently due to change and decontamination of cell equipment. It is expected that new cell equipment will be installed and operating in about one month.

Shipments (1/16/47 to 2/15/47)

Off Area: 0.1 mg 43^{99} to Chicago

On Area: 50 mc Ru¹⁰³⁻¹⁰⁶
3 mc 61
15 mc Zr-Cb

VII. BASIC CHEMISTRY OF HEAVY ELEMENTS

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

Work has been carried out on the hydrolytic behavior of neptunium(V). It is expected that the final results can be reported next month.

In MonN-211 (monthly report for period October 15 - November 15, 1946) the hypothesis was advanced that ferric salts catalyze the disproportionation of Pu(V) in 1 M HClO₄. Further work has now been carried out on this problem, and the hypothesis was verified spectrophotometrically. It was found that the initial disproportionation products are Pu(VI) and Pu(III). Pu(IV) forms only much more slowly, probably through reactions of the Pu(III) with Pu(VI).

Recovery of Plutonium (K. A. Kraus, F. J. Fitch, G. E. Moore, G. W. Smith) - P.A. CX3-3. The plutonium inventory was completed. Recovery work is being started.

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

Studies are continuing on the negative iodate complex of thorium, to which the formula $\text{Th}(\text{IO}_3)_{4n}^{n-}$ had been ascribed. The work at present involves a pH of 2 to 3 and an ionic strength of 0.5, with the lithium iodate concentration varying between 0.01 and 0.5 M; LiNO₃ is used to maintain the ionic strength constant with varying iodate. The number n now appears to lie in the range of 2 to 3; one might guess that two is the more likely figure, though an accurate experimental determination has not yet been made due to the difficulties involved. Trouble is being experienced in thorium analyses and in the great tendency to form colloids in these solutions of low acidity. To some extent at least the latter trouble appears to be circumvented by altering the temperature.

Thorium iodate in solutions containing excess iodate is definitely less soluble at higher temperatures than at 25°C. This may be due largely to an increasing instability of the negative complex with increasing temperature.

VIII. RADIOCHEMISTRY

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

Conditions for the successful electro-deposition of technetium from its aqueous solutions have been determined. The deposition was found to be rather strongly dependent on the acidity. At a pH \approx 1.5, 67% can be plated in about two hours; the addition of small quantities of NH₄HF₂ raises this to 76%. At pH \approx 5.0 - 6.0, 84% can be deposited in the absence, and 87-90% in the presence, of F⁻ ion. At a pH \approx 9 - 10 only 21% electrodeposition was observed.

One mg of Re as carrier was co-deposited in these experiments. Good metallic electrodeposits of Re were obtained from dilute (pH \approx 1.5) H_2SO_4 solutions.

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

Decay curves of the Rh activity obtained almost a year ago from bombarded Pd have been analyzed and show the known 36 h Rh^{105} and 210 d Rh^{102} activities as well as an unknown activity with a half life of about 48 days. The most likely assignment of this activity would be Rh^{101} formed as a daughter of the unknown Pd^{101} . Growth of Rh activity into Pd after bombardment is being checked as evidence for the presence of Pd^{101} .

Comparisons of the radiations of 17 d Pd^{103} and 42 d Ru^{103} with those of their daughter 56 min Rh^{103} have been made in a spherical ion chamber by G. J. Borowski. The data obtained with this instrument give a more consistent interpretation of the decay mechanisms than counter data. Aluminum absorption curves of Ru^{103} and Rh^{103} in equilibrium have been taken with several different arrangements of source, absorbers, and tube. Because of the uncertainty in extrapolation of the Ru beta curves to zero absorber the number of conversion electrons per disintegration was uncertain by a factor of two.

Radiochemical Studies - P.A. CX4-3

Hard γ -Emitters in Fission (H. A. Levy, M. H. Feldman). Design and development of automatic and remote control chemical apparatus continues. A neutron counter for detection and measurement of hard γ -emitters by $D(\gamma, n)$ is being built.

Cross-section Studies (M. H. Feldman). A preliminary measurement of the activation cross-section of Cr^{54} was unsuccessful.

Fission Product Decay Energies (H. A. Levy with B. Zemel of the Health-Physics Department). Preparations are under way for study of the decay energies of some shorter-lived fission products.

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

Decay Schemes. Most of the work during the month involved further work on the calibration of various beta standards in an attempt to determine absolute disintegration rates for geometry calibrations. Of particular interest was the scheme of Cs^{134} . This scheme does not appear to be completely elucidated as yet.

The machine work has been completed on the beta ray spectrometer and the parts have been delivered. Considerable work has been done on the voltage control circuit, and the vacuum system is being tested.

Beta Standards. Work on the RaD-E-F mixtures and UX_2 beta standardization is being continued in an attempt to correlate geometry measurements determined in this way with geometries determined by coincidence measurements. It is

felt that the seeming discrepancy will be resolved in the near future, and the secondary standards can then be made up for distribution to the laboratory.

Yield Measurements. A series of alloys of aluminum with gold, manganese, and cobalt is being made up for monitoring pile bombardments. The small quantities of the monitors necessary make them difficult to work with, so the plan is to make low percentage alloys of the monitoring materials in the aluminum which can then be made into strips and attached to each can or sample that is put into the pile. It is thought that this information can be correlated with the yield to give better agreement between the pile bombardment calculations and the experimental yield. The gamma bench is being moved to the pile building since the FP-54 circuit was too temperature sensitive for the hutments. It is planned to use a Beckman amplifier which has been modified to get greater sensitivity than the conventional instrument.

The investigation of the pure chemicals supplied to us by Mallinckrodt Chemical Company has been completed with the result that they are found to be considerably more pure than the standard C. P. chemicals. Measurements are also being made to determine the upper limit of sensitivity for the detection of impurities in material. The preliminary work is being done with very small quantities of manganese in aluminum. We expect to determine the accuracy with which we can measure impurities present at less than one part per million.

Preparation of Fe⁵⁹ of High Specific Activity (J. A. Swartout)

The possibility of producing Fe⁵⁹ in high specific activity by application of a Szilard-Chalmers reaction with continuous extraction of the recoiled iron is being investigated. In particular, bombardment of a circulating solution of K₄Fe(CN)₆ with extraction of the recoiled iron by ion-exchange is visualized. Preliminary ion-exchange experiments are in progress to indicate the capacity of Dowex-50 for Fe⁺³ and K⁺, the effectiveness of various elutriants, and the degree of separation of Fe⁺³ from K⁺ which may be expected. Since some doubt now exists as to the exact state of the recoiled iron in solutions of neutron bombarded K₄Fe(CN)₆, it is planned to determine whether and, if so, to what extent the iron is colloidal.

REPORTS ISSUED

- MonC-169 - "Studies on the Preparation and Properties of a Long-Lived Isotope of Element 43 Produced by the Neutron Irradiation of Molybdenum Metal" by G. E. Boyd and E. E. Motta. P.A. CX5-7.
- MonC-209 - "A Consideration of Complicating Factors in the Micro Analysis of Carbonate and Bicarbonate in Homogeneous Pile Solutions" by A. F. Stehney and D. N. Hume. P.A. CX7-2.
- CN-2830 - "Oxidation-Reduction Potentials of Plutonium Couples as a Function of pH" by K. A. Kraus. P.A. CX3-2.

MonC-173 - "Experimental Use of C¹⁴: (I) Investigation of Counting Methods Using G.M. Tubes; (II) Synthesis of Active Organic Compounds; (III) Analysis of Ammonium Nitrate Solutions from the Carbon Factory" by W. B. Leslie and G. E. Boyd. P.A. CX4-4.

Distribution of Technical Personnel

<u>P.A. No.</u>	<u>Description</u>	<u>No. of Men</u>	
		<u>Past Month</u>	<u>Next Month</u>
<u>Applications of Radioisotopes</u>			
CX4-4	Diffusion in Electrolytes	1/2	1/2
	Use of Radioisotopes in Organic Chemistry	4	4
	Surface Studies	1	1
<u>Physical Chemistry</u>			
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	1	1
	Chemistry of Solutions	1	1
<u>Chemical Physics</u>			
	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	1-1/2
	Neutron Energy Dependence of Cross Section	1/2	1/2
	Spectroscopy of Heavy Elements in Crystals and Solutions	1/2	1/2
	Theoretical Chemistry	1	1
<u>Analytical Chemistry</u>			
CX3-4	Development of Radiochemical Procedures	1/2	1/2
CX7-2	Research and Development Studies on Analytical Procedures	10	11
CX7-1	Analytical Service	24-1/2	24-1/4
<u>Instruments and Physical Measurements</u>			
CX11-1	Geiger Tube Development	1-1/2	1-1/2
CX11-4	Development and Construction of Alpha-Counting Equipment	1	1
CX11-5	Development and Construction of Special Instruments	3-1/2	4-1/2
<u>Separation Processes</u>			
	Basic Chemistry of Solvent Extraction	2	2
CX3-5	Basic Studies of Separations Processes	2	2
CX1-10	Isolation of C ¹⁴ from Beryllium Nitride	2-1/2	2-1/2
CX1-24	Rare Earth Separations	4	5
CX9-1	Isolation of U ²³³ from Thorium by Solvent Extraction	9-1/4	9-1/4
CX5-9	The Recovery of Uranium from Enriched Files	4	4
CX1-9	Preparation of Radioisotopes	7-1/4	8

Distribution of Technical Personnel (Continued)

<u>P.A. No.</u>	<u>Description</u>	<u>No. of Men</u>	
		<u>Past Month</u>	<u>Next Month</u>
<u>Basic Chemistry of Heavy Elements</u>			
CX3-2	Basic Chemistry of Plutonium	3-1/4	4-1/4
CX3-3	Recovery of Plutonium	2-1/4	1-1/4
CX10-22	Chemical, Physical, and Nuclear Properties of Heavy Isotopes	3-1/2	3-1/2
<u>Radiochemistry</u>			
	Chemistry and Radioisotopes of Element 43	1	1
	Activities Induced in Palladium by Neutron Bombardment	1	1
CX4-3	Radiochemical Studies	2	2
	Radiochemical Measurements and Standards	4-3/4	5-1/2
	General Radiochemistry	1-1/4	2
	Preparation of Fe ⁵⁹ of High Specific Activity	1/2	1/4
	Plutonium Project Record	1-1/2	1-1/2
	Supervision	3	3
	Design Engineering	2	2
	Research Center Committee	1/2	3/4
	Library Research	1	3/4
	On loan to Atomic Energy Commission	3/4	1/2
	On Leave	2	2
	Unassigned	3/4	1
<u>Total Number of Technical Personnel in the Division</u>		124-1/4	129-1/2

Technical Personnel Added: 6

Technical Personnel Terminated: 2

Technical Personnel Transferred to Office of Research Director: 1

Non-Technical Personnel: 51

Training Program Members Assigned to Chemistry: 5

129
56
185

