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UCRL 264

Chemistry-Transuranic Elements

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QUARTERLY REPORT

September, October and November, 1948

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Patent Advisor, Washington		52
Technical Information Division, CROO		53-67
University of California, Radiation Laboratory		
	Information Division	68-70
	I. Perlman	71
	B. Tolbert	72
	W. Latimer	73
	E. Segre	74
	J. G. Hamilton	75
	E. O. Lawrence	76
	M. Calvin	77
	Patent Dept.	78
University of Rochester		79-80
Office of Chicago Directed Operations		81

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TABLE OF CONTENTS

Title	Page
I QUARTERLY REPORT. PROJECT 48	
A. Chemistry of the Lanthanide Elements	
Preparation of Pure Rare Earths for Chemical and Nuclear Work.	4
Heat of Solution of Praseodymium Sesquioxide.	5
Preparation of Praseodymium Hydride	6
High Temperature Equilibria in the Oxide Systems of Praseodymium	7
Crystal Structure of Samarium Oxychloride (Correction)	8
Vapor Phase Hydrolysis of Lanthanum Trichloride	9
Absorption Spectrum of Solid $NdCl_3$	10
Ion Exchange Separation of Zirconium and Hafnium	11
Separation of Zirconium and Hafnium by TTA Extraction	12
B. Chemistry of the Actinide Elements	
Absorption Spectrum of Aqueous Am(III)	13
Absorption Spectrum of Aqueous Am(III) as determined with a Baird Grating Spectrograph	14
Collateral Alpha-Decay Chains	16
Mass Assignments of Light Bismuth Isotopes	18
Isotopes of Tin	20
Fission Cross Section with High Energy Particles	21
Properties of $Radium^{227}$	22
Yields of Mn^{52} and Mn^{56} in the Deuteron Bombardment of Various Elements.	23

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Table of Contents (Con'd)

Neutron Deficient Rare Earth Isotopes and those of Hf, Ta, W and Re. 24

Neutron Deficient Cesium Isotopes 26

Spallation Products of $_{33}As^{75} + D^{+}$ (190 Mev) 27

Neutron Deficient Isotopes of Transuranium Elements. 28

Pulse Analysis Using a Cathode-Ray Tube 29

Mass Spectrograph for Mass Assignment of Radioactive Isotopes 32

C. Chemistry of Astatine and the Preparation of Certain Compounds.

Preparation of BeF_2 33

Preparation of $Be^7 F_2$ and $Be^7 O$ 34

Astatine Chemistry 35

D. Bio-Organic Chemistry.

Synthethetic and Experimental Chemistry 36

Biological Chemistry 43

Photosynthetic Chemistry 48

II QUARTERLY PROGRESS REPORT. PROJECT 48B

A. Metals and High Temperature Thermodynamics 55

B. Basic Chemistry, Including Chelates 57

C. Ore Reduction 58

D. Engineering Development of Plutonium Separation 59

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I QUARTERLY PROGRESS REPORT. PROJECT 48

A. Chemistry of the Lanthanide Elements

I. Perlman, B. B. Cunningham and Co-workers

Preparation of Pure Rare Earths for Chemical and Nuclear Work

R. C. Lilly, D. C. Stewart and B. B. Cunningham

The use of synthetic ion exchange resins of improved type provides a means for the relatively rapid and efficient purification of the rare earths on a substantial scale, to a degree of purity hitherto impossible. An important part of the program of investigating the chemical and nuclear properties of these elements is the initial preparation of each element in highly purified form.

The purification of praseodymium for the chemical investigations described in succeeding sections of this report was carried out as follows:

The starting material consisted of about three grams of praseodymium oxide (Lab. No. 1533) marketed as highest purity material by Johnson, Matthey and Co., Ltd. Spectrographic analysis by Mr. J. G. Conway showed the sample to contain 0.6 percent Nd, but to be otherwise free of rare earth impurities.

The oxide was dissolved in 70 percent $HClO_4$, precipitated as the hydroxide by neutralization of the acid solution with NH_3 gas, dissolved in 3M $HClO_4$ and adsorbed on Dowex 50 resin (ammonium form, spherical, 250-500 mesh).

The resin containing the adsorbed praseodymium was transferred to the top of a cylindrical column of resin, 5.4 cm in diameter and 21 cm in length. The praseodymium was then eluted from the column with a 0.25 M solution of citric acid plus ammonium dihydrogen citrate (pH 3.0) at a flow rate of 0.061 ml/cm^2/min.

The praseodymium eluted from the column was precipitated from the citrate solution by the addition of oxalic acid. The oxalate was then ignited to the oxide. No impurities could be detected by spectrographic analysis of this material.

About 3 grams of fairly pure neodymium were further purified in similar manner starting with Nd_2O_3 furnished by Dr. Spedding of the Iowa State College, Institute for Atomic Research. Spectrographic analysis by Mr. J. G. Conway of the starting material showed 0.2 percent Pr and 0.1 percent Eu and after column separation no rare earth impurities could be detected.

A sample of terbium ($\sim$1 gram) was partially purified from a starting mixture containing 35 percent Tb and several percent each of Y, Gd, Dy, Ho and Sm. Column separation removed the rare earths other than dysprosium.

Heat of Solution of Praseodymium Sesquioxide

LeRoy Eyring and B. B. Cunningham

The heat of solution of Pr_2O_3(crystalline, c form) in 6M HNO_3 has been measured in an adiabatic microcalorimeter sensitive to $\pm$ 2 x 10^{-4} calories.

The mean value of the heat as determined in three runs is 106.03 $\pm$ 0.20 kcal/mole. The weights of the samples used in the different runs varied from about 4 to 7 milligrams.

The praseodymium used in these experiments had been purified as described in the preceding section of this report. Conversion to Pr_2O_3 was accomplished by reduction of the higher oxide (Pr_6O_{11}) with H_2 (1/3 atmos.) at 500°C.

Preparation of Praseodymium Hydride

LeRoy Eyring and B. B. Cunningham

Praseodymium hydride (probably PrH_3) has been prepared by reacting praseodymium metal with hydrogen according to the following reaction:

$$Pr \xrightarrow[240^{\circ}C]{H_2\ (1/3\ atmos.)} Pr\ hydride$$

The x-ray diffraction pattern has not yet been interpreted. The hydride was prepared from pure praseodymium metal which is being successfully made on the milligram scale according to the following procedure:

1) Reduction of highly purified praseodymium in the form of its higher oxide to the pure sesquioxide, by the reaction:

$$Pr_6O_{11} \xrightarrow[500^{\circ}C]{H_2(1/3\ atmos.)} Pr_2O_3$$

2) Conversion of the sesquioxide to the trifluoride by the reaction:

$$Pr_2O_3 \xrightarrow[700^{\circ}C]{H_2(0.5\ atmos.) + HF(0.5\ atmos.)} PrF_3$$

3) Reduction of the trifluride to the metal with Ba vapor in a double crucible system in vacuum:

$$PrF_3 \xrightarrow[\sim 1100^{\circ}C]{Ba} Pr$$

High Temperature Equilibria in the Oxide systems of Praseodymium

L. B. Asprey and B. B. Cunningham

Previous work (see UCRL 172) with a simple quartz cantilever balance loaded with milligram samples of praseodymium oxide, which were maintained at elevated temperatures in the presence of various partial pressures of oxygen indicated that there exist considerable ranges of solid solution formation between the oxides Pr_2O_3 and PrO_2. An apparatus has been constructed to investigate this phenomenon in more detail, and in particular to secure data from which to derive heat and free energy functions that will describe the thermodynamics of the system over the range of composition: $PrO_{1.5}$ - PrO_2.

The apparatus, illustrated in diagrammatic form in Figure 1, is constructed as follows:

The sample (a known weight of Pr_2O_3) is placed in a quartz capillary and connected through capillary tubing to a mercury manometer. A section of the connecting tubing dips into a cold trap designed to prevent mercury vapor from entering the hot section of the apparatus. The free volume of the system (at any level of mercury in the manometer) is known from previous calibration.

Following the introduction of the sample the system is evacuated through a side tube provided with a capillary stopcock. During this time the sample is kept hot to permit thorough degassing. The sample is then cooled and a known pressure of oxygen is admitted to the system. The sample is heated to promote reaction with the added oxygen, and cooled to room temperature. Any residual oxygen is pumped off at room temperature. The quantity of oxygen absorbed by the sample is computed. The temperature is then adjusted to some desired value and the pressure of oxygen at this temperature is measured by reading the manometer. Sufficient time is allowed for equilibrium to be established. A final computation of the composition of the sample in equilibrium with this measured pressure of oxygen is made.

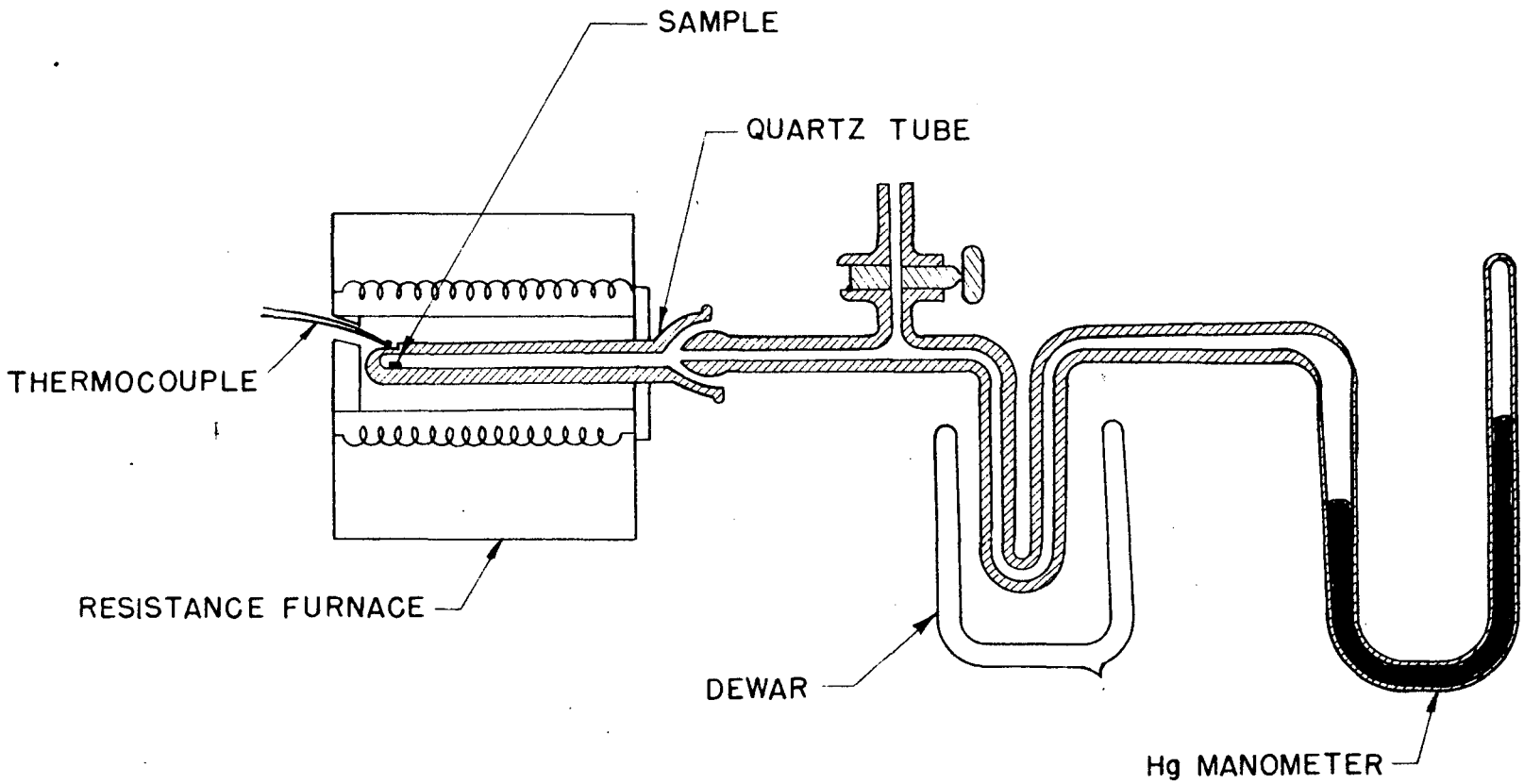
In preliminary runs to establish the general validity of measurements made with this apparatus, the vapor pressure of oxygen over the system CuO, Cu_2O was measured as a function of temperature. (There is no solid solution formation between these oxides). The data were used to compute the heat of the reaction:

$$CuO \longrightarrow 1/2\ Cu_2O + 1/4\ O_2$$

The value obtained was ΔH_{298} = 33.42 kcals/mole. The agreement with the accurate accepted value of ΔH_{298} = 33.490 kcal/mole is regarded as quite satisfactory.

Some preliminary data obtained on praseodymium oxide is shown graphically in Figure 2.

A very large number of measurements will be necessary in order to establish 1) the vapor pressure of oxygen over praseodymium oxides of various fixed compositions as a function of temperature, and 2) the vapor pressure of oxygen at various fixed temperatures as a function of composition.



APPARATUS FOR MEASURING THE VAPOR PRESSURE OF OXYGEN OVER PRASEODYMIUM OXIDE.

FIG. 1

13194-1

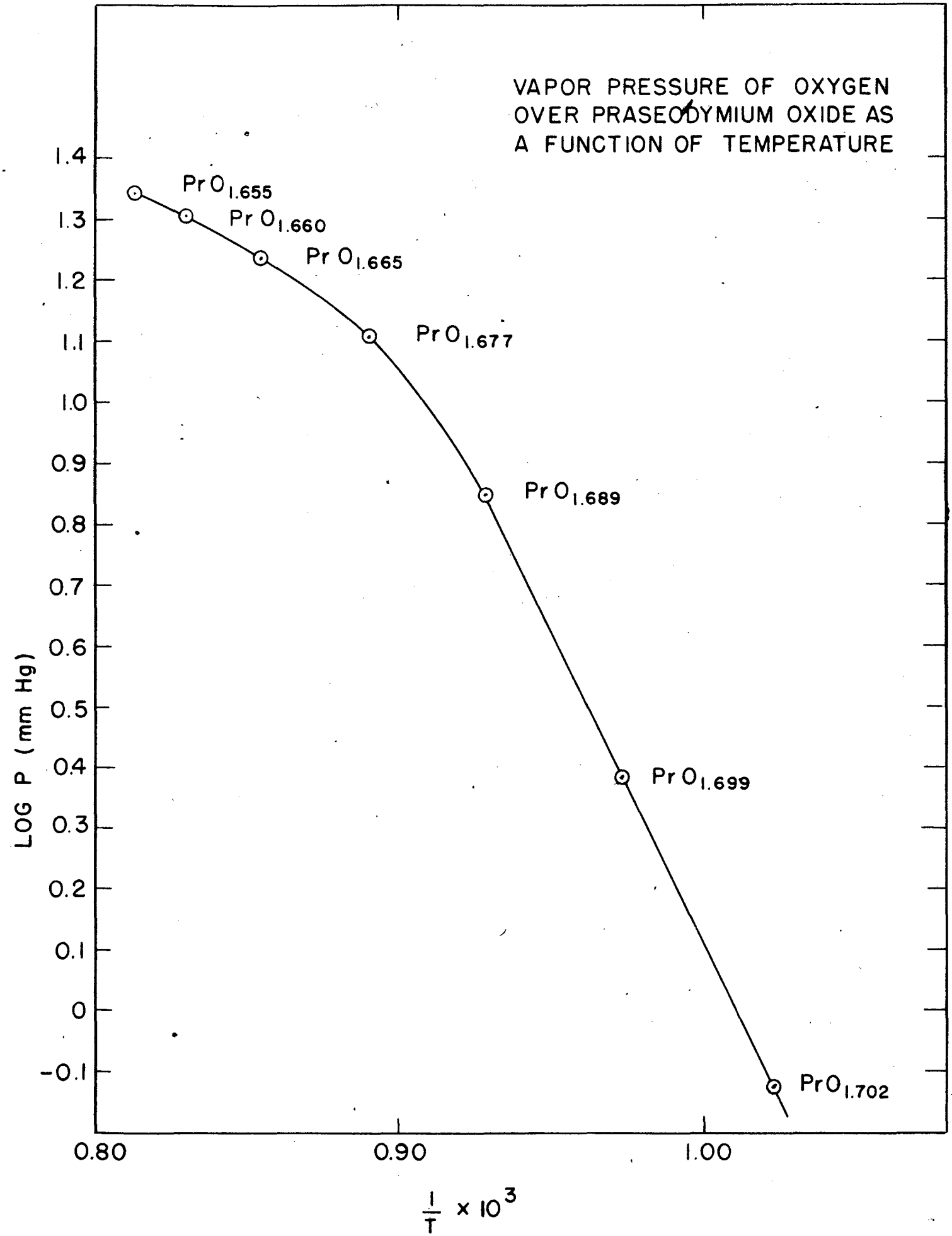

VAPOR PRESSURE OF OXYGEN
OVER PRASEODYMIUM OXIDE AS
A FUNCTION OF TEMPERATURE
PrO1.655
PrO1.660
PrO1.665
PrO1.677
PrO1.689
PrO1.699
PrO1.702
LOG P (mm Hg)
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
0.80
0.90
1.00
1/T x 10^3

FIG. 2

13193-1

Crystal Structure of Samarium Oxychloride (Correction)

In UCRL 172, page 6, the crystal structure of SmOCl was incorrectly reported as cubic. The structure is tetragonal, similar to other rare earth oxychlorides.

Vapor Phase hydrolysis of Lanthanum trichloride

Abraham Broido and B. B. Cunningham

A knowledge of the vapor phase hydrolysis constants of the lanthanide and actinide trichlorides would be of value in designing apparatus for the production of the trichlorides, since the greatest difficulty in the preparation of these compounds generally is due to formation of the oxychlorides.

An apparatus has been constructed for measuring the equilibrium constant for the reaction:-

$$LaCl_3 + H_2O = LaOCl + 2HCl$$

A preliminary run suggests that the equilibrium constant is of the order of magnitude of 13 at 500°C.

Absorption Spectrum of Solid $NdCl_3$

Betsy Jones and B. B. Cunningham

Considerable work has been done to determine the feasibility of using a microscope to project the image of a small rare earth crystal on the slit of the spectrograph.

The best results obtained with $NdCl_3$ and $EuCl_3$ indicate that the lanthanide absorption spectra are not sufficiently intense for this method to be applicable. The crystal thickness found necessary for lanthanides is ca. 2 mm, and with a solid of this thickness better results are obtained by placing it directly in front of the slit, which has been masked down to about 0.5 cm, than by projecting the image on the slit.

However, these results do not mean the elimination of the microscope method, since the estimated thickness required for actinide solids is only 0.2 mm.

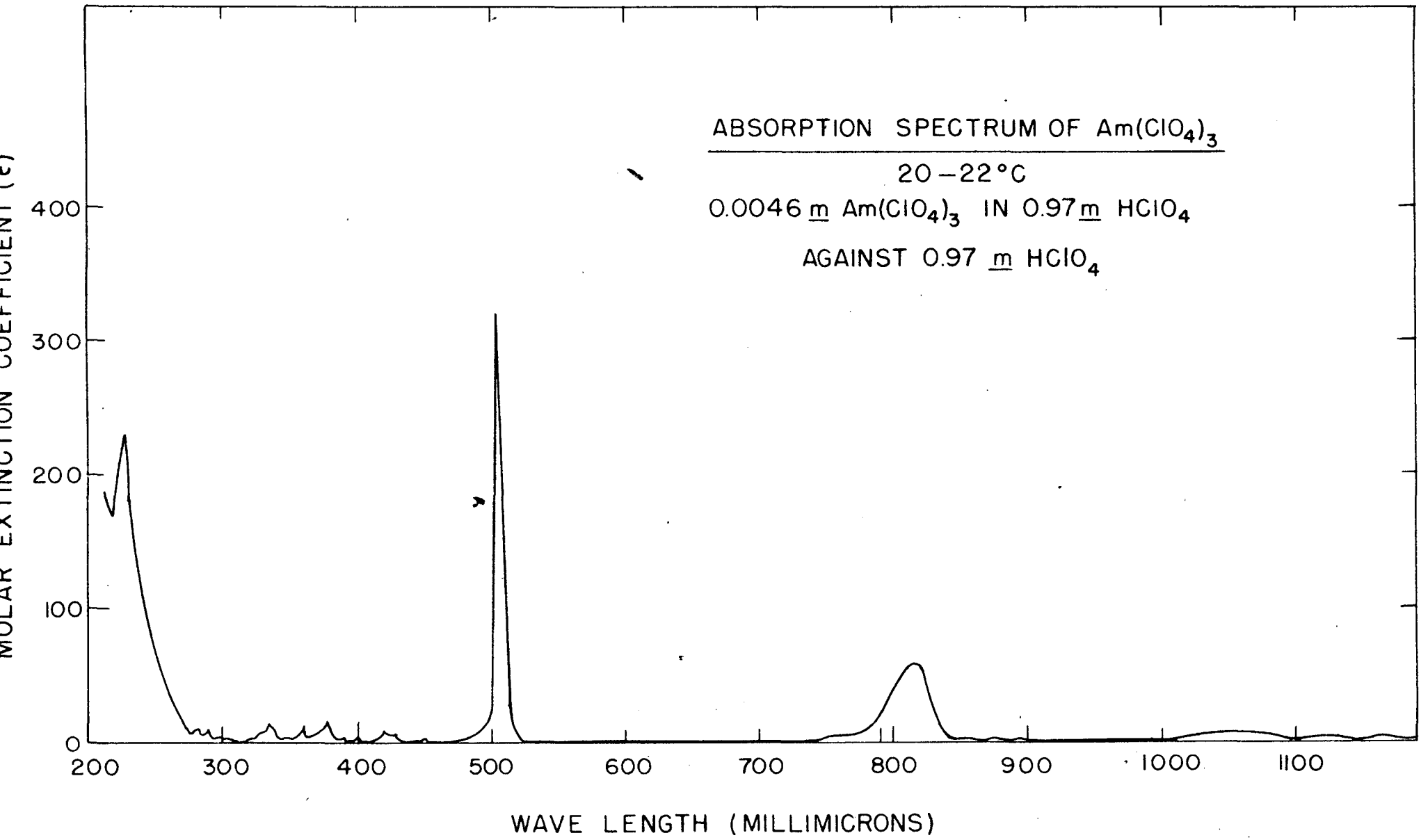

ABSORPTION SPECTRUM OF $Am(ClO_4)_3$
20 – 22 °C
0.0046 m $Am(ClO_4)_3$ IN 0.97 m $HClO_4$
AGAINST 0.97 m $HClO_4$
MOLAR EXTINCTION COEFFICIENT (ε)
400
300
200
100
0
200
300
400
500
600
700
800
900
1000
1100
WAVE LENGTH (MILLIMICRONS)

FIG. 1

Ion Exchange Separation of Zirconium and Hafnium

K. Street and G.T. Seaborg

In the course of a rather cursory examination of the elution of tetrapositive ions from the cation exchange resin Dowex 50 with hydrochloric acid solutions, we have found a very effective method of separating zirconium from hafnium.

The conditions which give satisfactory separation were first worked out using microgram amounts of material and the radioactive tracer technique. Subsequent runs with milligrams of material demonstrate the applicability of the method to the production of significant amounts of pure hafnium and zirconium (see Fig. 1).

The column used for the separation of 50 mg. amounts of zirconium and hafnium was 1 sq. cm in cross sectional area and 30 cm long, packed with 250 - 500 mesh Dowex 50, and converted to the hydrogen form by washing with 6 M HCl.

In the first few runs the ZrO_2 and HfO_2 were dissolved in mixtures of HF and HNO_3 or HF and H_2SO_4 and the oxychlorides crystallized from concentrated HCl. The material was put on the resin by dissolving approximately 50 mg. in 30 ml. 2 M $HClO_4$, equilibrating with 1 ml. of resin (~80 percent goes on resin), and placing the resin on top of the column. Since for a continuous flow process, it is necessary to put the material on the column in a narrow band by passing through a colloid-free solution of zirconium and hafnium; conditions under which this could be achieved were worked out. Although the above methods of solution apparently give colloid-free solutions with some samples of oxide, other require fusion with KHF_2. When the oxychlorides are dissolved in 4.5 M $HClO_4$ at concentrations of about 20 mg/ml and the solution passed through the column, the zirconium and hafnium are completely absorbed and subsequent elution with 6 M HCl gives effective separation.

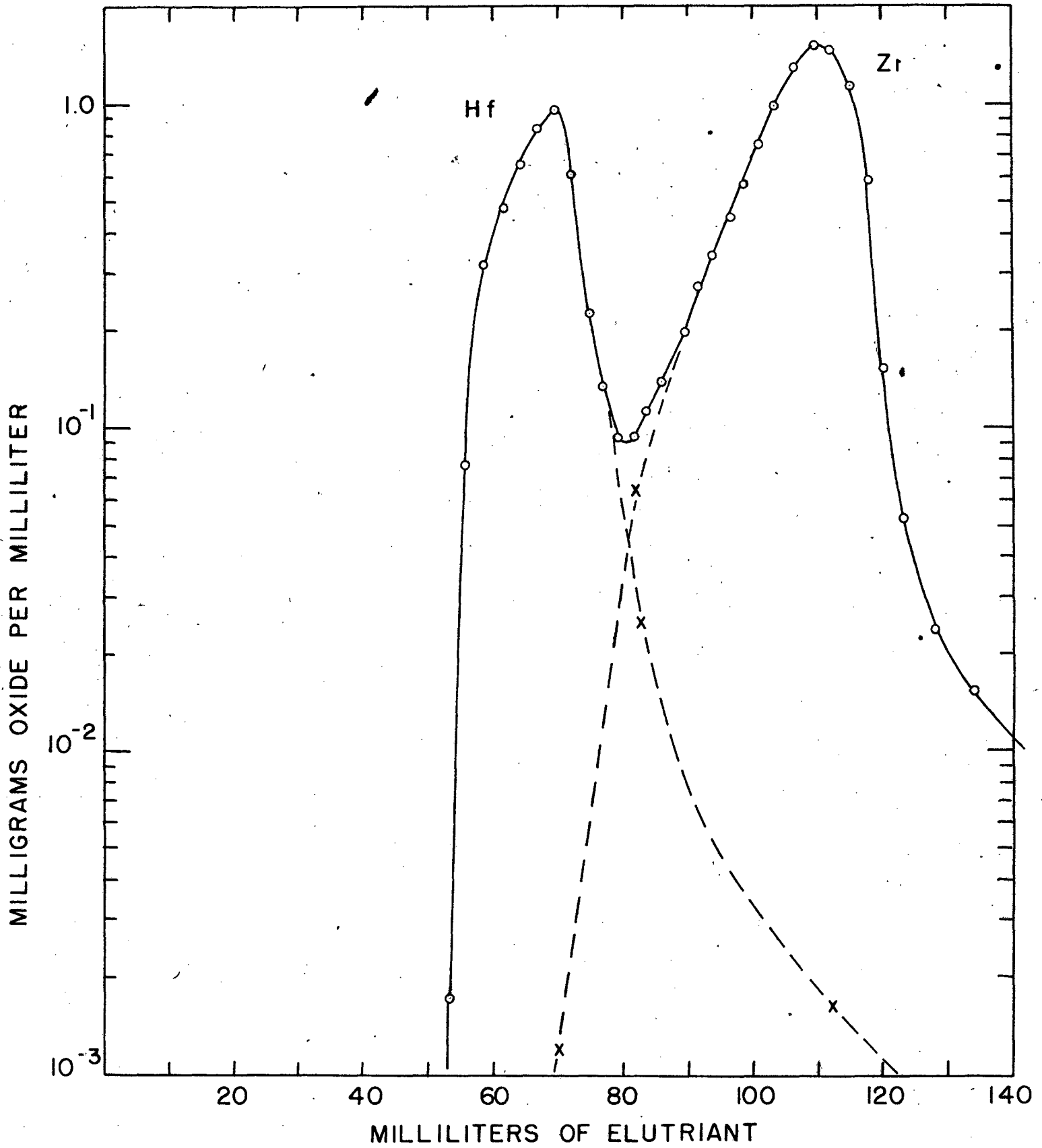


FIG. 1
ELUTION OF Zr AND Hf WITH 6.0 M HCl

1300

Separation of Zirconium and Hafnium by TTA Extraction

L. J. Beaufait and E. H. Huffman

A continuation of the studies on the extractions of Zr and Hf from 2 M $HClO_4$ has shown that the distribution ratio for Zr is about twenty times that for Hf for a given concentration of thenoyltrifluoroacetone (TTA) in benzene. In a constant acid concentration the equilibrium constant for the extraction may be expressed as

$$\log K = \log R - 4 \log [HT]$$

where R is the distribution ratio. After correcting for the solubility of TTA in the aqueous layer and using the activity coefficients for TTA in benzene found by King and Reas[1] the value for K_{Zr} was found to be 9.38×10^7 and for K_{Hf} 4.56×10^6 in 2 M $HClO_4$.

Successful purifications of Hf samples containing from 5 percent to 59 percent Zr have been made using this extraction.

---

[1] C. L. King and W. H. Reas Report BC-69 (July 1947)

B. Chemistry of the Actinide Elements

I. Perlman

Absorption Spectrum of Aqueous Am(III)

D. C. Stewart and B. B. Cunningham

The absorption spectrum of Am(III) in 0.97 M $HClO_4$ at an ionic strength of 1.0 has been determined in the region 214-1200 mμ, using the Beckman model DU spectrophotometer and special micro cells. The region 214-350 mμ had not been previously examined. The absorption curve is shown in Figure 1.

Absorption Spectrum of Aqueous Am(III) as determined with a Baird Grating Spectrograph

Betsy Jones and B. B. Cunningham

Use of the Baird grating spectrograph (see UCRL 172) permits the resolution of finer details of the absorption spectrum of Am(III) than does the use of the Beckman DU spectrophotometer, but does not yield a quantitative measure of the intensity of absorptions as readily as does the latter instrument.

As previously reported, using the Baird spectrograph, only the most intense absorption was observed with a 0.0046 M $Am(ClO_4)_3$ solution.

A new solution of Am(III) was prepared in which the concentration of Am^{+++} is ca. 0.042 M and that of $HClO_4$ ca. 0.51 M. americium solution with freshly prepared ammonium hydroxide. Then the precipitate was washed several times and dissolved in perchloric acid.

The absorption spectrum of this solution has been photographed in the region 2000A-9000A and the results are shown in Table I. The Am^{+++} spectrum lacks the structural detail observable in that of its 4f counterpart, Eu^{+++}. This appears to be the consequence of two factors. First, the solution is agitated by the radioactive decay, and, secondly, the 5f level appears to be relatively less shielded from external perturbations than the 4f level.

Table I

Absorption Spectrum of Am^{+++} (0.042 M)

λ (A)	Description
8133 ± 2	very broad
5165.7 ± 0.5	weak satellite
5103.7 ± 0.5	most intense absorption, resolved
5078.3 ± 0.5	only in more dilute solution (0.0046 M)
5030.0 ± 0.5	
4543.5 ± 0.5	4543.5 to 2432.6 are sharper and less intense
4287.4 ± 0.5	than those of longer wavelength and in appearance
4198.0 ± 0.5	are more similar to lanthanide absorption spectra.
4017.9 ± 0.5	
3784.0 ± 0.5	
3771.1 ± 0.5	
3756.0 ± 0.5	
3604.9 ± 0.5	
3391.5 ± 0.5	
3352.8 ± 0.5	
3311.5 ± 0.5	
2893.3 ± 0.5	
2861.2 ± 0.5	
2846.7 ± 0.5	
2825.6 ± 0.5	
2754.1 ± 0.5	
2705.4 ± 0.5	
2699.2 ± 0.5	
2650.7 ± 0.5	
2597.3 ± 0.5	
2536.9 ± 0.5	
2436.0 ± 0.5	
2432.6 ± 0.5	

Collateral Alpha-Decay Chains

W. W. Meinke, A. Ghiorso and G. T. Seaborg

Continuation of investigations previously reported [1,2] have led to numerous additions and revisions of energy and half-life values for the alpha decay chains. In addition, values for the electron-capture branching of Ac^{223} and Th^{225} have been determined by recoil collection methods.

More rapid chemical procedures have also been developed. It was found that by bombarding $Th(NO_3)_4 \cdot 4H_2O$ in the "jiffy probe" of the 184 inch cyclotron (at 1 atmosphere pressure and a beam reduction of ~ 10) and working with this salt rather than thorium metal, the time of solution and extraction of the target could be considerably reduced. It was found possible, by dissolving and extracting the target material in one operation to start counting an aliquot of a pure Pa fraction in the alpha particle pulse analyzer 3.3 min. after the end of bombardment. This extra speed made possible much better values for the Pa^{226} series.

Table I summarizes our latest values for these collateral series data. The assignment of all members of the Pa^{228}, Pa^{227} and U^{229} series is definite. The members of the U^{228} and Pa^{226} series (except U^{228} itself) have been assigned according to α-decay systematics in this region.[3] Also included in the table for those members where the half-lives have not been measured are values predicted according to recent correlations between α-particle energies and corresponding half-lives.[4]

Some work has also been done on determining the alpha half-life of Pa^{230}. From recent correlations[4] it was predicted that the alpha half-life should be a few thousand years. Actinium was separated from a large amount of Pa^{230}, and the Ac^{226} (from alpha decay of Pa^{230}) identified by the alpha energy of its 30-min. Th^{226} daughter, decaying with the 1 day half-life of the Ac^{226} parent.

We obtained $\sim 3 \times 10^7$ dis/min of pure Pa^{230} (plus probably an equal amount of Pa^{233}) by a low energy deuteron bombardment of Th metal (~ 10 microampere hours of 60 Mev deuterons on a thick target). From the Pa fraction (after the 1 day Ac^{226} had grown to equilibrium) we were able after several tries to obtain ~ 300 c/m of Th^{226} decaying with the half-life of the Ac^{226} parent. The Ac was separated by La^{+++} and Ce^{+++} fluoride precipitations and purified from thorium by repeated Zr phosphate precipitations. At the end of the procedure the Ce^{+++} was oxidized to Ce^{++++} by a bismuthate oxidation and the activity precipitated as a fluoride on the remaining small amount of La^{+++} carrier. The soluble chloride of the carrier gave a thin plate suitable for pulse analysis.

Rough chemical yield values, coupled with the value for the electron capture branching of Pa^{230}, $K/\beta - = \sim 10$, reported by Studier and Bruehlman[5] give a value of $\sim$ 2500 years for the alpha half-life of Pa^{230}. This value will eventually be checked with tracer to determine exactly the chemical yield.

---

1 W. W. Meinke, A. Ghiorso and G. T. Seaborg, UCRL-172 (Nov. 1948).
2 A. Ghiorso, W. W. Meinke and G. T. Seaborg, Phys. Rev. 74, 695 (1948).
3 I. Perlman, A. Ghiorso and G. T. Seaborg, Phys. Rev. 74, 1730 (1948).
4 I. Perlman, A. Ghiorso and G. T. Seaborg, unpublished work.
5 ANL-WMM-422 (Oct. 1948).

Table I

Collateral Series Data

Isotope	Radiation	Half-life	Energy (Mev)	K/α Branch
Pa^{228}	α	22 ± 1 hr.	6.09	50
Ac^{224}	α	2.9 ± .2 hr.	6.17	10
Fr^{220}	α	27.5 ± 1.5 sec.	6.69	
At^{216}	α	$\sim 3 \times 10^{-4}$ sec.	7.79	
Pa^{227}	α	38 ± 1 min.	6.46	.2
Ac^{223}	α	2.2 ± .1 min.	6.64	.001
Fr^{219}	α	~.02 sec.	7.30	
At^{215}	α	$\sim 10^{-4}$ sec.	8.00	
Pa^{226}	α	1.70 ± .15 min.	6.81	
Ac^{222}	α	~10 sec. (predicted)	6.96	
Fr^{218}	α	$\sim 10^{-2}$ sec. (predicted)	7.85	
At^{214}	α	$\sim 10^{-6}$ sec. (predicted)	8.78	
U^{229}	α	58 ± 3 min.	6.42	5
Th^{225}	α	7.8 ± .3 min.	6.57	.1
Ra^{221}	α	31 ± 1.5 sec.	6.71	
Em^{217}	α	$\sim 10^{-3}$ sec.	7.74	
U^{228}	α	9.3 ± .5 min.	6.72	.25
Th^{224}	α	~1 sec. (predicted)	7.20	
Ra^{220}	α	$\sim 10^{-2}$ sec. (predicted)	7.49	
Em^{216}	α	$\sim 10^{-5}$ sec. (predicted)	8.07	

Mass Assignments of Light Bismuth Isotopes

Henry Neumann and I. Perlman

A number of "milking" experiments have been performed on active Bi fractions obtained from bombardment of Pb with deuterons of high energy. The purpose of these experiments has been to obtain information as to the mass numbers of the light Bi α-emitters previously reported by observing genetic relationships with lead and thallium isotopes.

Bombardments of Pb were performed at deuteron energies of 60 Mev and 200 Mev. At 200 Mev, 4 α-activities are observed (1.7 min., 9 min., 25 min., and 62 min.), as was previously reported[1,2]. At 60 Mev only the 62 min. activity is observed in the α decay. The value for this half-life (62 ± 3 min.) is based on these α-decay measurements and is a better value than those previously reported.

The "milkings" were performed as follows: The Pb target was dissolved in HNO_3, the solution made 0.1N in acid by addition of KOH, and the active Bi electrochemically plated on a Ni foil immersed in the solution. The Ni foil (now containing Bi) was dissolved in HNO_3 and Pb periodically milked from Bi by precipitating BiOCl in presence of macro amounts of Pb and Tl, precipitating Pb from the resulting supernatant as $PbSO_4$ in presence of macro amounts of Bi and Tl, redissolving $PbSO_4$ and precipitating BiOCl from this solution, and precipitating $PbCrO_4$ from resulting supernatant. The Pb fractions so obtained were milked periodically for Tl by extraction of $TlCl_3$ into ether from solution 6N in HCl.

Bi fractions purified in time to contain the activities in question all yielded Geiger decay curves too complex to be resolved. The same was true for the Pb daughter fractions obtained from the 200 Mev deuteron bombardments. At 60 Mev the Pb decay resolved into 1 hr. Pb^{204M}, 52 hr. Pb^{203}, and an 8 ± 2 hr. activity.

Geiger decay of the Tl fractions was resolvable into various combinations of the known 1.8 hr. (Tl^{198}), 7 hr. (Tl^{199}) and 27 hr. (Tl^{200}) activities[3] (probable mass assignment in parentheses), and a 75 hr. activity. Only the 27 hr. and 75 hr. isotopes were observed in 60 Mev bombardments. Periodic milkings give a half-life value of 18 ± 4 hrs. for the Pb parent of 27 hr. Tl, and a value of 8 ± 2 hrs. for the Pb parent of 75 hr. Tl.

The same method gives a value of roughly 80 min. for the Pb parent of 7 hr. Tl. By following the decay of a Pb sample containing this activity through a 32 gm/cm^2 Pb absorber, fairly good resolution is obtained, giving a value of 100 min. for the half-life.

Because the Pb decay curves are in general not resolvable it has been impossible to obtain half-lives of Bi parents by milking experiments. The estimates of the Bi mass assignments have then been made on the basis of the Tl granddaughters obtainable from various Bi fractions. Thus Bi purified in time to contain the 9 min. activity has yielded 1.8 hr. Tl via the Pb intermediate, while Bi purified at times too late to contain the 9 min. activity does not yield 1.8 hr Tl. Bi fractions purified too late to contain the 62 min. activity have given 75 hr. Tl. Yields of all four Tl isotopes indicate that the half-lives of the corresponding Bi isotopes increase continually with increasing mass number.

From this evidence the most probable genetic relationships are:

	197	198	199	200	201	202	203
Bi	α,K(?) 1.7 min	K,α 9 min.	K,α 25 min.	K,α 62 min.	?	?	?
Pb	?	K <30 min.	K 70-100	K 18 hrs.	K 8 hrs.	? long	52 hrs.
Tl	?	K 1.8 hr.	K 7 hrs.	K 27 hrs.	? 75 hrs.	? 12 days	stable

75 hr. Tl has been placed at mass 201 with no positive evidence other than that Tl^{201} is unknown [the activity is not made with helium ions on gold (Au^{197})] , and that the 8 hr. half-life of the Pb parent is in accord with other evidence relating to Pb^{201}. 12 day Tl^{202} has never been observed in these experiments, confirming the belief that Pb^{202} is long-lived, and therefore making impossible any statement about the half-life of Bi^{202}.

Due to the low activity of the samples no accurate measurements of radiation characteristics have been made.

Aside from these light bismuth isotopes a number of those closer to Bi^{209} have never been observed and have been presumed to be long-lived. From some recent correlations of α-decay properties[4] it is obvious that Bi^{208} must be at least 2 Mev unstable with respect to Pb^{208}. This arises by closing the cycle involving the energies of α-decay and electron capture decay of At^{212} (estimated) and α-decay of ThC'^{212}. As a result of these predictions Bi^{208} (and by analogous reasoning, Bi^{207}) is being searched for as a short-lived electron capturing isotope.

Thus far, bombardments of PbO (natural isotopic composition) with ~18 Mev deuterons have been performed to investigate the possibility that Bi^{208} might be short-lived. No short activity was observed in a Bi fraction on which counting began 5-1/2 minutes after the end of a 2 min. bombardment. If short-lived, Bi^{208} must be less than 30 seconds, and such shorter periods are being investigated.

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1 D. H. Templeton and I. Perlman, Phys. Rev. 73, 1211 (1948)
2 Henry Neumann and I. Perlman UCRL 172, p. 40 (October 1948)
3 D. A. Orth, W. Heiman, L. Marquez, and D. H. Templeton, unpublished data (July 1948)
4 I. Perlman, A. Ghiorso and G. T. Seaborg, Phys. Rev. 74, 1730 (1948)

Isotopes of Tin

A. S. Newton and W. R. McDonell

A study of the beta-emitting isotopes of tin has made it possible to made some provisional isotopic assignments. A 28-hour period was previously assigned to Sn^{121} by Lindner and Perlman[1]. Other periods known to be formed in the bombardment of Sn are 10 minutes, 40 minutes, 10 days and 130 days. The 10-minute period was not studied in this research. Bombardments of separated isotopes of Sn, Sn^{120} and Sn^{124}, with deuterons have shown that the "40-minute" period is actually two periods of half-lives, 36 minutes and 39 minutes, respectively. The 36-minute period has a beta energy of about 3 Mev and is formed in comparable yield with the 28-hour period when Sn^{120} is bombarded with 14 Mev deuterons, no appreciable amount of longer-lived periods being formed. The 39-minute period formed by bombarding Sn^{124} (exact composition unknown) with 14 Mev D^+ has a beta energy of about 1.7 Mev, antimony x-rays are present as shown by critical absorption measurements in Cd, Pd and Ag. No 28-hour Sn is formed in this bombardment showing the Sn^{124} to be quite free from Sn^{120} contamination. The 39-minute period does not decay to the 2.7-year Sb^{125} since no Sb activity could be recovered from the tin fraction after decay of the 39-minute period. The 10-day and 130-day periods do not decay to a detectable Sb activity nor do they appear to emit x-rays of either Sn or Sb. Therefore at present, the best assignment appears to be to place the 36-minute and 28-hour periods as isomers at Sn^{121}, and the 39 minute, 10 day, and 130 day periods at Sn^{123}, the 39-minute period decaying to an excited state of Sb^{123} and the 10-day and 130-day periods decaying to the ground state of Sb^{123}.

A further check of these assignments will be possible when the longer-lived samples have decayed to the point where cross section calculations are possible.

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[1] M. Lindner and I. Perlman Phys. Rev. 73, 1124 (1948).

Fission Cross-section with High Energy Particles

R. L. Folger and G. T. Seaborg

The deuteron beam passing through a natural uranium foil target of known weight and area was measured for a one hour bombardment, and found to be 2.97×10^{-5} microampere-hour.

The target was dissolved in concentrated HCl containing 20 milligrams of Ba^{++} carrier. The barium was separated and purified, and then weighed as $BaCl_2 \cdot 2H_2O$. A chemical yield of approximately 90 percent was obtained.

The 12.8 day equilibrium decay curve was extrapolated back to zero time and corrected for counter geometry and growth of La^{140} daughter (growth factor 2.15). From the data obtained, the cross-section for the reaction $U\text{-}d_{(190\ Mev)} \longrightarrow Ba^{140}$ was determined to be 0.03 barn.

If the fission yield for Ba^{140} is assumed to be about 2 percent (the fission yield for Ba^{140} has been found to be approximately 2 percent from U + 380 Mev helium ions), the cross-section for the fission of natural uranium by 190 Mev deuterons is approximately 1.5 barns.

In the same irradiation R. Goeckermann obtained a cross-section of 0.2 barns for the fission of bismuth using for measurement Mo^{99} with its known fission yield.

Properties of Radium^{227}

R. L. Folger and G. T. Seaborg

The existence of Ra^{227} as a β^- -emitter of moderately short half-life had been predicted and its presence indirectly verified by the removal of Ac^{227} from neutron irradiated radium[1]. The reactions are:

$$Ra^{226} \quad (n, \gamma) \quad Ra^{227}$$

$$Ra^{227} \xrightarrow{\beta^-} Ac^{227}$$

The presence of radium and its decay products precluded the possibility of observing Ra^{227} from this method of production. However, it was considered possible to prepare this activity by spallation of thorium with high energy deuterons.

Strips of thorium foil were bombarded in the 184-inch Berkeley cyclotron for 1 hour with 190 Mev deuterons. The target was dissolved in concentrated HCl containing 1.5 milligrams of Ba^{++} carrier

The Ba-Ra fraction was separated from the target material and purified by means of sulfide insoluble scavengers and successive precipitations of $BaCl_2$ using HCl gas and HCl-ether reagent. The final precipitate (made with $CO_3^{=}$) was dissolved in 0.1 N HCl and the solution equilibrated with 140 mesh Dowex 50 resin.

The resin was mounted at the top of an ion-exchange column of similar material which was then eluted with 0.5M ammonium citrate at pH 7.75 (See Tompkins, E. R., AECD-1998). The radium fraction was located by means of its alpha-activity. On the basis of alpha-decay curves and alpha pulse analysis, Ra^{223} and Ra^{224} (ThX) were identified.

The beta-decay of the radium fraction showed the presence of a β^- emitter with half-life of approximately 2 hours and β^- energy in the range 0.7-1.2 Mev. This activity appears to be from the relatively short-lived Ra^{227} known as the parent of Ac^{227}.

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[1] S. Peterson PPR Vol 14B, Paper No. 19.9 (to be issued)

Yields of Mn^{52} and Mn^{56} in the Deuteron Bombardment of Various Elements

W. C. Orr

The yields of two isotopes of manganese (52 and 56) produced in the high energy deuteron bombardment of fourteen different elements have been determined relative to one another, in the expectation that such information may contribute to a better understanding of the nuclear reaction processes occurring.

All elements in the periodic table from chromium (atomic no. 24) to strontium (atomic no. 38), with the exception of krypton, have been bombarded with 190 Mev deuterons in the 184-inch cyclotron. The targets consisted of strips of metal foil where possible, but in other cases suitable samples were packaged in thin aluminum foil envelopes. The bombardments of chromium, manganese, iron, cobalt, nickel, copper, zinc, germanium, arsenic, selenium and strontium were previously described by N. A. Bonner[1]. More recently gallium, bromine and rubidium have been bombarded, and the bombardments of chromium, arsenic and selenium repeated.

In order to compare the yield obtained in one bombardment with that of another, a monitor foil of copper was cut to the exact area of each target and placed behind it in the deuteron beam. Whatever fraction of the beam penetrated the target in a given bombardment also passed through the monitor, and the activity of Cu^{64}, induced in the latter served, therefore, to measure the intensity of the bombardment and to relate the yield in one case with that in another.

Observation of the decay of certain of the samples is not complete, but the following table gives the results at present available. Many of the values are subject to future correction. The counting efficiency for Mn^{52} has been taken as 40 percent. The data is being presented here without interpretation.

Element Bombarded	Yield Relative to Cu^{64} from Copper	
	Mn^{52}	Mn^{56}
Chromium	0.094	0.000
Manganese	2.2	0.30
Iron	2.6	0.42
Cobalt	2.1	1.07
Nickel	2.2	0.31
Copper	0.55	0.33
Zinc	0.31	0.13
Gallium	0.047	0.13
Germanium	0.008	0.048
Arsenic	0.0027	0.013
Selenium	0.00055	0.019
Bromine	0.00020	0.0029
Strontium	<0.000018	0.00006

[1] N. A. Bonner, Report UCRL 172, p. 54 (October 1948)

Neutron Deficient Rare Earth Isotopes and Those of Hf, Ta, W and Re

G. Wilkinson and H. Hicks

The study of the light radioactive rare earth isotopes and those of Hf, Ta, W, and Re has been continued. The following isotopes have been characterized:

Isotope	Type of Radiation	Half-life	Energy of Radiation Particles	γ-rays	Produced by
Nd^{140}	K	3.3 days			Pr-d-3n
Nd^{141}	β^+ K, γ (3 %)	145 ± 4 min.	β^+ 0.7	K x-rays 1.05	Pr-p-n Pr-d-2n
Pm^{143}	K, γ	~350 days	no e^-	K, Lx-rays 0.95	Pr-α-2n
Pm^{144}	β^+	4.1 hours	β^+ 1.2		Pr-α-n
Lu^{173}	K	6.9 days	e^- 0.14 0.6		decay of Hf^{173}
Hf^{172}	K	22 hours	0.14 0.25		Yb-α-3n
Hf^{173}	K	>100 days	e^- 0.35		Ta-d-2zl0a
Hf^{175}	K, e^- γ	70 days	e^- 0.3	L, K 0.35, 1.5	Lu-p-n Lu-d-2n
Ta^{179}		~60 days	0.1 0.3		Hf-d-n, 2n-3n
W^{179}		38.5 min.			Ta-d-4n

Decays of activities from the following bombardments are still being followed and have not been resolved:

Pr + α, Nd + α, Sm + p, Eu + α, Gd + p, Dy + α, Dy + p,
Ho + α, Ho + p, Er + p, Tm + α, Yb + α, Ta + α, Ta + d, and Re + fast neutrons.

Neodymium Isotopes. The 145 minute β^+ and 3.3 day activities were proved to be neodymium isotopes by ion exchange resin column separations. The 145 minute activity was allocated to Nd^{141} and the 3.3 day activity, to Nd^{140} by results of bombardments of 10 and 20 Mev deuterons on praseodymium.

Promethium Isotopes. The 4 hour β^+ activity was allocated to Pm^{144} and the 350-day K-capture activity to Pm^{143} by results of bombardments of praseodymium with 38, 31 and 20 Mev He^{++}. It is probable that Pm^{142} is too short-lived to be seen in these

bombardments.

Lu^{173}. This 6.9 day K-capturing isotope was milked repeatedly from the >100 day hafnium activity mentioned below. The radiation characteristics are different from those of the previously reported 9 day Lu^{171}.

Hafnium Isotopes. A 70 day K-capturing isotope of hafnium was found by bombarding natural lutecium with protons and deuterons. No shorter periods have been found. The allocation made on the basis of these bombardments was Hf^{175}.

From the spallation of tantalum, as hafnium K-capture activity of greater than 100 days was separated. The lutecium daughter showed radiations characteristics and decay of 6.9 days, and on this basis, the isotope was allocated to Hf^{173}.

A 22 hr. K-capture activity was found in the hafnium fraction of the bombardment of ytterbium with 38 Mev He^{++}. The preliminary allocation is Hf^{172}.

Ta^{179}. A tantalum K-capture activity of half-life of about 60 days was found in the bombardment of hafnium with 20 Mev deuterons, and was allocated to mass 179.

W^{179}. The bombardment of tantalum with 40 Mev deuterons produced a 38.5 minute activity in the tungsten fraction. This was allocated to W^{179}. The 135 minute activity previously observed with 60 and 50 Mev deuterons has been reallocated to W^{177}.

Neutron Deficient Cesium Isotopes

R. W. Fink, D. H. Templeton and F. L. Reynolds

Two new neutron deficient isotopes of cesium have been prepared by bombarding I^{127} as ammonium iodide with 40 Mev alpha particles from the 60-inch cyclotron and 60 Mev alpha particles from the 184-inch cyclotron. These isotopes are tentatively assigned as follows:

$$Cs^{127} \xrightarrow[5.5\ h]{\beta^+} Xe^{127} \xrightarrow[34\ d]{K} I^{127}\ \text{(stable)}$$

$$Cs^{129} \xrightarrow[31\ h]{K} Xe^{129}\ \text{(stable)}$$

These assignments are based on the following observations. With 40 Mev alpha particles, only the 31-hour activity was found. At 60 Mev, both cesium isotopes were observed. The 34-day xenon was shown to be the daughter of the shorter-lived cesium isotope by its absence in the 40 Mev bombardment, its presence in all fractions which contained purified 5.5-hour cesium, and its absence in the same fractions if repurified after the 5.5-hour activity was dead. Gas pumped from the 5.5-hour cesium and sealed in a glass bulb showed the 34-day xenon activity and no other. The half-lives in cesium fractions were observed as about 20 days, due to loss of xenon by diffusion through the scotch tape covering the samples. The 34-day xenon has been assigned to Xe^{127} by previous work[1,2,3]. Thus the 5.5-hour cesium is Cs^{127}. The 31-hour activity must be heavier, and is therefore Cs^{128}, Cs^{129}, or Cs^{130}.

A mass spectrograph plate showed stable Cs^{133} and two faint lines at masses 127 and 129. There was not enough radioactivity to mark a transfer plate, so the identification of these lines with the radioactive materials has not been established, but the assignments to Cs^{127} and Cs^{129} are in agreement with all the observed facts.

A number of experiments with the mass spectrograph have resulted in failure. The difficulty seems to be an excessive loss of the radioactive cesium in the chemical separation from ammonium bromide without inactive cesium carrier. Experiments are in progress to improve these techniques.

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[1] E. Creutz, L. A. Delsasso, R. B. Sutton, M. G. White and W. H. Barkas, Phys. Rev. 58, 481 (1940).

[2] M. Camac, Plutonium Project Report CC-2409 (October, 1944)

[3] R. Overstreet, L. Jacobson, K. Scott and J. G. Hamilton, Plutonium Project Report CH-379 (December, 1942).

Spallation Products of $_{33}As^{75} + D^{+}$ (190 Mev)

H. H. Hopkins, Jr. and B. B. Cunningham

The last quarterly report (UCRL 172) described the work which has been carried out in the past months; namely the determination of isotopic yields with greater accuracy. Varying yields obtained in previous bombardments are believed to have been caused by the volatilization of target material during bombardment, with resultant variation in the specific activity of the monitoring isotope, As^{72}. To obtain true yields, bombardment was performed at 25 percent of normal beam intensity; the target weight was unchanged. Elemental fractions were separated and yields of the following isotopes obtained: Mn^{56}, Fe^{59}, Co^{61}, Ni^{65}, Cu^{64}, Zn^{69}, Ge^{66}, Ge^{71}, and As^{72}. Data from all previous bombardments was re-examined, and the yields of isotopes of each element calculated relative to the particular isotope examined above. After averaging these intra-elemental yields, the yields relative to As^{72} have been recalculated.

The As fraction from the above bombardment was milked periodically and yielded 11.4-day Ge^{71}. These milkings furnish a measure of the yield of electron-capturing As^{71} (which is hidden in the As fraction). A half-life for As^{71} of 60 ± 4 hours was obtained.

Milking Ga from the Ge fraction yielded Ga^{66} and Ga^{67}, hence yields of Ge^{66} and Ge^{67}, which are difficult to see directly.

Since the yields of Ga^{67} relative to Ga^{66} showed apparent variation from bombardment to bombardment, it became evident that the counting efficiency of Ga^{67} is critical to the amount of absorber. From a bombardment As + D^{+} (190 Mev) the Ga fraction was removed with no added carrier and careful absorption measurements performed using a windowless counter. Previously used counting efficiencies were found to be too low. After applying the appropriate counting efficiency, agreement was found for the yield of Ga^{67} relative to Ga^{66} and As^{72}.

The mass numbers of the 55-minute As and 60-hour As are believed to be 71 in both cases, but this must be verified for the 55-minute period. The bombardment $Ge^{69+7} + D^{+}$ (10 Mev) yielded too little activity from (α,2n) to be definitive. A repetition of this experiment using 18 Mev D^{+} and milking Ge^{71} from the As fraction is now in progress.

Neutron Deficient Isotopes of Transuranium Elements

K. Street, D. Orth, and G. T. Seaborg

A 3 hour bombardment of 20 mg. of Pu^{239} with 80 Mev alphas has produced a light curium α-activity. The half-life is approximately 2-1/2 hours and the energy 6.50 Mev. On the basis of α energy and method of production the activity is probably Cm^{238}.

In two bombardments of U^{233} with 37 Mev He^{++}, pure plutonium fractions have been prepared by use of ion exchange columns. The principal isotope made is Pu^{234}, which had been previously reported as $T_{1/2}$ = 8 - 8.5 hours, α energy = 6.2 with electron capture branching. The α peak was followed on the pulse analyzer and gave a half-life of 9.5 hours, and alpha energy = 6.2. Very few x-rays were associated with these samples but even so the plot of total Geiger counts (e^- plus γ-rays) turned into ~4 day period indicative of Np^{234} arising from electron capture branching. Based principally on the yield of Np^{234} the branched decay of Pu^{234} approximates the ratio K/α = 1, but this must be considered to be a very rough value.

Pulse Analysis Using a Cathode-Ray Tube

William E. Glenn, Jr.

An invaluable tool for the study of radioactive isotopes is the pulse analyzer. This is a device which makes it possible to plot a graph of alpha-particle energy against the number of particles emitted of that energy. Since a radioactive element which emits alpha-particles emits them in discrete energies, it is possible to detect the presence of extremely small quantities of such elements by analyzing the pulse height distribution of the pulses from an ionization chamber in which the sample has been placed.

The purpose of this project is to develop a pulse analyzer which is more reliable, more accurate, and faster than the ones used at present.

One of the outstanding difficulties with the present pulse analyzer is that of the drift of individual channels because of a drift in bias or tube characteristic in that channel. This is a much more serious difficulty than that of drift of the whole system, since it will give a false peak in the alpha spectrum which cannot be distinguished from a peak due to a radioactive isotope. By the use of a cathode-ray tube pulse height selector, this difficulty can be eliminated. Such a pulse height selector is shown in Fig. 1.

The pulse (a) from the ionization chamber (3) is shaped so that it has a flat top (b) and is applied to the deflection electrode (8) of the cathode-ray gun. The electron beam, which is normally off, is turned on at the peak of the pulse by a square pulse applied to the intensity grid (5) of the electron gun. The beam is then turned on at a position corresponding to the height of the applied pulse. A series of anodes (10) across the screen of the cathode-ray tube collect the current from the beam, and a series of mechanical registers(12) count the number of times the beam strikes a given plate. This gives a count of the number of pulses which occur between two given pulse heights.

Since the channel width and relative position is a function only of the physical width and position of the anodes in the tube, there can be no individual register drift. This type of pulse analyzer can be made to be much faster than the present one which is limited by the dead time of the thyratrons in the circuit. This system has the added advantages of being more easily stabilized and being more versatile in application than the present type.

The entire system seems to work satisfactorily. Test pulses of a constant height would trip a mechanical register connected to a plate corresponding to the pulse height. The device had sufficient resolution so that test pulses would always trip either one register or the adjacent but never both.

One of the more important circuits developed for this device was the pulse shaping circuit used in the pulse analyzer.

After the pulse from the ionization chamber has been amplified, it is a broad triangular pulse as shown in Fig. 2 (a). The pulse must then be shaped for two reasons:

(1) Since the pulse has a long decay time, a pulse occurring before the preceding pulse has returned to zero voltage, will register an incorrect pulse height. It is therefore necessary to have the pulse return to zero as soon as possible.

(2) Since the random noise is uniformly distributed over all frequencies, it has an RMS amplitude proportional to the square root of the band width. The signal to noise ratio will therefore be increased if the pulse height is preserved and the band width of the shaper is reduced.

The circuit diagram for the pulse shaper is shown in Fig. 2.

The pulse is applied to the grid (a) of the cathode follower shaper. Since the cathode follower has an impedance from cathode to ground of about 100 ohms, the cathode potential will rise to approximately the grid potential. The characteristic impedance of the lumped constant delay line (D_1) is 1000 ohms. The resistance R_1, is adjusted so that the output impedance from point (b) to ground without delay line connected is 1000 ohms. When the pulse is applied to the grid (a) of the triode, the voltage (b) across the delay line will rise to half the grid voltage. The signal reflects from the open end of the delay line 22 microseconds later in the same phase as the applied pulse. The voltage at point (B) will, therefore, rise to the full grid voltage 22 microseconds later, after the signal has traversed the delay line and returned. Since the impedance across the input of the delay line is its characteristic impedance, there will be no further reflections. The voltage appearing across R_1, and consequently across R_2 (since the same current flows through both), will be the difference of the voltage at (a) and the voltage at (b). This difference is a square pulse (c), which has a height proportional to the height of the input and a pulse width of twice the delay time of the delay line.

The signal to noise ratio of the signal is increased by this type of shaper, since it attenuates the low frequencies. The frequency response of this shaper for low frequencies (about a tenth the reciprocal of the delay time) is approximately proportional to the frequency. This attenuation of the low frequencies not only reduces the RMS value of the random noise but also attenuates hum and tube michrophonic noise considerably.

It is imperative that the pulse output be perfectly flat on top for the cathode-ray analyzer tube, since the beam must be stationary at the peak of the pulse while it is turned on. Using a flat pulse has also improved the stability of the biased thyratron-controlled pulse analyzer in use in this laboratory.

To insure that the pulse is flat on top but still preserves its pulse height, a pulse flattener circuit was developed. In this circuit, shown in Fig. 2, the pulse is applied to a cathode follower (T_5), and the pulse voltage is divided by two resistors (R_3 and R_4) in the cathode circuit of the tube. The pulse appearing at point (f) will be a constant fraction of that appearing at (e). When the pulse rises to its maximum, the condenser (C_1) will be charged by current through the crystal diode (D_1) to the maximum voltage of the pulse at point (f). This maximum occurs at the leading edge of the pulse. The voltage across C_1 will remain at this potential until it is lowered to zero by current through the diode (D_2) at the trailing edge of the pulse. The polarity of the diodes is such that while the pulse is at its top there is no current through either diode to the condenser (C_1), since

point (f) will be at a lower potential than point (g) after the leading edge of the pulse, and point (e) will be at a higher potential until the trailing edge of the pulse. This circuit, therefore, gives a pulse output which is flat on top and has a pulse height proportional to that of the input pulse. A cathode follower (T_6) is used as an output stage for the pulse shaper in order that the output impedance may be low.

A complete system of this type is now being constructed for use as a pulse analyzer. Further application of the general principles of this system are described below.

A system is being constructed, as shown in Figure 3. In this system an ordinary cathode-ray tube (a) is used instead of the pulse analyzer tube, and photo-tubes (b) and (c) are used, instead of anodes, to detect the position of the beam, when it is turned on. This system has only two channels and is used for short half-life determinations.

The position at which the pulses are detected is adjusted by varying the position of the slots (d) and (e) in front of the phototubes (b) and (c). The width of the channel can be adjusted by varying the width of the slots (d) and (e). An RF signal is applied to the vertical deflection plates to spread the spot in the vertical direction so that it may be detected by either tube.

The photo-tubes used are electron multiplier tubes, type 931 A. These tubes give a voltage pulse output of several volts when a pulse of light appears on the fluorescent screen in front of it.

For measuring short half-lives of certain isotopes one slot (d) is set at the energy of an isotope emitting an alpha-particle, and the other slot (e) is set at the alpha energy of the daughter product. An isotope will decay by emitting an alpha-particle to another isotope, which will emit another alpha-particle. The time between these two alpha-particles is a measure of the half-life of the second isotope.

The pulse analyzer tube may be used as a device for measuring the time between these two pulses. A linear-triggered sweep may be tripped by the first alpha-particle pulse so that the beam of the cathode ray gun will sweep at a constant rate from one end of the series of anodes to the other. The beam, which is normally off, can then be turned on by the second alpha-particle pulse. The beam will then be turned on to an anode corresponding to the time between the two pulses. A plot of the counts appearing on the mechanical registers connected to these anodes will give a plot of the number of counts versus the time between pulses that is an exponential. This corresponds to the exponential decay of the second alpha-emitter. From this curve the half-life of this isotope can be calculated.

The pulse analyzer tube may have further application in the field of pulse modulation and electronic computors.

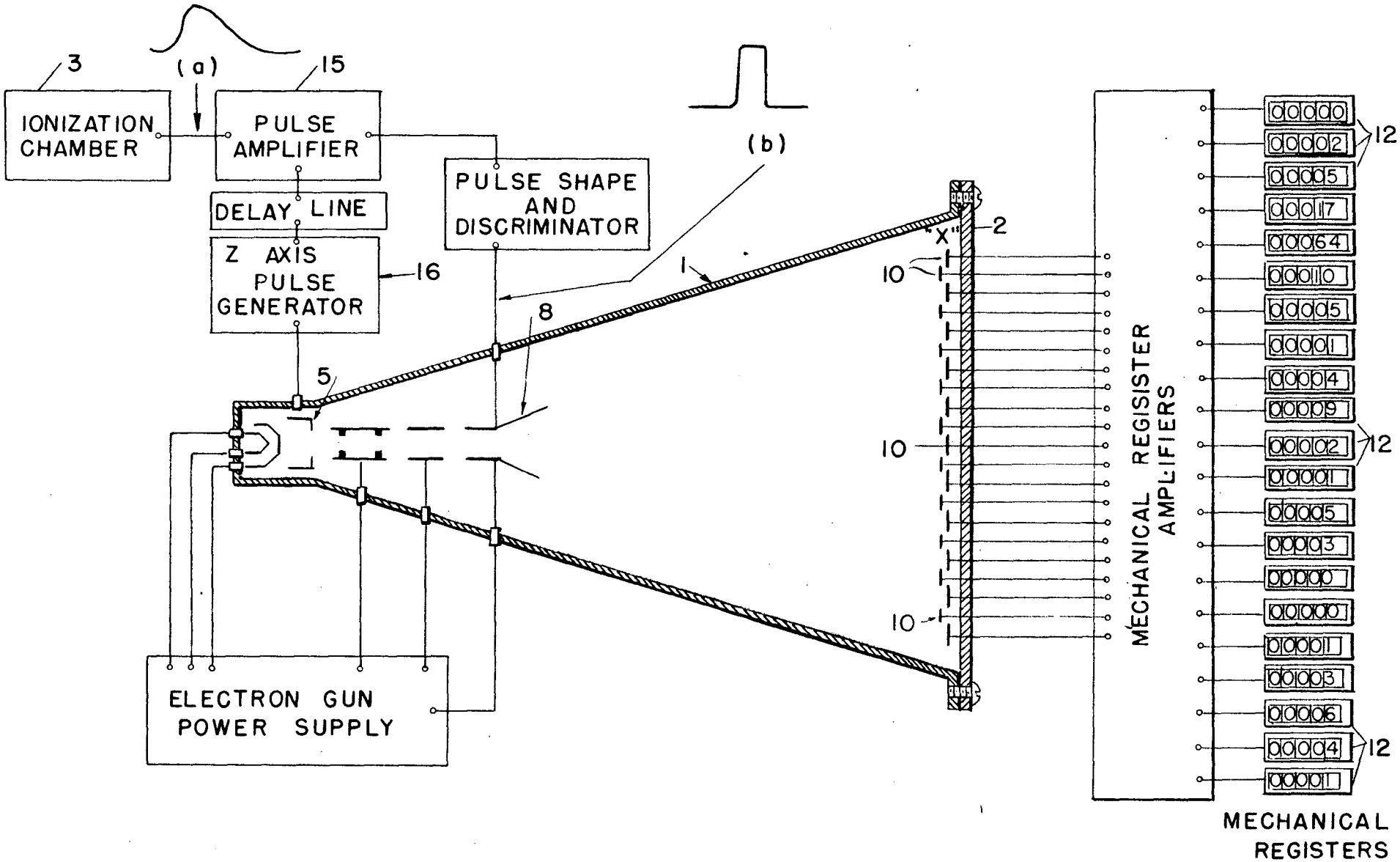


FIG. 1

MECHANICAL REGISTERS

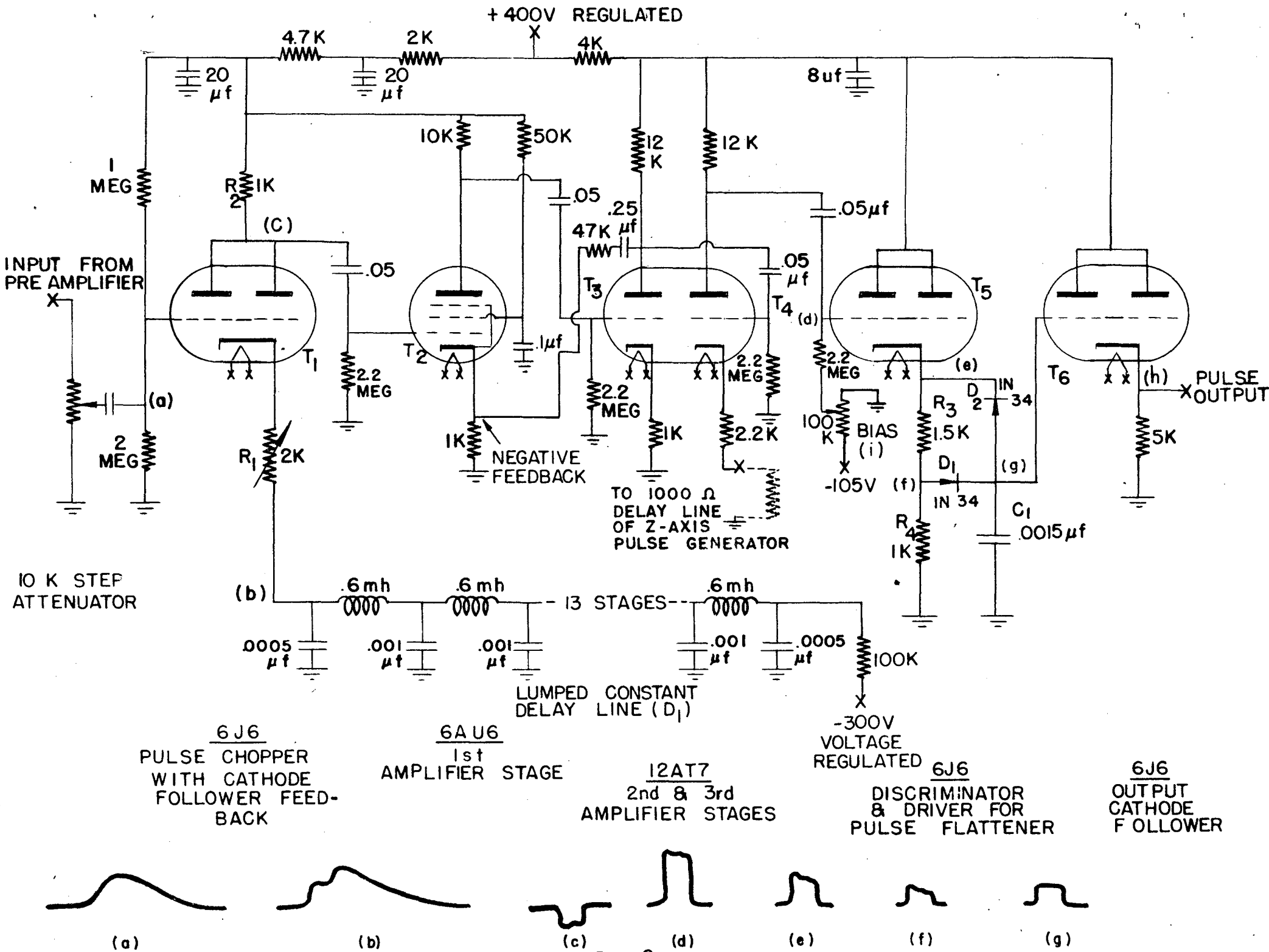


FIG. 2
PULSE SHAPER

13176-1

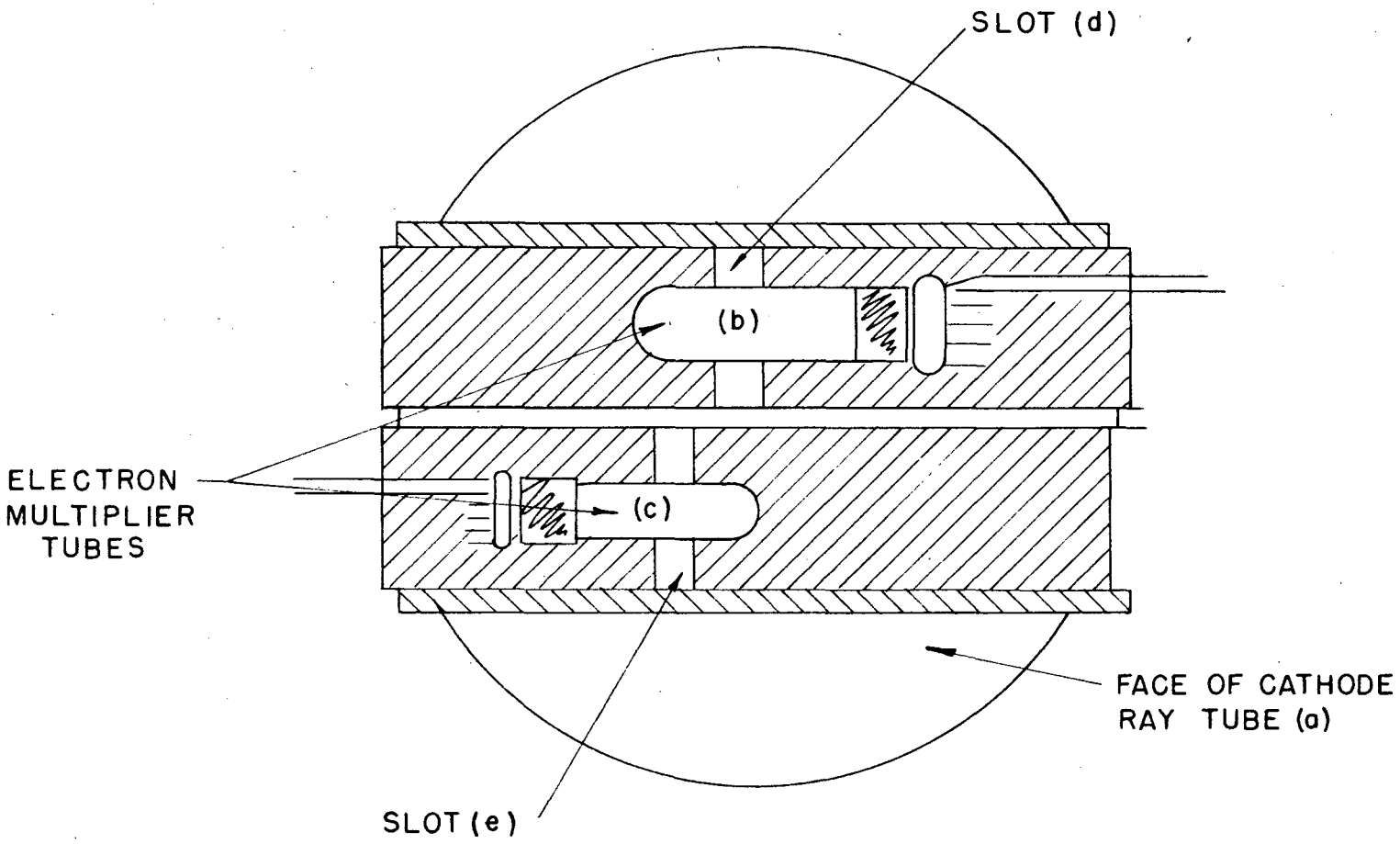


FIG. 3

PHOTOELECTRIC CELL SYSTEM

13174-1

Mass Spectrograph for Mass Assignment of Radioactive Isotopes

F. L. Reynolds

Most of this period has been devoted to the study of the efficiency of ionization of various substances using a thermal source as an ionization medium. The efficiency is the ratio of the amount of material in grams placed on the thermal source to the amount of material in grams collected at the receiver. This ratio, known as the "loss factor", differs for each substance and is probably a function of the ionization potential of the sample material, the surface work function of the filament and the temperature of the filament. The "loss factor" also includes the instrument transmission which is a fixed quantity with a given slit system. Some results are as follows:

Sample	Ion Species	Loss Factor
$RbNO_3$	Rb^+	8.7×10^1
$Ba(NO_3)_2$	Ba^+-BaO^+	1.6×10^6
$BaSO_4$	Ba^+-BaO	3.3×10^4
$Bi(NO_3)_3$	BiO^+	6.4×10^7
$PbSO_4$	PbO^+	$1. \times 10^6$
$TlNO_3$	TlO^+	$2. \times 10^8$
$Tl(NO_3)_3$	TlO^+	1.7×10^5
$SrSO_4$	Sr^+	1.7×10^5

This mass spectrograph was built primarily for the mass assignment of radioactive isotopes from cyclotron bombardments. We have in addition been able to use the instrument for rough abundance measurement work.

C. Chemistry of Astatine and the Preparation of Certain Compounds

R. F. Leininger and E. Segrè

Preparation Be F_2

The experiment by which the half-life of Be^7 was to be altered by chemical means (Segrè and Wiegand) is being repeated. Since inconclusive results were obtained when the half-lives of Be (metal) and BeO were compared the experiment is to be repeated using BeO and BeF.

To this end a method of preparation of pure BeF_2 was sought. The method listed by Gmelin was tried. It involved the thermal decomposition of $Be(NH_4)_2F_4$ in CO_2 at 800°C. The yields were low and the product difficult to recover due to its glass-like nature.

The method finally used was supplied by Dr. Wilhelm of Iowa State. The beryllium was precipitated from nitrate solution by ammonium hydroxide, washed and dried in a platinum boat at 100-120°C. When dry the sample was heated in a stream of anhydrous hydrofluoric acid for two hours at 200-225°C and finally sintered at 375-400°C for one hour. Yields approaching 100 percent were obtained.

Preparation of $Be^7 F_2$ and $Be^7 O$

Lithium was bombarded by protons from the 60 inch cyclotron to Be^7. The lithium was dissolved by HCl containing 20 milligrams of inactive Be. The beryllium was separated from the lithium by precipitation with ammonium hydroxide. The beryllium was purified by repeated separation from all possible active contamination. Finally the beryllium was converted to the basic acetate and extracted into chloroform, worked 3x with water, the chloroform evaporated, the residue beryllium converted to the hydroxide.

One-half of the hydroxide was ignited at 1000°C for 2 hours to produce the oxide and the other one-half was converted to the fluoride. The final samples have been prepared and the relative half-lives are being observed by E. Segrè and C. Wiegand.

Astatine Chemistry

Preliminary experiments indicate that astatine is taken up by Dowex 50 resin but that the absorption does not appear to be due to ion exchange.

Previously the carrying of astatine by Te when precipitated by SO_2 from 3NHCl was reported. By drying samples at constant geometry with respect to a Geiger Mueller counter it has been shown that the loss on drying amounts to less than 2 percent. This is a good technique to prepare samples of At for quantitative studies.

A detailed investigation of the distribution of astatine between aqueous and organic phases has been started. The astatine is being stabilized with respect to oxidation or reduction by using Fe^{++}-Fe^{+++} in H_2SO_4 0.1M to maintain equilibrium. No quantitative results have been obtained, however a dependence of the partition ratios upon astatine concentrations has been observed.

D. Bio-Organic Chemistry

B. M. Tolbert

Synthetic and Experimental Chemistry

M. Calvin, B. Tolbert, J. Reid, P. Adams, J. Bassham,

F. Christenson, A. Fry, D. Hughes, R. Ostwald, R. Selff and W. Tarpey

Distribution of C^{14} Labeled Compounds.

It is believed that the research work of the whole country will be greatly expedited and aided if labeled compounds from Project laboratories can be made available to workers in chemistry, biochemistry, biology, medicine and other sciences before development work would permit them to be available through non-government sponsored organizations. Therefore, a program for the synthesis of C^{14} labeled compounds to be distributed through the Isotopes Division of the Atomic Energy Commission has been set-up and we are preparing from 5-20 mc. batches of the following compounds for such distribution:

Glycine-1-C^{14}	Alanine-1-C^{14}
Glycine-2-C^{14}	Alanine-2-C^{14}
Sodium propionate-1-C^{14}	Calcium glycolate-1-C^{14}
Sodium propionate-2-C^{14}	Calcium glycolate-2-C^{14}
Sodium propionate-3-C^{14}	Propanol-1-C^{14}
Sodium butyrate-1-C^{14}	Propanol-2-C^{14}
Sodium valerate-1-C^{14}	Propyl bromide-1-C^{14}
Sodium caproate-1-C^{14}	Propyl bromide-2-C^{14}
Sodium heptanoate-1-C^{14}	Benzoic acid, carboxyl-labeled

Additional compounds will be added to the list from time to time as procedures for their preparation become routine in the laboratory.

Calcium Glycolate-C^{14}.

Glycolic acid, an important plant and animal biochemical intermediate, has been prepared labeled with C^{14} in the one-position and in the two-position in good yield on a 15 mmole scale. Sodium acetate labeled in either the one or the two-position was used as the starting material:

$$CH_3CO_2Na + HCl_{(g)} \longrightarrow CH_3CO_2H + NaCl$$

$$CH_3CO_2H + Cl_2 \xrightarrow[P_4,\ I_2]{\text{acetyl chloride}} ClCH_2CO_2H + HCl$$

$$2\ ClCH_2CO_2H + CaCO_3 \longrightarrow (HOCH_2CO_2)_2Ca + CaCl_2 + CO_2$$

The purity of the calcium glycolate was checked by (a) recrystallization from water and measurement of the specific activity, (b) paper chromatographic separation of the product which revealed only one radioactive compound, and (c) an elementary analysis which agreed well with the calculated values.

The data for the preparations of the two compounds are listed in Table I and Table II.

Table I

Preparation of Calcium Glycolate -1-C^{14}

		M.equiv.	Wt.,Mg.	Sp. Activity
Starting Materials	Sodium acetate	12.40	1001.5	0
	Sodium acetate	0.94	77.0	6.5 µc/mg
	Acetyl chloride	5.65	443.0	0
Product	1st crop 2 H_2O	8.69	982.0	0.24 µc/mg*
	2nd crop 2 H_2O	3.65	411.8	0.21 µc/mg

* - Theoretical = 0.23 µc/mg

Yield: 65.0 percent based on acetate used to begin synthesis or 61.7 percent based on $\overset{*}{C}O_2$. The yield of sodium acetate-1-C^{14} was 95 percent based on $\overset{*}{C}O_2$.

Table II

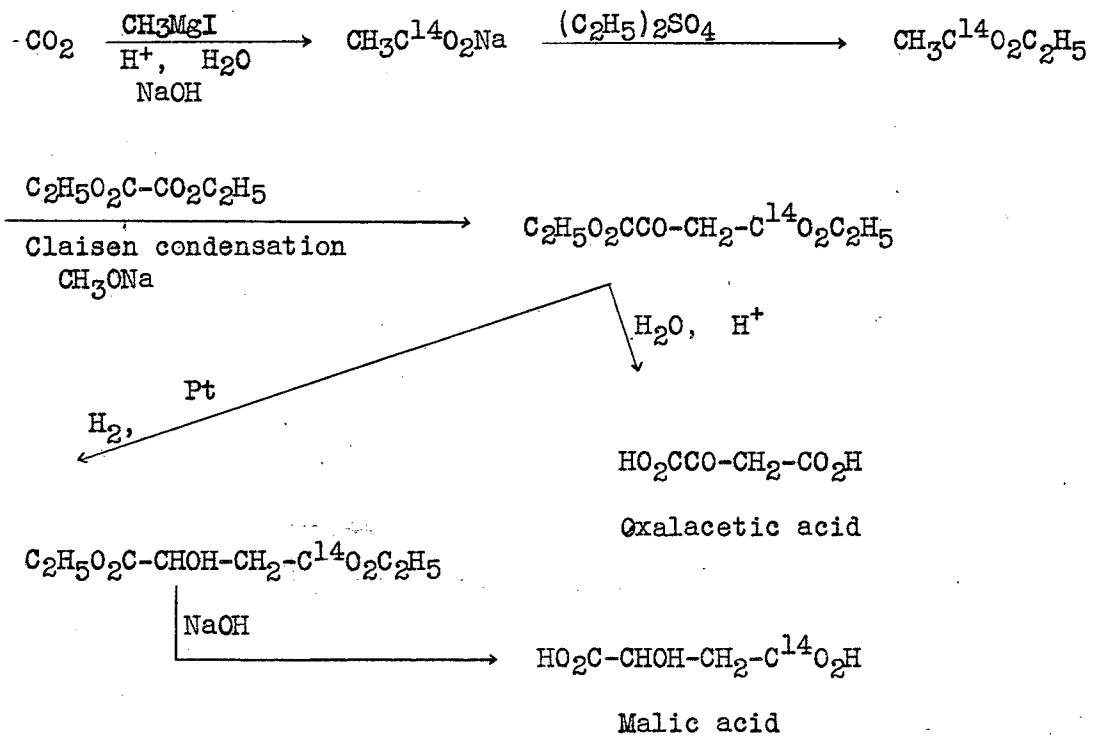
Preparation of Calcium Glycolate-2-C^{14}

		M.equiv.	Wt.,Mg.	Sp. Activity
Starting Materials	Sodium acetate	12.40	1000.3	0
	Sodium acetate	1.35	110.5	4.88 μc/mg
	Acetyl chloride	5.65	443.0	0
Product	1st crop [.0 H_2O]	8.70	828.4	0.30 μc/mg*
	2nd crop [.2 H_2O]	3.05	344.7	0.23 μc/mg

* - Theoretical = 0.29 μc/mg

Yield: 60.5 percent based on acetate used to begin the synthesis or 42.5 percent based on $\overset{*}{C}O_2$. The yield of sodium acetate-2-C^{14} was 70 percent based on $\overset{*}{C}O_2$.

Oxalacetic Acid-C^{14} and Malic Acid-C^{14}. Oxalacetic acid diethyl ester has been prepared from carbon dioxide, and this compound has then been converted to malic acid and oxalacetic acid by the following series of reactions:



Barium carbonate was converted to the carboxyl-labeled sodium acetate (97 percent yield), and 1 g. of the thus prepared anhydrous sodium acetate-1-C^{14} containing 6.1 mc. of C^{14} was converted to 1.161 g. of labeled malic acid which corresponded to 71.5 percent yield based on sodium acetate or 69 percent based on barium carbonate. The specific activity of the resulting malic acid was 3.77 μc/mg.

Experimental - Malic Acid. Ethyl acetate was prepared by treating sodium acetate with an excess of diethyl sulfate and the ethyl acetate distilled out. The ester condensation was carried out in a 120 ml. flask equipped with a mercury sealed stirrer and a condenser protected with a calcium chloride tube. Fifty ml. of dry ether was distilled into the flask, after which 1.3 g. sodium methylate and 1.9 ml. diethyl oxalate were added with stirring. The flask was stoppered and the ether warmed to reflux temperatures for several minutes. The ethyl acetate (1.02 g. or 95 percent yield from sodium acetate) was then transferred to the flask and the reaction mixture refluxed for 16 hours and then poured onto 10 ml. 6 N sulfuric acid kept below 0°C. After shaking, the ether phase was removed and the aqueous phase washed twice with 20 ml. of ether.

The combined ether extracts were concentrated to about 3 ml., taken up in 40 ml. 95 percent ethanol and transferred to a 120 ml. flask equipped with a sealed-in induction stirrer and a hydrogen inlet tube. After the addition of 400 mg. platinum oxide, the flask was closed and hydrogen bubbled in at 22°C, 1 atmosphere pressure. In 2 hours the hydrogen uptake was complete, and the reaction mixture was transferred to a 500 cc. flask where 50 ml. 1 N sodium hydroxide was added and the mixture shaken for 12 hours at room temperature.

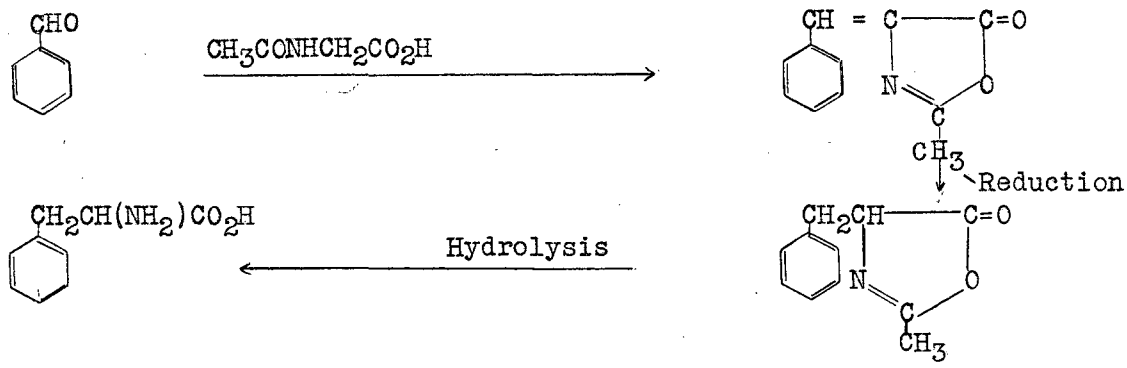
After the mixture was neutralized at 0°C with 6 N sulfuric acid, the solution was concentrated to about 20 ml. and a slight excess of molar calcium chloride solution added. The precipitated calcium oxalate was removed by centrifugation and the supernatant liquid acidified to pH 1 and extracted overnight with ether. The ether extract was evaporated to dryness and reduced and the residue of malic acid recrystallized from a mixture of ethyl acetate and toluene.

Experimental - Oxalacetic Acid. Oxalacetic acid diethyl ester prepared as just described was hydrolyzed in 12 N hydrochloric acid at 5°C for 4 days. At the end of that time, the mixture was evaporated to dryness at room temperature and reduced pressure. The residue containing the oxalacetic acid was recrystallized from ethyl acetate and benzene to give 0.437 g. oxalacetic acid from 0.775 g. of sodium acetate, or a 35 percent yield. The specific activity of the oxalacetic acid was 0.014 μc/mg.

Phenylalanine-β-C^{14}.

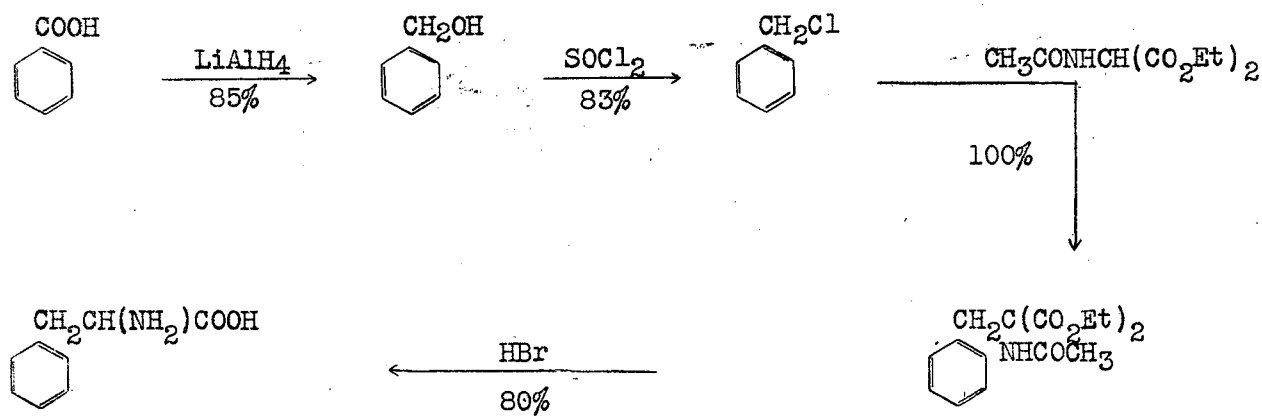
Preliminary work on the synthesis of phenylalanine-β-C^{14} is nearly complete. Synthetic routes to this compound may be divided into three classes: (a) those involving the condensation of labeled benzaldehyde with compounds related to glycine, such as acetylglycine, hippuric acid, hydantoin and acetylthiohydantoin; (b) those involving the condensation of labeled benzyl chloride with compounds related to aminomalonic acid, such as acetylaminomalonic ester, phthalimidomalonic ester and ethyl acetylaminocyanoacetate; (c) others - Knoop reduction of phenylpyruvic acid, etc. Examination of the literature suffices to exclude (c) from consideration.

Experimental trials of methods in category (a) using acetylglycine, hydantoin and acetylthiohydantoin indicate a rather low overall yield. A typical sequence of reactions in this series may be illustrated with acetylglycine:



The yields in the condensation reaction do not exceed 75 percent. The overall yields for reduction and hydrolysis do not exceed 70 percent, whether the procedure is carried out in two steps (catalytic reduction followed by acid hydrolysis) or in one (reduction and hydrolysis with red phosphorus and hydriodic acid). Since the expected yield of benzaldehyde (made by the Rosenmund reduction of labeled benzoic acid) is about 70 percent, the indicated yield is not better than 37 percent based on benzoic acid.

Somewhat better results can be obtained with category (b). The method which has finally been selected is given below:



When the entire sequence has been checked with low-activity benzoic acid, a high-activity run will be carried out.

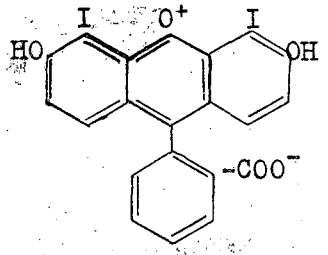
Compounds Being Studied.

Among the new compounds being studied are: alanine-3-C^{14}, codeine-C^{14}, Demerol-C^{14}, fumaric acid-C^{14}, succinic acid-C^{14} (by two different methods), morphine-C^{14}, butyric acid-1-C^{14}, valeric acid-1-C^{14}, hexanoic acid-1-C^{14} and diiodo^{131}tyrosine.

Diiodo^{131}fluorescein.

The preparation of 4,5-diiodofluorescein labeled with I^{131} has been carried out for investigation of its localization in brain tumors. Although the iodination

of fluorescein (by ammonium hypoiodite) has been described in the literature, some difficulty was encountered in obtaining material with the correct analytical values. The remedy has been found in modification of the relative amounts of reactants and of the ammonia concentration.



4,5-diiodofluorescein

A satisfactory product was obtained by treating one molar equivalent of purified fluorescein with four times the theoretical requirement of iodine prepared by oxidation of excess iodide^{131} with the calculated amount of hydrogen peroxide. An excess of iodide sufficient to make the reaction mixture 0.4 M in iodide was used. The ammonia concentration was 2.5 M. The reaction was allowed 3 hours for completion at 6-8°C. The product, obtained by acidification with phosphoric acid, was recrystallized 3 times from dilute acetone. The yield was 72 percent based on fluorescein and 9 percent based on iodide. The excess iodine can be recovered, if desired, by distillation in a current of nitrogen from the phosphoric acid filtrate after adding enough red phosphorus to reduce the free iodine. The recovery is 95 percent.

This synthesis was developed before the report of Boyach, Clasesson and Moore (Nucleonics, 2, Oct. 1948, p. 62) was published. At present a preparation is in progress to test this modified method since it will produce the desired compound with a much smaller use of the radioactive iodine. A variation of this procedure will probably be used in the preparation of diiodo^{131}-tyrosine.

Experimental Chemistry-Decomposition of Acetyl Peroxide in Acetic Acid.

Kharasch and Gladstone (J. Am. Chem. Soc., 65, 15 (1943)) reported that the decomposition of acetyl peroxide in glacial acetic acid at 85-95°C resulted in the formation of succinic acid, methane, carbon dioxide and some methyl acetate. In order to study the mechanism of this reaction, unlabeled acetyl peroxide was decomposed in glacial acetic acid labeled with C^{14} in the methyl group.

As a preliminary step, the exchange reaction between acetyl peroxide and acetic acid was studied. Unlabeled acetyl peroxide was dissolved in C^{14} labeled glacial acetic acid and after standing for 1 hour, and later after standing for 1 week at room temperature and 6 hours at 50°C, the acetyl peroxide and acetic acid were separated by repeated partitions between carbon tetrachloride and water. In both of the above experiments, the recovered acetyl peroxide showed no activity within experimental error, while the recovered acetic acid had a specific activity only slightly lower than that of the original acetic acid. The lower value is probably due to hydrolysis of the acetyl peroxide to acetic acid during the extraction process. During the time allowed for possible exchange, the peroxide titre did not change.

Following this experiment, acetyl peroxide was decomposed in methyl-labeled glacial acetic acid at 90° in a reaction flask fitted with a water condenser. The gaseous reaction products were swept out with purified nitrogen first through a trap at -80°C to

remove any entrained acetic acid and methyl acetate, then through a bubbler containing 2 N sodium hydroxide to absorb the carbon dioxide, through a furnace to oxidize the methane to carbon dioxide, and finally through another sodium hydroxide bubbler to collect this carbon dioxide. The acetic acid remaining in the reaction flask was removed by steam distillation and the residue extracted with ether to remove the succinic acid. The ether was then evaporated and the resulting crude product recrystallized from water.

The specific activities of the various products are shown in Table III. These preliminary results indicate that the succinic acid comes from two molecules of the acetic acid while the methane, and probably the carbon dioxide, come from the acetyl peroxide. The mechanism proposed by Kharasch and Gladstone when applied to the decomposition of unlabeled acetyl peroxide in methyl-labeled acetic acid would give the same distribution of activity as we have found.

Table III

Decomposition of Acetyl Peroxide in Acetic Acid-2-C^{14}

Source of Barium Carbonate	Specific Activity, cts/min/mg of carbon
Original acetic acid	1177
Succinic acid	1151
Carbon dioxide	0 *
Methane	1.6

* - Less than counter background

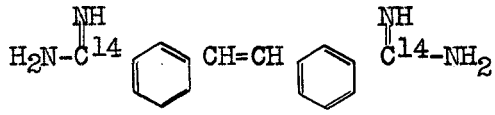
Biological Chemistry

M. Calvin, J. Reid, M. Kirk, C. Krone, M. Meinke, G. Nardi

L. Skiff, Y. Stone and J. Weaver

Metabolism of C^{14} Labeled Stilbamidine.

Stilbamidine has been observed to form granules (associated with nucleic acid) in cases of human multiple myeloma as well as improving the general condition of the patient. In order to investigate this localization, C^{14} labeled stilbamidine has been prepared



and its metabolism studied in a series of preliminary experiments to obtain data for actual patient treatments. In these experiments, one normal dba female mouse was given 0.70 mg. (436,000 cpm) intravenously and sacrificed after 96 hours. The body was dissected, and the dried tissues assayed for radioactivity. All were found to be active. The values obtained are shown in Table I.

Table I

Tissue Activities After the Administration of Stilbamidine-C^{14}

Tissue	Specific Activity Cts/min/mg	Tissue	Specific Activity cts/min/mg
Liver	31.1 (This discrepancy not yet resolved) 183	Pelt	21.0
Bone	14.4	Kidney	414
Feces	230,000 (total act.)	Intestines	193
Lung	42.7	Spleen	21.7
Heart	112	Salivaries	22.9
Muscle	10.1	Brain	8.00
Skin	10.6	Plasma solids	22.9
Pancreas	27.0	Urine	25,000 (total act.)
Ovaries	6.40	Breath	~0

This experiment was performed primarily for the purposes or orientation and the data from a single mouse cannot be pushed very far. However, the animal was killed long enough after the injection that the initial transient effects should have largely died out,

and the data no doubt give a valid picture of the overall distribution. Of particular interest is the high kidney uptake, which may be related to kidney damage described in clinical reports of toxicity observed in therapy with amidines.

The uptake of the heart, high with respect not only to the other body tissues but also to ordinary striated muscle, is striking. As the number of labeled compounds studied increases, the great metabolic activity of the heart manifests itself more and more emphatically.

The high activity of the erythrocytes which are relatively inert to other compounds studied is noteworthy. The absence of activity in the breath and the major role played by the feces as a route of excretion has been reported previously. Studies with this compound are continuing.

Fate of C^{14} Injected as Methyl-Labeled Glycine in "A" Strain Mice.

It has been felt that C^{14} presented certain limitations in its use as a tracer in human beings because of its long half-life and suggested evidence that it might deposit in the bones for long periods of time. In an attempt to determine its actual fate in bone, a series of quantitative experiments was carried out to ascertain the activity of the bones after the injection of glycine-2-C^{14} in mice. At the same time, the activities in most of the other important tissues in the body were followed.

The labeled glycine was injected intravenously in tail veins of adult "A" strain male mice. Breath, urine and feces samples were collected and the animals were killed at intervals and dissected. All tissues were dried *in vacuo* and the dried tissues combusted. Water extract from the tissues on drying showed a negative activity in all cases.

There was a uniform rise in the activity of all the tissues which reached a peak in about 3-4 days and gradually dropped at about equal rates over a period of 6 weeks. The data for a number of the more interesting body parts are compiled in Table II.

In an attempt to determine the actual turnover rate of C^{14} in each tissue, the specific activity/mg. of carbon in each tissue was determined. These values were plotted on semi-log paper and the curves analyzed. The data are tabulated in Table III; K equals 1/turnover time in minutes. From these values one can see that the rate of turnover is practically identical for the medium component for all the tissues analyzed, and in the slow component liver, bone, pancreas and heart are only slightly slower than the other tissues. Brain had a single component which was slowest of all, but still showed a definite C^{14} turnover rate with a half-life of 21 days.

Rate Studies on the Metabolic Oxidation to Carbon Dioxide of Labeled Compounds.

A series of experiments have been carried out to determine the rate of oxidation and elimination from the body as carbon dioxide of a number of simple C^{14} labeled compounds. In this group the following compounds have been studied: Sodium formate-C^{14}, sodium acetate-1-C^{14}, sodium acetate-2-C^{14}, glycine-1-C^{14}, glycine-2-C^{14}, sodium propionate-1-C^{14}, potassium pyruvate-3-C^{14} and alanine-2-C^{14}.

The studies have been made with both normal and pathological (mammary carcinomas and sarcomas) mice. The rate of $C^{14}O_2$ elimination was measured by passing the breath

Table II

Fate of C^{14} from Methyl-Labeled Glycine

Percent of Administered Dose of C^{14} Remaining in Organ

Time	Bone+	Brain	Heart	Intest.	Kidney	Liver	Stomach	Spleen	Panc.	Colon	Lungs
6 h	2.0	0.3	0.04	10.0	4.9	14.0	3.0	9.0	5.0	1.2	1.4
18 h*	0.5	0.5	0.04	6.0	3.0	6.7	4.3	2.0	1.5	8.5	1.4
25 h	1.3	0.5	--	6.0	2.9	17.0	2.3	0.9	2.3	6.6	1.4
41 h	1.0	0.3	0.5	9.0	2.5	12.0	3.4	1.9	1.0	1.5	0.3
68 h	0.5	0.2	0.4	2.3	1.9	9.0	1.0	0.7	0.8	2.8	0.5
96 h	0.6	0.5	0.4	5.5	2.1	8.0	0.7	0.5	0.5	2.6	0.6
6 d	0.5	0.3	0.4	2.2	1.8	5.3	0.6	0.4	0.6	1.0	0.6
12 d	0.25	0.3	0.1	1.0	0.7	2.0	0.2	0.25	0.3	0.4	0.2
14 d	0.25	0.3	0.2	1.0	0.6	2.2	0.3	0.2	0.3	0.3	0.2
17 d	0.3	0.3	0.2	0.3	0.6	1.4	0.15	0.2	0.2	0.4	0.2
21 d	0.1	0.2	0.2	0.3	0.3	0.6	0.1	0.1	0.1	0.2	0.1
26 d	0.13	0.1	0.1	0.2	0.2	0.6	0.07	0.15	0.08	0.2	0.1
34 d	0.10	0.1	0.09	0.2	0.2	0.3	0.02	0.07	0.06	0.1	0.1
43 d	0.05	0.1	0.05	0.08	0.05	0.2	0.04	0.04	0.1	0.07	0.04

+ - both legs, tibia and femur

* - this animal may have been sick

h - hours

d - days

Table III

C^{14} Turnover in Mouse Tissues

	Rapid Component		Medium Component		Slow Component	
Tissue	K	Percent Inj.C^{14}	K	Percent Inj.C^{14}	K	Percent Inj.C^{14}
Liver	--	--	0.217	6.7	0.0447	1.8
Bone*	0.835	8.24	0.217	6.5	0.0447	3.7
Stomach	0.992	4.02	0.252	0.79	0.0616	0.27
Colon	--	--	0.248	2.67	0.0554	0.52
Intestine	--	--	0.266	7.56	0.0554	1.19
Kidneys	2.31 ?	3.39 ?	0.277	2.5	0.0787	1.73
Spleen	2.31	7.83	0.248	0.6	0.0630	0.39
Lungs	0.925	1.95	--	--	0.0603	0.68
Pancreas	0.867	9.14	0.248	1.19	0.0408	0.26
Heart	0.521	1.97	--	--	0.0470	0.37
Brain	--	--	--	--	0.033	0.45

* - Liable to correction for percent of body weight. Tentative figures used.

of the mice through an alkali solution which was changed at from 1-minute to 2-hour intervals, depending on the rapidity with which the compound was oxidized by the animal. Ten normal and ten tumor mice were measured for each compound.

In most of the compounds the metabolic oxidation rates were essentially the same for the two types of mice, but in the cases of the pyruvate, the sodium propionate-1-C^{14} and alanine-2-C^{14} there were marked differences. In the case of the propionate and pyruvate, the metabolism rate in the period of 1/2 to 2 hours after injection was faster for the tumor mice than for the normal mice. With alanine, the metabolic rate during the first hour was much slower in the tumor than in the normal mice. There was quite a difference in the time required to reach the peak of elimination in this latter case.

The experiments are being continued with additional labeled compounds. It appears not at all unlikely that as a result of this investigation a new diagnostic method for cancer may be evolved.

Copper in the Study of Melanoma.

A tracer study of the distribution of copper ion in a case of human melanoma has been made. This experiment was suggested by the fact thay tyrosinase, the enzyme responsible for the heavy production of melanin by the melanoma, is a copper-bearing protein. It is therefore practically certain that copper administered parenterally will appear to a certain extent in the tumor. If the uptake relative to the rest of the body were large enough to be called selective, then the possibility of radiotherapy by the administration of a radioactive copper isotope would be open. Even if the concentration taken up were no larger than that of the most active of the normal body tissues, this mode of radiotherapy would entail no greater destruction of healthy tissue than does irradiation from an external source. Moreover, it would have the great virtue that metastases would be sought out and destroyed. Once the melanoma has begun to metastasize, cure by surgery or external irradiation is practically hopeless. In addition to the possibility of therapy, copper might be used diagnostically, particularly if the isotope used emitted radiation of a type permitting counting *in vivo*. Such a method of diagnosis would be especially valuable if it furnished a criterion for distinguishing between malignant growth and benign pigmented areas.

An ideal isotope for this type of experiment is available in $_{29}Cu^{64}$, which decays with a 12.8 hour half-life and emits a 0.66 Mev positron (and a negatron and K-capture gamma). Its formation by the reaction $_{28}Ni^{64}$ (p,n) $_{29}Cu^{64}$ permits the preparation of material free of carrier except for the amount of copper present as impurity in the nickel target.

The experiment was performed on a male patient suffering from advanced melanoma with a few small pigmented surface lesions, multiple subcutaneous tumors and extensive metastases to internal organs. The copper was administered intravenously in saline and the activity of various regions was followed with external directional gamma-ray counters. The data obtained suffer from the defect that the amount of activity obtained from the target (ca. 100 μc) was insufficient for accurate counting and so will not be discussed in detail. Insofar as they can be interpreted, they show (a) no significant difference between the activity of either cutaneous or subcutaneous neoplasm and the activity of surrounding tissue; (b) a high uptake by the liver, which, however, contained metastases; (c) rapid removal (15 minutes) of the administered dose from the blood; and (d) slight urinary excretion. The experiment was repeated with more activity and the results were substantially in agreement with those found before.

Photosynthetic Chemistry

M. Calvin, A. Benson, V. Haas, J. Bassham, T. Goodale,

R. Lemmon, W. Routson and J. Weigl

The nature of the processes involved in photosynthesis by green plants is being investigated in this laboratory. By using radioactive carbon and phosphorus it is possible to examine the products formed under given conditions without interference by larger amounts of non-radioactive compounds of the same structure. This report will deal with two of these applications of radioisotopes.

The first is the determination of the overall rates of photosynthesis and the concomitant respiration process using $C^{14}O_2$. Heretofore, this measurement could not be made directly. By the use of suitable analytical apparatus developed in this laboratory, it is now possible to measure the rates of both processes simultaneously. The difference in rates of photosynthesis of $C^{12}O_2$ and $C^{14}O_2$ accounting for a considerable isotope effect is reported here. An understanding of this phenomenon is essential to interpretation of subsequent data involving photosynthetic rates.

The second phase of the work deals with the determination of the path of carbon from CO_2 in the air as it passes through the chemical processes performed by the plant. Several series of experiments have been performed in which the amounts of radioactive photosynthetic intermediates and products have been determined for shorter and shorter periods of photosynthesis.

The present method of separation of these intermediates has been described in previous reports. This method of paper partition chromatography is ideally suited for the separation of the soluble intermediates. By applying a solution to be analyzed in a small circle near the corner of a large sheet of filter paper and allowing a suitable solvent (water-saturated phenol) to flow through the length of the paper, the compounds in the original spot are separated into a row of spots since each compound has a different rate of movement (designated as R_f value). The paper is dried and the adjacent edge is immersed in a different solvent (butanol-propionic acid-water mixture) which further washes the row of spots as it travels the other direction in the paper. A map of spots characteristic of the compounds involved is formed. For extracts of plants which have been fed radioactive CO_2 some of these spots will be radioactive while those formed prior to the radioactive experiment will be inactive. The position of the radioactive spots is determined by exposing an x-ray film to the paper for a suitable time (1 hour to 3 weeks). The developed film reproduces the active spots exactly and is termed the 'radiogram' in this report. The identification of the unknown radioactive compounds, indicated by spots on the film is being investigated in this laboratory.

The Path of Carbon in Photosynthesis.

Our present concept of the path of carbon in photosynthesis is given in Fig. 1. The compounds marked with two asterisks have not been identified as yet, while the ones with one asterisk have been either partially identified or partial evidence for their presence has been obtained. Unmarked compounds have been identified unequivocally. The combination of reactions involving the identified compounds has been published, (M. Calvin and A. A. Benson, Science, 107, 476 (1948); W. Stepka, A. A. Benson and

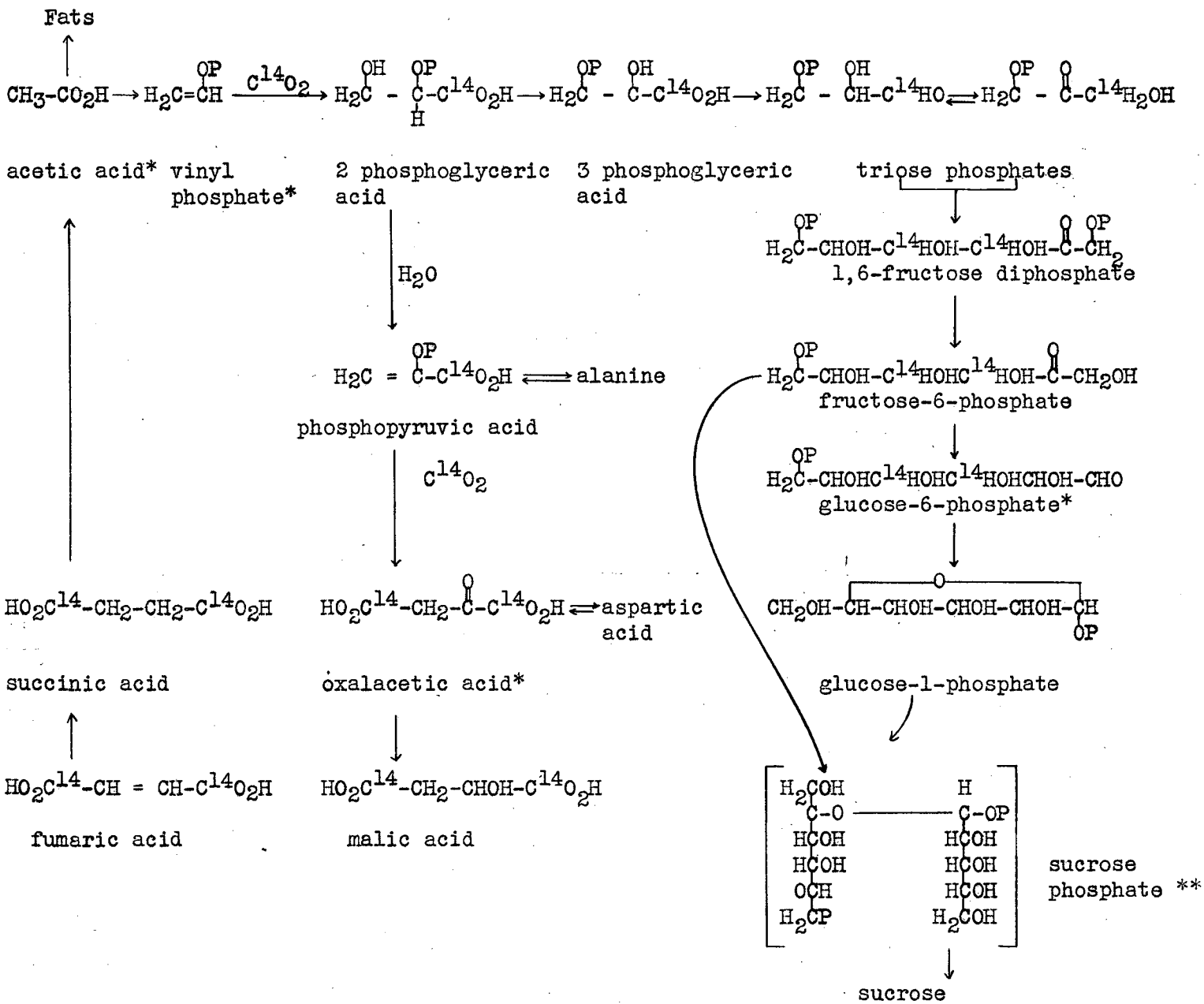

Fats
acetic acid*
vinyl phosphate*
2 phosphoglyceric acid
3 phosphoglyceric acid
triose phosphates
1,6-fructose diphosphate
fructose-6-phosphate
glucose-6-phosphate*
glucose-1-phosphate
phosphopyruvic acid
alanine
aspartic acid
oxalacetic acid*
succinic acid
fumaric acid
malic acid
sucrose phosphate **
sucrose

Figure 1

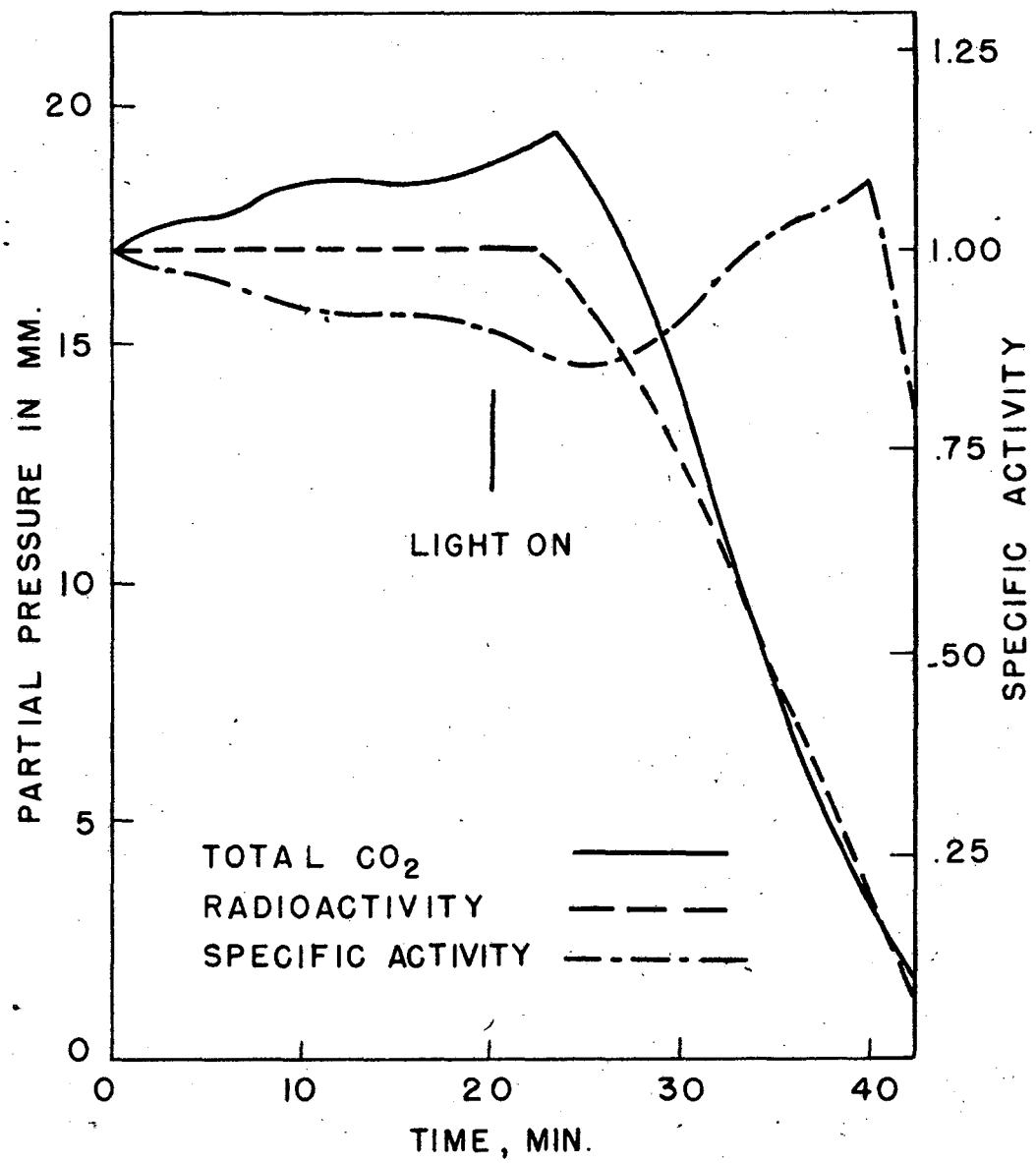

PARTIAL PRESSURE IN MM.
SPECIFIC ACTIVITY
TIME, MIN.
LIGHT ON
TOTAL CO_2
RADIOACTIVITY
SPECIFIC ACTIVITY
0
5
10
15
20
.25
.50
.75
1.00
1.25
0
10
20
30
40

FIG. 2

13119-1

M. Calvin, Science, 108, 304 (1948)) and the evidence accumulated since that time has substantiated the original suggestion. The direct path from CO_2 to sugar is found to involve the known intermediates of sugar metabolism. The cycle which continuously regenerates the CO_2 acceptor molecules is shown in the left-hand part of the diagram. The degradation of a number of intermediates to determine the distribution of C^{14} in the molecule gives evidence for the sequence of reactions as written: thus, in short periods of photosynthesis, the major part of the fixed $C^{14}O_2$ is in the carboxyl groups of the carboxylic acids and in the middle pair of carbon atoms of the hexoses.

The amino acids which have been identified in plant material have confirmed this concept. Thus, the following amino acids are formed in photosynthesis: aspartic acid, alanine, serine and smaller amounts of phenylalanine, β-alanine, asparagine and phosphoserine. When plants were allowed to respire in the dark, appreciable amounts of glutamic acid are formed. This occurs extremely slowly in the light. Since glutamic acid is related to α-ketoglutaric acid, a tricarboxylic acid cycle intermediate, it is apparent that this cycle functions in dark respiration and not in photosynthesis.

The CO_2 Acceptor.

Our earlier work showed that a plant could fix up to fifty times as much CO_2 in the dark if it was preilluminated in the absence of CO_2. That this was not merely a shift of equilibria involved, but a formation of a true reducing agent was shown by work in this laboratory. It is now shown by the radiogram of the extract of dark fixation products by preilluminated algae that the radioactive compounds fixed in 15 seconds dark are the same as those synthesized in an equal or longer time of steady state photosynthesis. The distribution of radioactivity among these compounds is also similar. Evidently, some reduced compound of considerable ability to reduce CO_2 can be stored for short times by the plant.

To isolate such a reduced CO_2-acceptor the following experiment has been performed. Algae which have photosynthesized $C^{14}O_2$ for 2 minutes were flushed with helium for 3 minutes to remove all CO_2. The radioactive intermediate of the cycle should then build up considerable concentrations of compounds up to the point of CO_2 addition. Incomplete results indicate the formation of a new compound under these conditions which forms acetaldehyde upon acid hydrolysis. The source of this reduced CO_2 compound is uncertain.

The First CO_2 Addition Compound in Photosynthesis.

By choosing shorter and shorter times of exposure to $C^{14}O_2$ the number of labeled products is shown to diminish. The shortest exposure, 5 seconds, gives a radiogram showing only one compound in major amount. This is now fairly well established to be 2-phosphoglyceric acid. Another compound, 3-phosphoglyceric acid, is found to have less than half the activity, while a spot tentatively identified as phosphopyruvic acid has one-seventh the total activity. A trace of active malic and aspartic acids is also apparent. This indicates that carboxylation via Wood-Werkman carboxylation of pyruvic acid is also occurring. A series of experiments at lower temperature (5°C) have been performed which give as few as two labeled intermediates. These are the 2-phosphoglyceric and phosphopyruvic acids. We have observed that dark respiration produces active glutamic acid at 0°C. Hence lowering the temperature may not decrease the rate of respiration as rapidly as it decreases the rate of photosynthesis.

Plant Respiration Processes.

By allowing algae to respire in the dark with $C^{12}O_2$ after fixing $C^{14}O_2$ in the light, it is shown that a considerable amount of glutamic acid is formed as well as a new carboxylic acid, presumably a member of the tricarboxylic acid cycle. In the dark respiration, the amount of aspartic acid is diminished considerably. This means that oxalacetic acid which is in equilibrium with aspartic acid is being used in respiration. Sucrose is not rapidly diminished by respiration while certain of the sugar phosphates apparently are respired.

When algae respire in the light the products do not include glutamic acid. This is shown by a radiogram of an experiment identical to the above experiment except that it had no dark treatment. The glutamic acid (the major free amino acid in algae) was found to possess only very slight activity.

These results confirm kinetic experiments with barley seedlings performed in this laboratory. During photosynthesis the respiration CO_2 is found to be of low specific activity. It does not involve photosynthetic intermediates. In the dark the immediately previously formed radioactive photosynthetic intermediates are rapidly respired and the respiration CO_2 has a high specific activity. In other words, the effect of light is to shift the nature or location of the respiration process in green plants.

Sucrose - the First Free Sugar Synthesized.

The formation of sucrose without simultaneous or prior formation of free hexoses as shown in the chromatograms is evidence that sucrose is directly formed by combination of glucose and fructose phosphates. An effort will be made to find the postulated sucrose phosphate which should exist unless its hydrolysis is simultaneous with sucrose formation.

Acid hydrolysis of sucrose synthesized in 90 seconds by Chlorella shows that the glucose and fructose have equal specific activity. It is necessary, therefore, either that the reservoirs of the intermediates be very small or that sucrose be formed from a single hexose phosphate. The first possibility is the most plausible, since both glucose-1-phosphate and fructose-6-phosphate may exist in very minute amounts in plant tissues.

An Isotope Effect in Photosynthesis.

In the course of some kinetic studies of photosynthesis of barley seedlings, it has been found that plants utilize $C^{12}O_2$ faster than $C^{14}O_2$. The plants were placed in a closed system containing infra-red absorption cell for the analysis of total CO_2 and an ionization chamber for the determination of $C^{14}O_2$ in the gas phase, both instruments recording continuously.

Carbon dioxide, containing about 2 percent $C^{14}O_2$, was introduced in the dark and the specific activity at this point taken as unity. After a short dark period, the lights were turned on and photosynthesis was allowed to take place. Figure 2 shows the result of a typical experiment.

During the initial dark period the specific activity fell because of dilution

by inactive respired CO_2. However, as photosynthesis proceeded, the specific activity of the residual CO_2 rose until, when only one-sixth of it remained, the specific activity reached a peak some 20 percent higher than it had been at the start of photosynthesis. At this point, the steady respiratory dilution became an appreciable fraction of the total remaining CO_2, and the specific activity dropped rapidly.

Two other possible explanations of the rise in specific activity were (1) a difference in the response times between the instruments of the order of a minute or two and (2) the conversion of the CO_2 into some other volatile compound. Independent determinations of the response time to changes in the system revealed no appreciable time lags. The interpretation as an isotope effect was confirmed by removing samples of CO_2 during the course of a run and determining its specific activity by counting as $BaCO_3$, reconverting to CO_2, and measuring in a separate ionization chamber.

As a further check, a 200 mg. "isotope farm" was grown from a 2 mg. inoculum in a large quantity of dilute $C^{14}O_2$ (initial pressure 4 mm.). When 70 percent of this carbon had been converted into organic matter, the reaction stopped, the three phases (air, solution and algae) separated, and the carbon in each converted into $BaCO_3$ under an inert atmosphere. The carbonate was counted; the resultant specific activities were: air phase, 99; water phase, 106; algae, 81. The large difference in the specific activities between the organic and inorganic carbonate fractions further confirms the reality of the isotope effect.

A similar selectivity favoring $C^{12}O_2$ over $C^{13}O_2$ has been observed by Nier and Urey in steady state systems, in which the net effect is considerably smaller than that reported here.

Fate of Pyruvic Acid in Plant Metabolism.

C^{14} methyl-labeled pyruvic acid has been fed to Scenedesmus D_3, both in the dark and during 5-minute illumination. The preliminary fractionation of the fixed activity recovered from the algae is summarized in Table I.

Table I

	5-min. dark fixation		5-min. photosynthesis	
Total C^{14} fixed, cpm x 10^{-5}	4.41		6.16	
C^{14} fixed, water soluble	2.23	100%	2.10	100%
I Ether ext. acids	0.74	34%	0.81	42%
II Cationic (amino acids)	1.13	51%	0.31	15%
III-A Anionic, ammonia elutable	0.26	12%	0.46	23%
III-B Anionic, not ammonia elutable	0.05	2%	0.26	13%
IV Neutral substances (sugars)	0	0	0.01	0.4%
C^{14} fixed, water insol. alc. ext.	2.18		4.06	

No fractionation of the ether extractable acids (I) has been carried out. Paper chromatograms have been prepared on aliquot portions of the amino acid fractions (II). These papers have enabled us to identify radioactive aspartic acid and alanine from both the dark fixation and the five-minute photosynthesis. In both cases, the amount of aspartic acid was vastly greater than that of alanine. In addition, both experiments showed a considerable fraction of a radioactive amino acid, the identity of which could not be established with certainty but which may be glutamic acid.

No further work was carried out on Fraction III-A. Paper chromatograms of the III-B fractions revealed no spots which could be identified.

No sugar was obtained in the case of the dark fixation and not enough was obtained from the 5-minute photosynthesis to permit identification.

The lipid material contained in the alcohol soluble portion of the 5-minute photosynthesis experiment was distributed between ether and water at pH 9 and again at pH 1. Eighty percent of this material was found to be acidic in nature. The distribution coefficient (ether/water = pH 1) for the single compound which constituted about 75 percent of the alcohol soluble material was 650. The coefficient for the same compound in benzene/water = pH 1 was 95. The compound contained no unsaturation as shown by the failure to observe any change in the distribution coefficient after adding bromine to the solution. That the compound was not a simple fatty acid was shown by comparing its distribution constants and volatility with those of fatty acids. A plot was made of the change of distribution coefficient with change in pH value; this plot indicated the presence of two acidic groups with dissociation constants of about 10^{-5} and 10^{-9}. This information indicated that the acidic substance was possibly a β-keto acid. A decarboxylation was then carried out but the CO_2 which was evolved was not radioactive. An iodoform test in the presence of 2-octanone as carrier was carried out on the decarboxylated material. The iodoform was inactive.

Analytical Techniques in Photosynthesis.

Paper Chromatography. A major portion of the chromatography work involves chemical identification of the labeled intermediates as evidenced by darkened spots on the x-ray film in the radiogram. Identification has been done in the following ways:

Synthesis. The authentic compound is synthesized using C^{14} or P^{32} and applied to the paper alone and with the plant extract. Complete identity of the synthetic activity and that synthesized by the plant constitutes unequivocal identification. Malic acid containing C^{14} has been synthesized in this laboratory for this purpose. The synthesis is separately described on page 38 of this report. The intermediates of sugar metabolism have been labeled with P^{32} phosphate and isolated in the classical manner. Concurrence of the P^{32} activity of the synthetic material and the C^{14} activity in the mixed chromatogram constitutes unequivocal identification.

Synthetic Radioactive Compounds. Glucose-1-phosphate was obtained by action of potato phosphorylase on glucose in presence of radioactive phosphate.

Glucose-6-phosphate, fructose-6-phosphate, fructose-1,6-diphosphate and phosphoglyceric acids were produced by yeast fermentation of glucose in the presence of radioactive phosphate and fluoride.

Location of these phosphorylated compounds was determined on paper chromatograms (a) by radioactivity and (b) by formation of blue spots when sprayed with ammonium molybdate reagent. Inorganic phosphate, glucose-1-phosphate and hexose diphosphate and phosphopyruvic acid reacted to give such blue spots since they can be readily hydrolyzed on the paper.

Acetyl phosphate decomposed when developed in the butanol-propionic acid solvent which is used in preparation of our chromatograms. The fact that synthetic oxalacetic acid is also too unstable to undergo paper chromatography precluded the possibility of finding a corresponding spot.

Color Tests. The amino acids were identified by spraying the chromatogram with ninhydrin solution and observing correlations between the colored areas denoting amino acids and the radioactive areas in the radiogram. A test for phosphate on the paper has been developed in this laboratory for identification of easily hydrolyzable phosphate esters and anhydrides. It consists of spraying with the conventional reagents to produce molybdenum blue on the paper wherever free phosphate exists.

Phosphate Compounds. By allowing algae to photosynthesize in a nutrient containing labeled phosphate it has been possible to prepare a radiogram of the compounds synthesized. This result, which gave the general location of phosphate compounds on the paper, led to the identification of the unknown C^{14} spots as phosphorylated sugar intermediates.

Chemical Tests. A radioactive spot on the chromatogram may be easily eluted with water. Chemical tests can then be performed on the solution. Carrier crystallization, distribution coefficients, hydrolysis rates and hydrolysis products may be determined. Properties of the following compounds have been determined in such tests: phosphopyruvic acid, fructose diphosphate, malic acid, sucrose and phosphoglyceric acid. This type of work is being continued in order to complete the identification of the major intermediates of photosynthesis.

Separation of Phosphate Esters by Ion Exchange.

The use of ion exchange resins in separating organic compounds as developed in this laboratory has now been extended to include the phosphorylated glycolysis intermediates. The results indicate that these compounds may be readily and completely separated on a large scale. This is a promising possibility in view of the difficulty involved in the classical separations of these important biological intermediates.

Labile phosphate esters are unstable in alkaline solution and cannot be absorbed on the base form of an anion exchange resin. Hence the compounds are absorbed on the chloride form of a strong base quaternary ammonium type resin in neutral solutions. Elution is carried out with suitable concentration of sodium chloride solutions. Elution curves have been obtained for several compounds and these are listed in the order of increasing resistance to sodium chloride elution: inorganic phosphate, glucose-1-phosphate, 3-phosphoglyceric acid, fructose-1,6-diphosphate. The bands obtained upon elution are sharp and will allow separation of the compounds named. Analysis of elution samples is being done by phosphate determinations and by radioactivity determinations. The method will provide another physical property by which to establish the identity of a labeled compound with an authentic sample.

II QUARTERLY PROGRESS REPORT. PROJECT 48B

W. M. Latimer, Director

A. Metals and High Temperature Thermodynamics

L. Brewer, L. A. Bromley, N. Lofgren, A. Searcy, L. Templeton

R. Edwards, R. McKissen and G. Elliott

Thermodynamics Papers.

Vol. 19B of the Plutonium Project Record, which consists of ten papers based on work done by the Manhattan District group of the Chemistry Department during the war, is in the final stages of editing and is expected to be published shortly. The papers to be published are as follows:

1. "Investigations in the Liquid-Solid Equilibria of the Two Component Systems Composed of the Bromides and Iodides of Strontium and Barium", by E. D. Eastman, N. C. Melchior, and Ernest Strickland.

2. "Temperature-Composition Diagrams of Metal-Metal Halide Systems", by E. D. Eastman, Daniel Cubicciotti, and Carl Thurmond.

3. "The Thermodynamic and Physical Properties of the Elements," by Leo Brewer.

4. "Thermodynamic and Physical Properties of Nitrides, Carbides, Sulfides, Silicides, and Phosphides", by Leo Brewer, LeRoy Bromley, Paul Gilles, and Norman Lofgren.

5. "The Thermodynamic Properties of Common Gases", by Leo Brewer.

6. "The Thermodynamic Properties of the Halides", by Leo Brewer, LeRoy Bromley, Paul Gilles, and Norman Lofgren.

7. "The Fusion and Vaporization Data of the Halides", by Leo Brewer.

8. "The Thermodynamic Properties of Molybdenum and Tungsten Halides and the Use of These Metals as Refractories", by Leo Brewer, LeRoy Bromley, Paul Gilles and Norman Lofgren.

9. "The Heats of Formation of CeS, Ce_3S_4, and Ce_2S_3 at 25°C.", by Marjorie Evans.

10. "The Heat of Reaction of the Cerous-Ceric Couple in 0.5 Molal Perchloric Acid at 25°C.", by B. Fontana.

Thermodynamics of Gaseous Cuprous Chloride and Molybdenum Chloride Systems.

The copper work has been completed and a paper will be submitted for publication in the Journal of the American Chemical Society shortly. The lack of a satisfactory method of analysis for very small amounts of molybdenum has delayed work on the molybdenum chloride system, but a satisfactory method of analysis has now been worked out. It has been found that the color of the $Mo(CNS)_5$ complex is intensified and stabilized by the presence of Fe^{++} ion which tends to indicate a complex containing both metals. With the availability of a satisfactory analytical method, work is progressing on the determination of the molybdenum chloride gaseous species.

Thermal Conductivity of Gases.

Construction of the apparatus for the determination of thermal conductivities of gases at high temperature is underway.

Thermodynamics of CN gas.

Further determinations of the heat of formation of CN gas are being made in an endeavor to definitely fix the stabilities of CN and N_2 gases.

Vapor Pressures of Metals.

Work is progressing on the determination of the vapor pressure of aluminum. TaC, $TaSi_x$, BeO, and Al_4C_3 are the only possible container materials which are found for molten aluminum at high temperatures. It is believed that use of these materials will make possible an accurate determination of the vapor pressures and heat of sublimation of aluminum using an effusion method.

Preliminary work on the determination of the vapor pressures of various refractory methods such as Re, Os, etc. by spectroscopic methods has been carried out.

Liquid Metal Systems.

The construction of a new high temperature calorimeter for determination of heats of formation of metal alloys at high temperature is under way. The study of the U-Bi-Na system is continuing. A new technique of using a high temperature x-ray camera to speed up study of ternary phase diagrams is being tried. A new high temperature x-ray camera is under construction. A method of sealing capillaries containing samples for x-ray analysis in a dry box is being tried out.

Thermodynamics of Gaseous Oxides and Hydroxides.

The study of the vapor pressure of Al_2O_3 by the effusion method has indicated the vapor pressure to be lower than previously believed and the volatility may be due entirely to AlO(gas) formation. Spectroscopic studies will be necessary to confirm these conclusions.

B. Basic Chemistry, including Metal Chelates

R. E. Connick, Z. Z. Hugus and K.L. Mattern

Exchange of Iodine Atoms Between Iodine and Iodate Ions.

Attempts were made to investigate the iodic acid ionization and dimerization spectrophotometrically. The results obtained were, however, found to be irreproducible, and it was further found that a solution of sodium iodate showed large changes in absorption with temperature. The system is being investigated further and an attempt to eliminate impurities which might cause such a temperature dependent absorption is being made.

In order to correlate the iodine-iodate exchange rate with kinetic measurements the rate of oxidation of I^- by IO_3^- is being studied under conditions similar to those used by Abel and Hilferding. Preliminary results indicate that their rate law was in error and that the kinetic rate law and the exchange rate law are identical.

Lanthanum Chemistry.

The spectrophotometric study of equilibrium conditions in lanthanum chelation requires the accurate determination of the molar extinction coefficient of the (LaK^{++}) species. A preliminary investigation of the conditions under which one would have a maximum amount of (LaK^{++}) present, with a minimum (or measurable amount) of other absorbing species, showed that one could most favorably work at a pH≈6. A great deal of trouble has arisen from precipitation in attempting to attain this (H^+) concentration.

Attempted purification, as well as spectrographic analyses, of the La_2O_3 used as a source of lanthanum has not overcome these difficulties, as yet. Though the spectrographic analysis shows less than 1 percent of any other metal and qualitative tests indicate the lack of (IO_3^-), ($SO_4^=$), ($PO_4^{\equiv}$)--which seemed to be the most possible acid-insoluble compounds--, the La_2O_3 will not dissolve in aqueous solution with an (H^+) below $\sim 10^{-4}$ M. Titration curves, in the literature (Moeller, 1946) showed much greater solubilities for the rare earth oxides. Attempts to work at the desired pH have only removed (La^{+++}) from solution and reduced its concentration below that required by the experiments.

A solid sample of $La(NO_3)_3$ was recently located which will go into solution at the required pH. Lanthanum hydroxide prepared from this source will also dissolve at pH 6.5.

C. Ore Reduction

E. F. Orlemann, M. Riley and L. Myers

A preliminary study of the solubilities of U^{VI} and U^{IV} phosphates has been made. Uranium solutions in varying concentrations of $HClO_4$ were precipitated with NaH_2PO_4 and after shaking the supernatant analyzed for uranium by the fluorescence method. Solubility products were calculated assuming UO_2HPO_4, $UO_2(H_2PO_4)_2$, $U(HPO_4)_2$, and $U(H_2PO_4)_4$ to be the solid phase. Results would indicate that the precipitate is of a more complex nature. Visual comparison has been used in the fluorescence analysis, but a fluorimeter is being constructed to increase the accuracy of further investigations of this nature.

An apparatus for the storage and use of chromous ion (Cr^{++}) solutions of known strength has been constructed for direct titrations of U^{VI} solutions in analytical work. At present the determinations are being carried out on macro scale but it is hoped that the method will give satisfactory results when reduced to micro scale.

D. Engineering Development of Plutonium Separation

T. Vermeulen, T. Hicks, Barney Rubin and Milton Davis

Pilot Scale Synthesis of TTA.

One hundred seventy pounds of purified TTA has been prepared. Production is continuing in order to satisfy needs of various project centers.

Experimental work has shown that TTA residues which previously were considered unreclaimable have been purified by steam distillation. Some difficulty due to the formation of TTA hydrate during the steam distillation has been experienced.

Physical chemical data concerning the various steps in TTA production is being organized in report form.

Solvent Extraction Utilizing Chelate Process.

Work has continued on construction and operation of a two-column counter-current extraction column for separation and decontamination of Pu by the chelate process. A second 5 stage 1 inch diameter column has been completed and placed in series with the column reported previously.

Four runs with Pu tracer solution have been carried out in the equipment with results in good agreement with theoretical prediction. Extraction efficiencies of 85-90 percent per stage were obtained with Pu loss of 1 percent or less.

It is desired that hydraulic characteristics of both columns be improved in order to attain better reproducibility of data and more accurate flow control. Work now in progress includes insertion of weirs between each mixing stage in order to improve interface level control; construction of a rotameter panel is under way to insure more accurate flow metering.

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