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QUARTERLY REPORT

September, October and November, 1949

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I QUARTERLY PROGRESS REPORT. PROJECT 48

A. Chemistry of the Rare Earth and Actinide Elements

Chemistry of Plutonium

J. C. Wallmann and B. B. Cunningham

Previous measurements of the specific alpha-activities of several samples of plutonium (MUC-GTS-2042, 2075, 2082) irradiated with neutrons for various lengths of time have indicated that the specific alpha-activity of Pu^{240} might change with neutron irradiation (MB-IP 425). Since any such hypothesis depends upon the accuracy of the specific activity measurements, the specific activities of several samples of plutonium have been remeasured. The technique used has been to dissolve a weighed piece of Pu metal in acid, diluted to the desired concentration, and plate a weighed aliquot of about 10-20 μgms. Except in the case of sample 49NH the metal samples are produced by Ba micro-scale vacuum reductions of PuF_3 prepared from purified stocks. Sample 49NH was obtained as metal and was simply cut up, weighed, and dissolved. A low geometry vacuum counter with a geometry factor of 1408 was used for counting the plates. Table I presents the data obtained to date.

TABLE I

Sample	Pu^{239} Atom %	Pu^{240} Atom %	Sp. Act. c/m/ug
12B	58.1	34.0	1.4×10^5
49NH	92.76	6.86	83,300
2gt-M-1	99.98	0.02	72,150
2gt-M-2	99.98	0.02	71,400
2gt-M-3	99.98	0.02	71,100
2gt (average)			71,600

(All the specific activity values except that for 49NH have been corrected for impurities as determined by spectrochemical analysis. The isotopic composition of the 49NH and 2gt materials was determined at Los Alamos; Mr. F. L. Reynolds of this Laboratory determined the 12B abundances.)

These data differ somewhat from results obtained previously and, if real, these discrepencies have no obvious explanation. The 12B specific activity checks the result obtained earlier in this laboratory but the values for 49NH and 2gt are 1.6 percent lower and 1.1 percent higher than previous specific alpha-activity determinations. It should be pointed out, however, that no spectrochemical analysis has been obtained for 49NH and presence of impurities might raise our value a fraction of one percent.

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A higher value for the specific activity of Pu^{239} reduces appreciably the inconsistency between the calculated half-life values for Pu^{240} based on mass analysis and specific activity determinations on samples of various Pu^{240} content.

No final figure for the half-life of Pu^{240} can be given, however, until the mass analysis can be done with the same precision as the specific activity.

Chemistry of Lanthanum,

The Vapor Phase Hydrolysis of Lanthanum Trichloride

A. Broido and B. B. Cunningham

The flow method described in the last Quarterly Report, UCRL 460, has been used to determine the thermodynamics of the reaction

$$LaCl_3 + H_2O \longrightarrow LaOCl + 2\ HCl$$

Briefly the method consists of passing N_2 - H_2O - HCl mixtures of known composition over a sample of the lanthanum compound mounted on a quartz fiber cantilever-type microbalance which is contained in a pyrex tube. The sample is maintained at the desired temperature by an electrically-heated tube furnace. If the HCl/H_2O ratio exceeds the value of the equilibrium constant at a particular temperature, the sample is converted to the trichloride; if not, the oxychloride results.

Since the writing of the last Quarterly Report, values of the equilibrium constant at several additional temperatures were obtained and ΔH and ΔS were calculated for the reaction. In addition, the iron-constantan thermocouple mounted in the furnace has been calibrated by comparison with a previously standardized platinum-platinum-rhodium thermocouple mounted inside the reaction tube.

The experimental values for the equilibrium constant are recorded in Column 3 of Table I. These values and the temperatures given in Column 2 have been used to calculate the experimental values of ΔF given in Column 4. In calculating ΔH and ΔS, values were estimated for Cp of LaOCl and $LaCl_3$ and these were combined with equations for Cp of the two gases to give

$$\Delta Cp = -4.11 + .0039\ T - .00\ 000\ 222\ T^2$$

Using this equation, the following values were obtained from the data:

$$\Delta H_{298} = 33.2$$

$$\Delta S_{298} = 42.8$$

$$\Delta H_o = 34.2$$

The value of ΔS_{298} is higher by about eight entropy units than that estimated by analogy with similar compounds. X-ray diffraction data and the fact that no change was obtained in the value of the equilibrium constant with change in composition of the initial solid phase both indicate that the range of solid solution formation is negligibly small at room temperature. The fact that the same value for the constant was obtained at flows of ~5 cc/min. and ~50 cc/min. together with the fact that no change resulted in substituting argon for nitrogen as the inert gas were taken as indications that no appreciable error in computing partial pressures of the gaseous species inside the furnace was introduced by thermal diffusion effects.

As a further check on the value of ΔS it is intended to determine ΔH for the reaction by calorimetrically obtaining ΔH of formation for the two solids.

TABLE I

Experiment Number	T (° K)	K	ΔF Expt'l	ΔF Calc. ⊠
1	641	0.0079	6.1_6	6.1_5
2	683	0.036	4.5_1	4.4_5
3	720	0.136	2.8_6	2.9_5
4*	759	0.40	1.3_8	1.3_8
5°	760	0.47	1.1_4	1.3_4
6	764	0.45	1.2_1	1.1_8
7	798	1.14	-0.2_1	-0.1_8
8	838	2.94	-1.7_9	-1.7_8

*Argon used as inert gas in this experiment.

°Probably this temperature is in error.

⊠ Calculated on the basis of

$$\Delta Cp = -4.11 + .0039T - 0.00000\ 222T^2$$

$$\Delta H_{792} = 31.83$$

$$\Delta S_{792} = 40.12$$

$$\Delta F_{792} = 0$$

The Crystal Structures of CeB_4, ThB_4 and UB_4

Allan Zalkin and D. H. Templeton

The compounds CeB_4, ThB_4 and UB_4 have been shown to crystallize in a new structure, which has been worked out from x-ray diffraction patterns. This structure is designated as the "ThB_4-type structure", since that was the compound first observed. These borides were prepared by D. L. Sawyer and L. Brewer of this laboratory, who heated the metals and boron together in vacuum at about 1500°C. Powder diffraction patterns were obtained of the three compounds. Rotation and Weissenberg patterns were obtained for (110) and (001) axes of a small single crystal of ThB_4. The patterns were indexed on tetragonal lattices whose dimensions are listed in Table I

TABLE I

Lattice Parameters

	CeB_4	ThB_4	UB_4
a	7.205 ± .008 Å	7.256 ± .004 Å	7.075 ± .004 Å
c	4.090 ± .005 Å	4.113 ± .002 Å	3.979 ± .002 Å
c/a	0.568	0.567	0.562
x-ray density	5.74 g/cm^3	8.45 g/cm^3	9.38 g/cm^3

Consideration of the intensities leads to the following structure for the metal atoms:

Space group D_{4h}^5-P4/mbm

4 Ce, Th, U in 4(g): ± (u, 1/2 + u, 0; 1/2 - u, u, 0)

u = 0.31

These metal atoms are coplanar, with each having five nearly equidistant neighbors in the plane. Each metal atom has two neighbors in adjacent planes, but these are at a greater distance. This structure has holes, between the layers, which are best filled by boron atoms as follows:

$$4 \text{ BI in } 4(e): \pm (0, 0, \underline{v}; 1/2, 1/2, \underline{v})$$

$$\underline{v} = 0.2$$

$$4 \text{ BII in } 4(h): \pm (\underline{w}, 1/2 + \underline{w}, 1/2; 1/2 - \underline{w}, \underline{w}, 1/2)$$

$$\underline{w} = 0.1$$

$$8 \text{ BIII in } 8(j): \pm (\underline{x}, \underline{y}, 1/2; 1/2 + \underline{x}, 1/2 - \underline{y}, 1/2;$$

$$\underline{y}, \underline{x}, 1/2; 1/2 + \underline{y}, 1/2 + \underline{x}, 1/2)$$

$$\underline{x} = 0.2$$

$$\underline{y} = 0.04$$

Thus the compounds were assigned formulas of the type MB_4, in agreement with the deduction, from the phases observed in various preparations, that the composition is between MB_2 and MB_6.

This structure can be considered as a combination of two other more simple structures. Each atom BII is in a hole bounded by six metal atoms at corners of a triangular prism, as is the case with boron in the isostructural compounds AlB_2[1], ZrB_2[2], TiB_2[3], CrB_2, NbB_2, TaB_2[4], VB_2[5], and UB_2[6]. The atoms BI and BIII are grouped together as octahedra in holes bounded by metals at the corners of square prisms, analogous to the arrangement in the compounds CaB_6, CeB_6, ThB_6, and others,[7] in which a simple cubic array of metal atoms is interpenetrated by boron octahedra. The distances in the MB_4 compounds are in reasonable agreement with the corresponding ones in the MB_2 and MB_6 compounds.

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The YF_3-type Crystal Structure

Allan Zalkin, Carol H. Dauben, and D. H. Templeton

For some time we have had x-ray powder diffraction patterns of YF_3, SmF_3, EuF_3, GdF_3, TmF_3, and YbF_3 which showed them to be isomorphous with an unknown crystal structure. Recently single crystals of YF_3 were prepared by slow cooling from above the melting point in high vacuum. The crystal fragments were transparent and colorless, but showed no crystal faces. Oscillation and Weissenberg patterns provided information which made possible the indexing of the powder patterns. The intensities show that the cell is orthorhombic, space group D_{2h}^{16}-Pnma, and that the structure is the same as that of Fe_3C. The lattice parameters are as follows:

	a Å	b	c	P gm/cc calc.
YF_3	6.33	6.86	4.39	5.20
SmF_3	6.66	7.07	4.40	6.65
EuF_3	6.61	7.01	4.41	6.79
GdF_3	6.52	6.93	4.36	7.21
TmF_3	6.29	6.79	4.39	8.02
YbF_3	6.15	6.71	4.41	8.39

It is interesting to note that SmF_3, the first one of the rare earth fluorides to exhibit this structure, is dimorphous crystallizing also in the hexagonal LaF_3 structure.

Professor W. H. Zachariasen (private communication) has in dependently indexed a powder pattern of YF_3 using the values a = 4.37 Å, b = 6.42, and c = 6.89, in good agreement with our values.

Magnetic Susceptibility of Vitamin B_{12} and the Rare Earths

J. C. Wallmann and B. B. Cunningham

Magnetic susceptibility measurements have previously been made on vitamin B_{12} and several rare earth compounds (UCRL-460). Since an absolute calibration of the magnet and balance is not feasible, a more accurate investigation of the relative standard, Mohr's salt, has been undertaken. The literature lists several values for the specific susceptibilty of ferrous ammonium sulfate $\cdot$ $6H_2O$ (e.g., Pauling, "Nature of the Chemical Bond," and Selwood, "Magnetochemistry") and by measuring the susceptibility of $NaSO_4 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, and $CuSO_4 \cdot 5H_2O$, it has been possible to choose the value $X = 29.45 \times 10^{-6}$ as the most reliable at the present time: eleven separate measurements indicate that using this figure as the balance calibration gives the best agreement with literature values for the susceptibility of the nickel and cupric salts. Our previously reported observations on B_{12} and rare earth compounds are not appreciably altered because $X = 29.6 \times 10^{-6}$ was used for the Mohr's salt standard.

Anion Exchange Separation of Zirconium and Hafnium

E. H. Huffman and R. C. Lilly

The separation of zirconium and hafnium by Amberlite IR-400 has been reported previously, and subsequent work has been to study the effects of varying HCl and HF concentrations on the elution. The following experiments were carried out with 2.0 mg of zirconium and 1.0 mg of hafnium adsorbed from 0.06M HF and eluted from a column 10 cm long and 0.3 cm^2 in cross section.

In Figure 1 are given the results for 0.19, 0.20, and 0.23M HCl eluting solutions each 0.01M in HF. In each case the first peak represents zirconium and the second peak hafnium.

Very small increases in the concentration of HCl are thus seen to influence both the rate of elution and the sharpness of the peaks in a marked manner. At higher concentrations of HCl, still using 0.01M HF , the rate of elution is still faster (results not shown), but the degree of separation is still less pronounced. The greatest separation with 0.01M HF appears to be attained with the 0.19M HCl, although for some purposes the higher rate of elution shown by 0.23M HCl might be preferred.

In Figure 2 are given the results for 0.01M HF and 0.02M HF, both 0.23M in HCl. A result for 0.04M HF is not drawn in as the curve was broad and low, beginning at about 109 ml, and showed an indefinite degree of separation.

The result for the mixture of 0.23M HCl and 0.02M HF is very similar to that for 0.19M HCl and 0.01M HF as shown in Figure 1, but with somewhat sharper peaks.

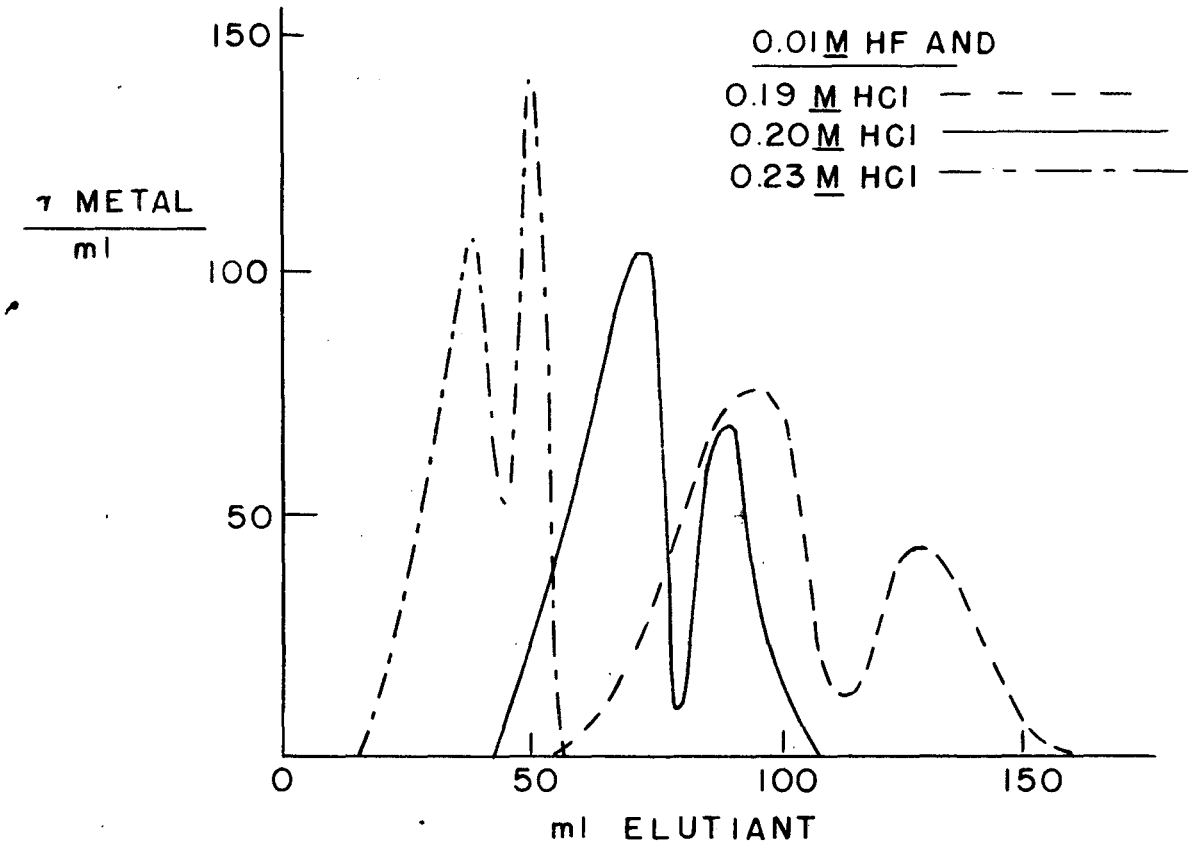

0.01 M HF AND
0.19 M HCl
0.20 M HCl
0.23 M HCl
γ METAL / ml
150
100
50
0
50
100
150
ml ELUTIANT

FIG. 1

14512-1

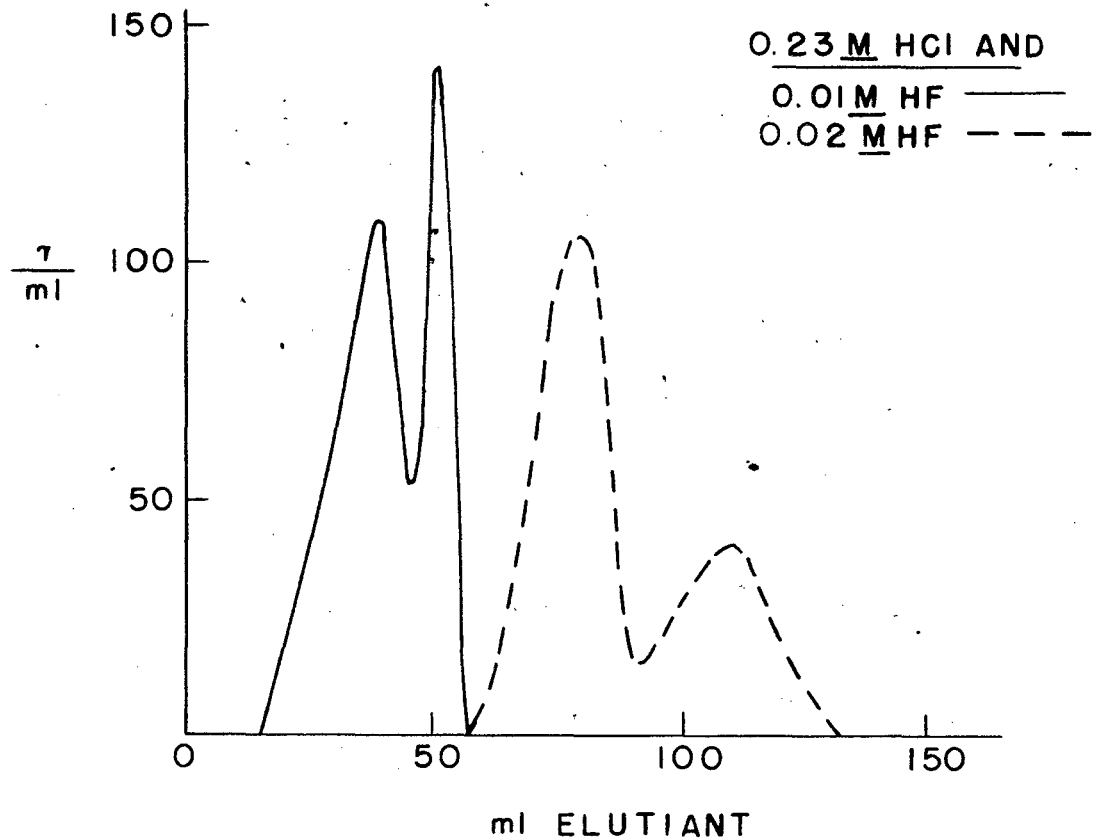

150
100
50
0
50
100
150
γ/ml
ml ELUTIANT
0.23 M HCl AND
0.01 M HF
0.02 M HF

FIG. 2

14513-1

Extraction and Paper Chromatography of Zirconium and Hafnium

E. H. Huffman and Dorothy B. Stewart

Some experiments have been carried out to use the alizarin colorimetric determination of Liebhafsky and Winslow on a tributyl phosphate (TBP) extract of zirconium in order to shorten the separation procedure. Although no final method has been decided on, the following observations indicate the possibilities of such a scheme.

Zirconium is extracted completely by fresh TBP from HCl solutions of 7 molar strength or greater. The degree of extraction drops off on lowering the HCl concentration to 4 molar and becomes negligible below this concentration. However, if the TBP is allowed to stand for some time in contact with HCl of, say, 6 molar strength and then used to extract zirconium from 6M HCl, the degree of extraction is increased. If the TBP-6M HCl mixture is boiled and then used to extract zirconium, extraction is complete. The extraction coefficient for zirconium appears to be about three times that for hafnium from 6M HCl and fresh TBP.

The extraction with TBP is not specific for zirconium. Some extractions not previously reported have been investigated for the elements listed in Table I which are known to interfere with the alizarin method as generally used.

These extractions were made from 6M HCl with a solution of one part TBP, (after boiling with 6M HCl) and three parts dibutyl ether. Standard colorimetric curves were made from zirconium solutions which contained the same amount of organic solvent as in the aliquots used.

At present the only method of determining small amounts of hafnium in zirconium is by means of the spectrograph. The use of paper chromatography for the separation, followed by colorimetric determination of hafnium might offer another method, and some attempts at such a separation have been tried. Very appreciable differences in R_f, as measured by the leading edges or by the center of density of zirconium and hafnium spots have been attained by three different developing solutions. A solution of 50 percent n-butanol - 50 percent 6M HCl moves the hafnium spot faster than it does the zirconium. The opposite result is obtained with a 50 percent ethylacetoacetate - 50 percent 6M HCl mixture, as is also the case with a half and half mixture of 2 percent β-nitroso-α-naphthol in ethyl alcohol and 6M HCl. Although the differences in the R_f values themselves are appreciable, there is too much tailing of the spots to allow of satisfactory separations. The method is not usuable until this difficulty is overcome.

TABLE I

Ratio of Element to Zirconium	Degree of Extraction	Interference of Extract with Color
2:1 Fe	100 %	Negligible
2:1 Al	None	None
1:1 Ti	30-50 %	Slight positive
2:1 Cd	None	None
3:1 Cu	Slight	None
2:1 Cr	None	None
2:1 Co	None	None

B. Nuclear Properties and Transformations

Neutron Deficient Radioactive Isotopes of Cerium and Lanthanum

Betsy Jones and B. B. Cunningham

To look for new light isotopes of Ce and La, La_2O_3 was bombarded with 50, 60, 70 and 80 Mev protons on the 184-inch cyclotron. Three new activities were observed and assigned to Ce^{133}, Ce^{134}, and La^{134}. The half-life and positron energy of Ce^{135}, which had been known only approximately, were determined, and an error in the conversion electron energy of Ce^{137} was noted.

Chemical identification of these activities was made by first subjecting the bombarded material to fluoride-hydroxide cycles to exclude any elements other than rare earths. The La-Ce separation was affected by oxidizing Ce with $KBrO_3$ in HNO_3 and then precipitating $Ce(IO_3)_4$ with HIO_3 at 0°C. Spectrographic analysis of the $Ce(IO_3)_4$ showed La to be beyond the limit of detection. Interfering lines in the rare earth region limit spectrographic analysis, but the above results show that more than 98 percent of the La was separated from the Ce.

Ce^{137}. The 36-hour Ce^{137} was reported by Chubbuck to have a conversion electron of 0.20 Mev, this value being a weighted average of 0.23 Mev obtained on the bender and 0.16 Mev from Be absorption. In the present work 0.24 Mev was measured both on the bender and by Be absorption. Re-examination of Chubbuck's Be absorption data revealed an error in interpretation.

Ce^{135}. A half-life for Ce^{135} of approximately 18 hours was estimated from bender sweeps by Chubbuck who also showed it to be the parent of the 19.5-hour La^{135}. Resolution of decay and absorption data is complicated both by the growth of La^{135} and the high yield of Ce^{137}. Sufficient Ce^{135} was made to follow decay of the positron on the bender, and decay through about 5 half-lives gave a value of 22 hours. Bender and Be absorption data give 0.75 Mev for the positron energy and show a very small $\beta+/K$ ratio.

Ce^{134} and La^{134}. After all other Ce activities had decayed out and their La daughters removed, a 72-hour Ce remained, and La milkings revealed a 6.5 min. La daughter. Since La^{133}, La^{135}, and La^{137} have been assigned mass spectrographically, and La^{136} by yield considerations from bombardments on separated Ba isotopes, the 6.5 min. was assigned to La^{134} by elimination. This assignment is consistent with the relative yields of the 72-hour Ce parent.

The radiations of Ce^{134} and La^{134} in equilibrium, and of separated La^{134} were characterized by Be and Pb absorption and bender data.

equilibrium

$Ce^{134} + La^{134}$ = 2.7 Mev $\beta+$: 0.5 Mev γ : K
0.44 : 0.44 : 1.56

separated

La^{134} = 0.4 : 0.4 : 0.6

That the positron is emitted by the La^{134} was shown by checking energy and half-life on the bender. These data permit a rough decay scheme determination. Ce^{134} decays 100 percent by electron capture; La^{134}, 56 percent by electron capture and 44 percent by positron emission.

Ce^{133}. The mass assignment was made by milking the 4-hour La^{133}. Ce^{133} is the only isotope among the light Ce's and La's under observation which emits a very hard gamma, and this property permitted a good half-life determination. Decay of the 1.4 Mev γ through 7.5 half-lives gave 6.3 hours. Other radiations are a 1.4 Mev $\beta+$ K-x-rays, and possibly a conversion electron of about the same range of that of Ce^{137} and a 0.38 Mev γ.

Bi Activities from Neutron Irradiated Bi

I. Perlman and H. M. Neumann

The Bi activity resulting from neutron irradiation of Bi, reported in UCRL-382 has been studied further. The presence of a 5.03 Mev α-emitter, leading to a 4.2 min. Tl daughter was reported at that time. The alpha-emitting Bi was assigned to an excited state of Bi^{210} on the basis of this information.

A large portion of this irradiated Bi was intensively purified and the specific activity determined. The resulting values for the specific activity are 1.9 ± 0.1 α-disintegrations/min. per mg and 2.0 ± 0.2 Geiger counts/min. per mg.

An aluminum absorption curve indicated 95-99 percent of the Geiger activity to be due to a β^- particle of maximum energy 1.5 ± 0.3 Mev. This activity is the 4.2 min. Tl^{206} daughter in equilibrium with the parent. The remaining 1-5 percent of the activity was electromagnetic in character, and a crude Pb absorption of the few counts available indicated an energy in the range 30-400 Kev. This radiation could conceivably be x-rays from Bi^{208}.

If Bi^{208} were present one might expect some conversion electrons to be seen. Because of the low specific activity of the sample, self-absorption effects are large in samples with moderate counting rates (~400 counts/min.), and counting errors are large in samples with small self-absorption. Thus the failure to observe conversion electrons does not mean they cannot be present.

A portion of the Bi was carefully purified from Po, and then allowed to stand for 63 days. Since Bi^{210m} is unstable with respect to Po^{210} one might expect Po^{210} to grow into the sample. This growth could result from β^- decay of Bi^{210m}, or by isomeric transition to Bi^{210} followed by β^- decay of the latter. The amount of Po^{210} found at the end of the growth period indicates the half-lives for I.T. and β^-decay to be each greater than 2×10^3 times the half-life for α-decay. The measured half-life (from decay of alpha particles over a period of 15 months) is greater than 25 years.

Light Polonium Isotopes

David G. Karraker and D. H. Templeton

Light Polonium Isotopes. The thallium orbital electron-capture daughters of the lead alpha-decay daughters have been identified for three polonium isotopes; Po^{205}, Po^{203}, and Po^{202}. In each case, the genetic relation between parent and daughter was established by successive separations of the thallium daughter, such that the amounts of thallium activity separated decreased with the half-life of its chain parent. The activities separated and their parents are shown in Table I.

TABLE I

Parent	Tl activity	α-decay daughter
1.5 hr Po^{205}	72 hr Tl^{201}	8 hr Pb^{201}
37m Po^{203}	7 hr Tl^{199}	~80m Pb^{199}
40m Po^{202}	1.8 hr Tl^{198}	~25m Pb^{198}

The alpha-particle energy of 4-hr Po^{204} has been redetermined as 5.37 Mev, and that of Po^{203} as 5.62 Mev. This alpha-group has been assigned to Po^{203} instead of Po^{202} because the separation of alpha-decay daughters has shown that about 100 times as many alpha-particles belong to Po^{203} as Po^{202}. No alpha-group which can be assigned to Po^{202} has been found.

The branching ratio of Po^{205} has been determined as $K/\alpha \cong 1000$, by counting the decay of the alpha-particles, and separating the bismuth orbital electron capture daughter. A counting efficiency of 2 percent was used for Bi^{205} in the calculations.

Low Mass Isotopes of Astatine

George W. Barton and I. Perlman

The alpha-branching ratio of the lighter astatine isotopes has been found to be high enough to permit the use of recoil methods in mass assignment. A sample of several million counts of At on a 1 inch silver disc is placed in vacuum 1/16 inch away from a standard Pt counting plate which is used as a catcher. The recoiling bismuth atoms from the At alpha emission are caught on the Pt plate. The Bi atoms are then changed to the sulfate and that At which has volatilized onto the catcher is flamed off. By replacing the catcher plate with a new one at uniform intervals, it is possible to take data in essentially the same form as in chemical milking experiments. Recoil activities were observed which can be attributed to the 52 hour Pb^{203} ($At^{207} \xrightarrow{\alpha} Bi^{203} \xrightarrow{k} Pb^{203}$) and to the fourteen-day Bi^{205} ($At^{209} \xrightarrow{\alpha} Bi^{205}$). These experiments confirmed the assignment of the 5.5 hr. At activity to At^{209} and the 1.7 hr. activity (α-energy 5.75 Mev) to At^{207}.

Protron Excitation Cross Sections in Uranium Fission

R. L. Folger, P. G. Stevenson and G. T. Seaborg

Preliminary Results. A series of bombardments were made in the internal beam of the 184-inch Berkeley cyclotron in order to determine the excitation function for the fission of uranium^{238} with high energy protons. In order to measure the proton beam through the U foil, advantage was taken of the reaction: $Al^{27}(p,3pn)\ Na^{24}$. The target consisted of a 2-mil U foil (depleted in U^{235}) sandwiched between 1/2 mil Al foils protected from fission recoils by 1 mil Al as illustrated in Fig. 1.

After bombardment the target was cut (with shears) in the position indicated in order to eliminate error due to Cu spallation products and secondary neutrons from the target holder.

The Al monitors were removed and the front and back foils counted separately in order to observe any mechanical errors which might have been introduced by faulty cutting (i.e., area of Al obtained might have differed slightly from area of U). The U targets were dissolved in conc. HNO_3 containing carriers and allowed to stand for 4-1/2 hours (in order for all Pd^{111} to decay to Ag^{111}). Ba, Sr, and Ag were separated chemically by standard fission product procedures.

The cross section for the reaction $Al^{27}(p,3pn)Na^{24}$ was determined by calibration against the reaction: $C^{12}(p,pn)C^{11}$ (whose cross section has been determined by Peterson, et al referred to in a private communication, for energies from 10-350 Mev). 20 mil graphite blocks, backed by 1 mil Al foils, were bombarded at various energies for 2 min. each in the internal proton beam of the 184-inch cyclotron. See Fig. 2.

The effect of recoils from the Al into the C was negligible as evidenced by the counting data which showed that <.01 percent of the activity of the graphite was long-lived activity.

Self-absorption in the graphite was measured by comparing the activity of a known weight of 20 mil graphite to the activity of a known weight of thin polystyrene. These were bombarded simultaneously in the circulating beam with the intensity reduced to prevent thermal distortion of the polystyrene. Peterson, et al have shown (private communication) that self-absorption in thin polystyrene is negligible.

Preliminary values of the fission cross section for formation of mass 111 (measured as Ag^{111}) and mass 89 (measured as Sr^{89}) were obtained as functions of bombardment energy. The experimental data scatter about smooth curves; this scatter is due to treatment of the target before solution, since corresponding points for Ag^{111} and Sr^{89} deviate from their respective curves in the same sense in every case. The ratio of these two cross sections as a function of bombardment energy does not exhibit this pronounced scatter.

Indications are that the cross section for formation of mass 111 is constant at about 0.5 barns above 175 Mev, decreasing at lower energies; the cross section for formation of mass 89 is constant at about 0.33 barns above about 125 Mev, decreasing at lower energies; and the ratio (σ 89/σ 111) is roughly constant at energies greater than 150 Mev, and increases at lower energies. Assuming that the total fission cross section for uranium is approximately the geometric cross section the fission yields for mass 111 and mass 89 are respectively 19 percent and 13 percent at high energies. More precise data will be forthcoming.

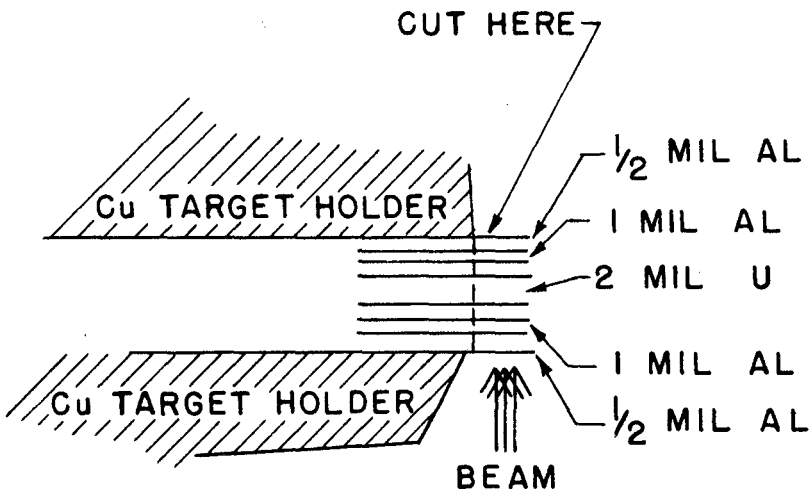

CUT HERE
1/2 MIL AL
Cu TARGET HOLDER
1 MIL AL
2 MIL U
1 MIL AL
Cu TARGET HOLDER
1/2 MIL AL
BEAM

FIG. 1

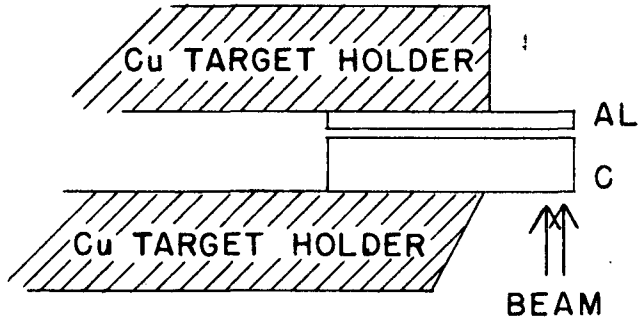


FIG. 2

Mass Spectrograph

F. L. Reynolds

Most of the work done during this period has been on abundance ratio determinations of Pu and Am samples. These ratio determinations are of importance since they can contribute to the estimation of half-lives and cross sections.

Sample 12B, a Pu sample, gave the following relative atomic percentages:

Mass	239	240	241	242
Percent	58.1	34.0	6.8	1.02
Average Dev.	±.48	±.48	±.32	±.11

Sample 12B was also used in an attempt to determine the half-life of Pu^{240} by the following method. Several exposures of the above spectra were made, collection being on Ilford Q photographic plates. Eastman N.T.A. alpha-track plates were then placed, emulsion to emulsion, for a period of time. The ratio of the number of tracks between Pu^{239} and Pu^{240} gave a measure of the half-life of Pu^{240} as 6,600 years ± 250. This work is not completed.

An Am sample, 51NB, gave the following percentages, which are an average of thirty determinations:

Mass	241	242	243
Percent	99.0	0.6	0.4

The value for Am^{242} is still uncertain.

Both the above and the Pu determination were accomplished by using a thermal source. The "loss" factor for Pu as oxide on a Ta filament is 6.6×10^5. Pu is emitted as Pu+ and PuO+ from the Ta filament, Pu+ being the heavy beam at around 1800°C. The "loss" factor for Am, as oxide on a Ta filament, is 1×10^5. Emission beams are Am+ and AmO+.

Attempts were made to use the instrument for the collection of very small amounts of the Pu isotopes for subsequent fission studies. The results of this work will be reported elsewhere in this report.

In conjunction with the Eastman Kodak Company, work is progressing in the development of more suitable and sensitive plates for positive ion spectra detection.

Heavy Plutonium, Americium, and Curium Isotopes

S. G. Thompson, K. Street and A. Ghiorso

12B Plutonium Sample. Pu^{239} was bombarded in a Hanford pile from September 27, 1944 to June 14, 1945 at a total nvt of 1.3×10^{20}. The resulting Pu was purified and the isotopic composition determined at Los Alamos with a mass spectrograph. The results were 92.8 percent Pu^{239}, 6.86 percent Pu^{240} and 0.38 percent Pu^{241}. Approximately 54 mg of the purified Pu was further bombarded at Hanford as follows:

Period of Bombardment	Reported nvt
5/25/46 - 7/16/47	2.04×10^{20}
5/25/48 - 5/25/49	1.95×10^{20}

At the end of the bombardment, the sample was shipped to Berkeley where chemical separation and decontamination of the Pu, Am and Cm fractions were performed. The elemental composition of the bombarded material was approximately as follows:

Element	Wt (mg)
Pu	~20
Am	~ .03
Cm	~ .0045

Pu Isotopes of Mass 242 and 243. The isotopic abundances of the 12 B Pu were determined in the mass spectrograph. These results are reported in the mass spectrographic section of this report. It should be noted that observation of Pu^{242} represents the discovery of a new Pu isotope.

The existence of the isotope Pu^{243} which decays by beta-particle emission to Am^{243} has been proved by observing a larger amount of Am^{243} in the Am fraction than could have been produced by the reaction Am^{242} (n,γ) Am^{243}. Am^{243} has been observed previously by Street and Seaborg in samples of Am bombarded with pile neutrons according to the above reaction. Its observation is made possible through its α-decay to Np^{239} which is separated. The ratio of Am^{243} to Am^{242} in the 12B Am was found to be >10 times the corresponding ratio observed in a comparable irradiation of Am with pile neutrons.

Alpha-energy of Pu^{240}. Examination of the plutonium fraction from the 12 B bombardment in a differential pulse analyzer shows that the α-energy of Pu^{240} is less than 10 Kev different from that of Pu^{239} (5.16 Mev).

Alpha-energy of Pu^{241}. The plutonium fraction also shows an alpha of 4.91 Mev energy in an abundance of 0.2 percent. This α is probably due to Pu^{241} and if this is assumed to be the case the alpha-half-life is 3×10^5 years from the mass spectrographic data.

Alpha-energy of Am^{243}. The milking of Np^{239} from the americium fraction of 12B as mentioned above showed that 0.3 percent of the α disintegrations are due to Am^{243}. Examination of the americium fraction in the pulse analyzer showed an alpha of 5.21 Mev energy and in 0.3 percent abundance which is thus assigned to Am^{243}.

The Isotope Cm^{244} (?). Examination of the α's in the curium fraction of a 15-mo. neutron irradiation of Am^{241} (51NB. Isotopic composition given in Mass Spectrographic Section of this report) showed an α of 5.78 Mev energy in 0.3 percent abundance (after 28-mo. decay of curium fraction). The curium fraction of the 12B bombardment showed the same α in an abundance of 0.1 percent. Considering the periods of irradiation and the subsequent decay of the 51NB curium it seems most likely that the observed alpha(5.78 Mev) is due to Cm^{244} formed by the path

$$Am^{243}\ (n\gamma)\ Am^{244} \xrightarrow{\beta^-} Cm^{244}.$$

A curium alpha of this energy was previously reported by Thompson, Cunningham and Ghiorso, in the curium fraction of an alpha particle bombardment of Am^{241} and tentatively assigned to curium 243 or 244.

Half-Life of Pu^{241}. The Pu fraction from sample 12B was milked for Am^{241} to determine the beta-half-life of Pu^{241}. The half-life obtained using the mass spectrograph analysis reported in the Mass Spectrograph section of this report, (6.8 percent Pu^{241}) is 14.2 ± 1 year.

The Isotope Am^{244} (?). Irradiation of the americium fraction of sample 12B with neutrons in the Argonne pile produced a new beta-emitting americium activity of ~25 min. half-life. This activity is probably Am^{244} and if this is the case the capture cross section of Am^{243} is ~50 barns.

Fission Cross Sections. Fission measurements made at the Argonne pile using samples of the plutonium isotopes separated with the mass spectrograph (UCRL 460) allow the following limits to be placed on the fission cross sections.

σ_f Pu^{240} <50 barns

σ_f Pu^{241} 500 to 1000 barns

Fission measurements on the americium fraction from the 51 NB bombardment give a fission cross section for Am^{242} of 4000 to 6000 barns.

X-ray Spectrometer

G. W. Barton and I. Perlman

The new detection system for the x-ray spectrometer has been installed and experiments are being carried on. The system now consists of an end-window xenon-filled counting tube working at 1 atm. Xe pressure in the proportional region. The pulses are fed from the tube into a linear amplifier and into a discriminator circuit which permits the rejection of all pulses which are not of the size corresponding to the x-rays of interest. The desired counts are then fed into a scaler and also to a counting rate meter. This system has succeeded in reducing the background count to ca 10 c/m while at the same time increasing the sensitivity to the desired radiation by a good factor.

Beta Spectrometer

G. D. O'Kelley and F. L. Reynolds

The magnet power supply for the β-spectrometer has been improved, and the regulation is now about 1/5000 for normal line voltage fluctuations, which are held below 1 percent by a 5 kva Stabiline regulator.

No changes have been made in the counter, since the present window (0.4 mg/cm^2 nylon) has been in service for ten weeks without leaking seriously.

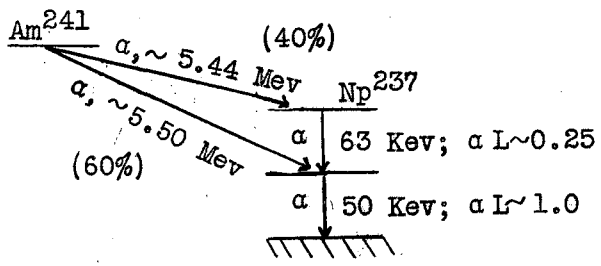
The pressure in the vacuum tank is about 4 x 10^{-6} mm of Hg Electron Spectrum of Am^{241}. The sample for this investigation was prepared by W. W. Crane, and had a disintegration rate of 3.7 x 10^7 d/min. Since the sample was mounted on mica, the lowest electron line was smeared somewhat, but the energy assignments should be fairly good. Table I indicates the results found.

TABLE I

Electron line, Kev	Relative Activity, e^- c/m	Interpretation	Binding Energy (Np), Kev	E_γ, Kev
30	88,700	L_{II}	20.4	50.4
33	17,000	L_{III}	16.7	49.7
46	10,800	L_{III}	16.7	62.7

The two γ-lines have thus been assigned values of 50 and 63 Kev. A 62-Kev γ-ray is seen by absorption, and one would expect the 50 Kev γ-ray to be almost completely converted, since it is not seen in absorption measurements.

A possible decay scheme might be:



The estimations for the conversion coefficients and degree of branching were made by correcting for the geometry of the machine, and choosing the most consistent values. The α L ≃ 0.25 for the 63 Kev γ-ray is in agreement with an estimate by A. Ghiorso based on other evidence.

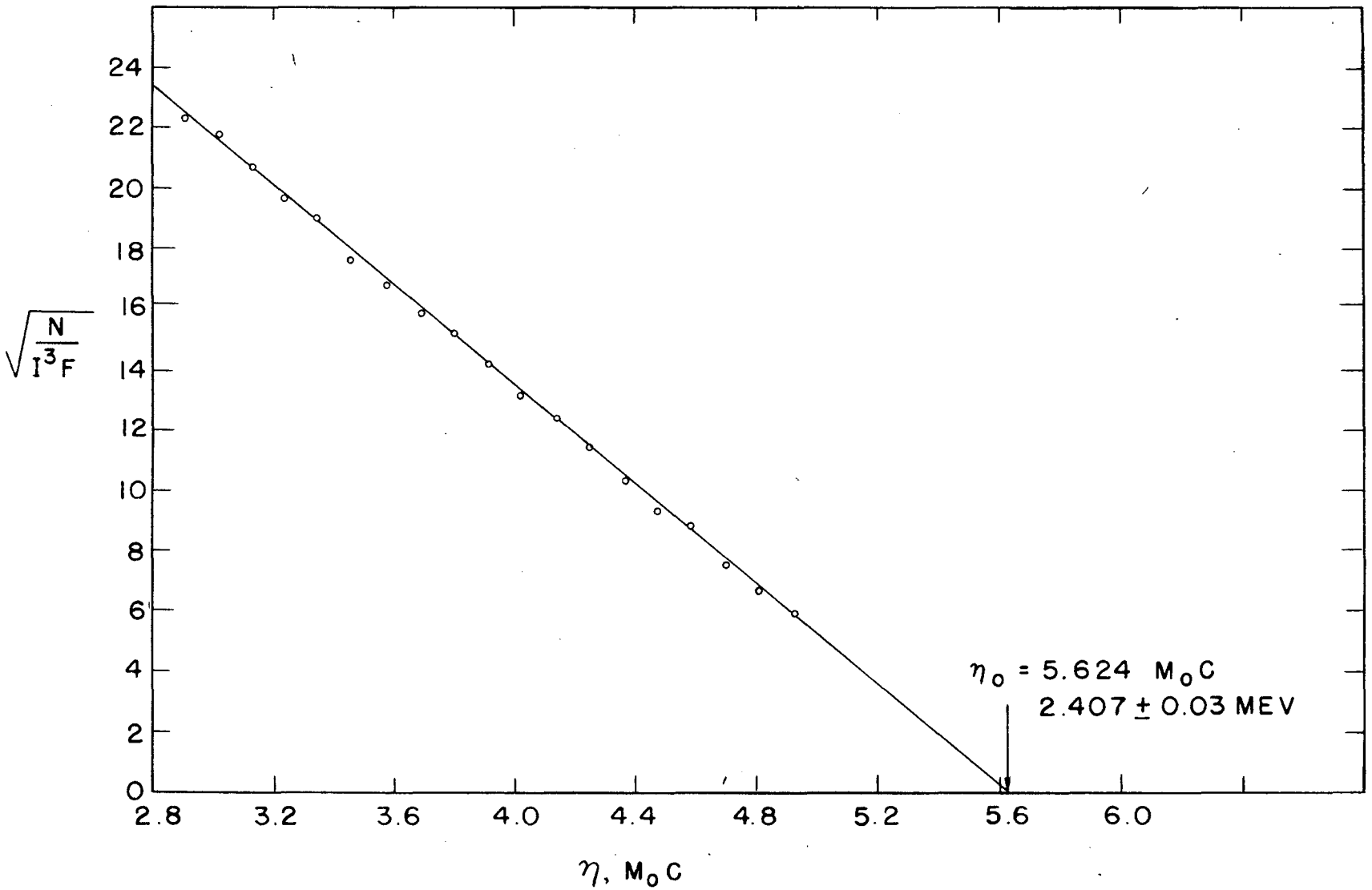


FIG. 1

FERMI - KURIE PLOT OF $Zr^{87(?)}$ β^+ SPECTRUM, NO SCREENING CORRECTION

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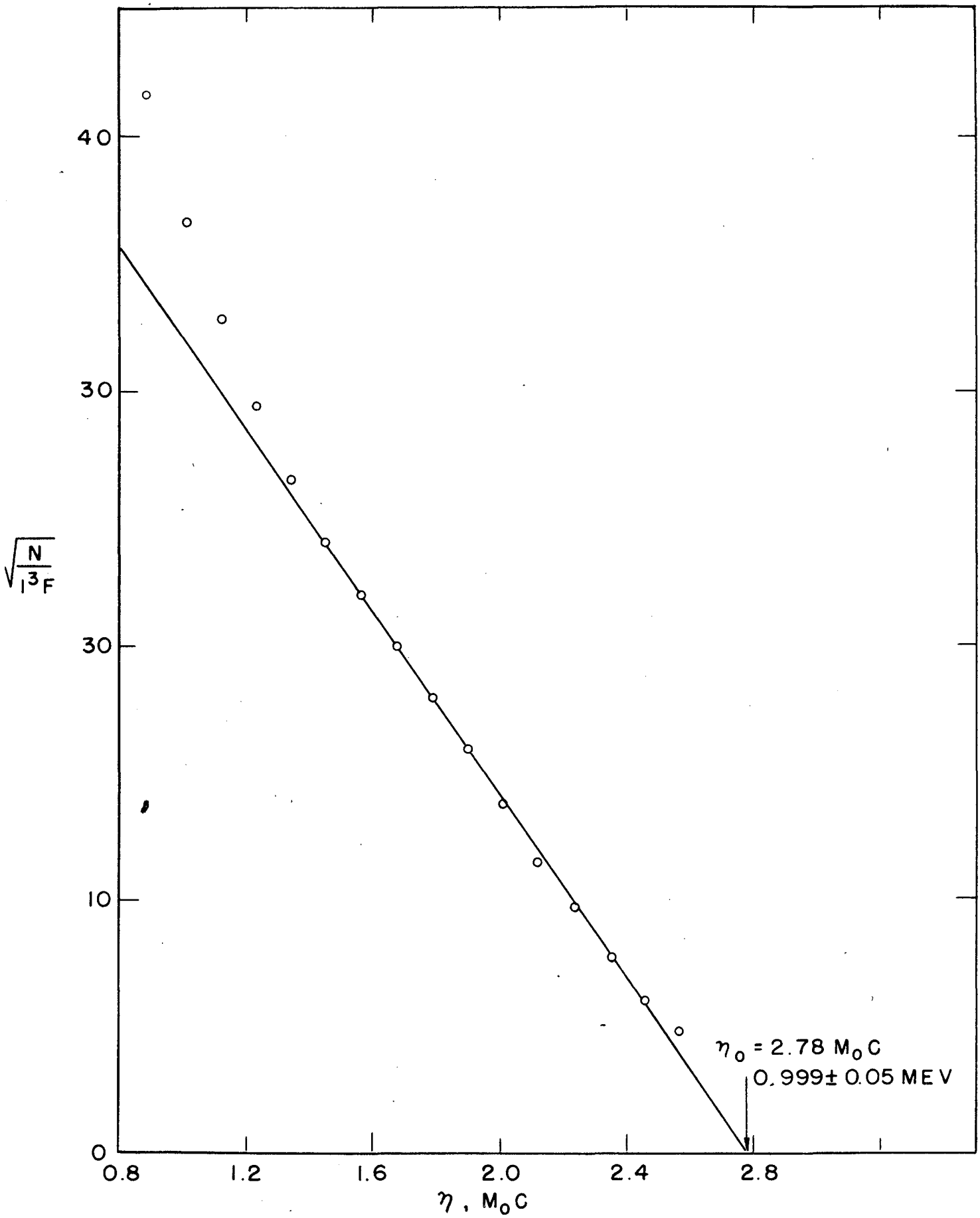

FIG. 2

FERMI-KURIE PLOT OF β^+ SPECTRUM OF Zr^{89}, NO SCREENING CORRECTION

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The binding energies in the heavy region were extrapolated by W. W. Crane from known binding energies below Z = 91.

Electron Spectrum of U^{231}. We have previously reported electron lines at 30, 34, 44, 56 Kev. The results are summarized in Table II.

TABLE II

Electron Line, Kev	Relative Intensity	Interpretation	Binding Energy, Kev	Eγ, Kev
30	9.3	L_{II}	20.4	50.4
34		L_{III}	16.7	50.7
44	2.5	L_{II} (?)	20.4	64
56	1.0	L_{II} (?)	20.4	76

Although the U^{230} present in the sample was down by at least a factor of five, a sample of pure U^{230} of comparable activity was run as a precaution, and no electrons were detected. We thus assign these observed electrons to U^{231}.

Electrons from Cm^{242}. A sample of Cm^{242} was prepared by W. W. Crane on mica (~3 mg/cm^2). To investigate the effect of heavy sample backings, a sample was also mounted on 1/4 mil platinum. Tables III and IV show the results obtained

TABLE III

Mica Backing

Electron Line, Kev	L-Edge	Eγ Kev	Ave., Eγ Kev
17.6	L_{II}	39.8	39.9 (A)
21.9	L_{III}	40.0	
35.2	L_{I}	58.1	58.1 (B)
(36.1)*	L_{II}	(58.3)	
39.9	L_{III}	58.0	

*Not accurately determined.

TABLE IV

Pt Backing

Electron Line, Kev	L-Edge	Eγ Kev	Ave. Eγ Kev
~16	L_{II}	~38.2	) 38.8 (A)
21.2	L_{III}	39.3	)
34.4	L_{I}	57.3	) 57.2 (B)
38.9	L_{III}	57.0	)

It is seen that the introduction of a heavy backing lowers the energy measured by about 1 Kev. However, the use of platinum backings is convenient, especially in the case of the Cm^{242} samples, since the intense α radioactivity attacks mica or plastic.

The relative intensities of electron groups (A) and (B) are in the ratio 1.0/1.8, respectively.

Positron Spectra of Zr^{87} (?) and Zr^{89}. E. K. Hyde has observed a new 90-minute β^+ activity in the Zr fraction isolated from bombardments of Nb with high energy protons. The mass assignment is tentatively Zr^{87}. A considerable quantity of 80-hour Zr^{89} is also formed, and the $\beta+$ energies of both isotopes have been measured in the β^- spectrometer.

A Fermi-Kurie plot of the 90-minute $\beta+$ activity is shown in Figure 1. Two experiments yielded end point values of 2.407 and 2.405 Mev. We have thus assigned an energy of 2.41$\pm$ 0.03 Mev to the 90-minute isotope. An automatic recording of the spectrum was made, using a motor-driven magnet current sweep and a counting rate meter in conjunction with a Leeds & Northrup dot-type Speedomax. The end point in this case was simply read off the spectrum; a value of 2.40 Mev was obtained, which is in agreement.

After decay of the 90-minute component, the spectrum of the remaining 80-hour Zr^{89} was investigated, and a Fermi-Kurie plot made as shown in Fig. 2; further work is being carried out on the spectrum of Zr^{89}. The value of 0.999$\pm$ 0.03 Mev should be fairly good.

Spontaneous Fission

R. L. Shuey

This report will discuss the equipment that has been constructed for the measurement of sponteneous fission rates. Theory and design information that is not well known at present has been included.

The construction of this equipment was undertaken primarily for two reasons: first, to study and solve the problems that were likely to be encountered in the construction of equipment to study the energy distribution of spontaneous fission: second, to construct a machine that would be useful for analysis and research in the Chemistry Department. The present equipment which can be mounted in a standard Bud cabinet seems to fullfil both of these aims. Its main asset is its simplicity and the ease of reproducing it.

This report will limit itself to a discussion of the instrumentation and equipment involved and will not discuss the applications and uses of the fission counter.

General Block Diagram. Figure 1 is a general block diagram of the equipment; this diagram will be referred to in the text of this report.

Ionization Chambers. a) Most discussions of ionization chambers analyze them by considering the charge induced on the collection plate.[1] We have chosen to use an equivalent analysis used in vacuum tube studies because we believe that once having proved a basic theorem the important features of how an ionization chamber acts are immediately apparent. It may be shown that given any number of conductors, n, (Figure 2) and a charge traveling through space with velocity $\overline{V}$, the current induced in the i-th conductor is:[2]

(1) $I_i = g\overline{V} \cdot \overline{E}_a$ All values MKS unite

I_i = current induced in i-th conductor

where: g = charge

$\overline{V}$ = velovity

$\overline{E}_a$ = field at q if all conductor but i-th grounded and one volt applied to the i-th.

Integration of (1) gives the charge on the collecting electrode which we see is a function only of position as expected. (All of this analysis is of course assuming magnetic effects and relativity are second order)

(2) $\int I_i \, dt = \int g\overline{V} \cdot \overline{E}_a \, dt = \int g \, \frac{\overline{dS}}{dt} \cdot \overline{E}_a dt = g \int \overline{dS} \cdot \overline{E}_a$ = function of position or potential

Let us assume an infinite plate parallel-plate chamber. Figure 3 shows that current induced in the collection plate and the voltage developed across the chamber capacity assuming the time constant of the load resistance and chamber capacity is infinite. Two cases of alpha particles with the same energy but at different angles are shown. Unfortunately, we cannot avoid the integration of the current by the chamber and input tube capacity; the possibility exists however of differentiating the resulting signal at a low impedence level and then clipping the result of the differentiation. This is shown in Figure 4 and we see that it results in a signal which is proportional to the number of ions originally formed or the particle energy. As the ion formation takes place in a time less than 10^{-8} seconds we can theoretically get this signal in a time very short with respect to the collection time.

Rossi and Staub[1] indicate that there is a plateau in the velocity vs E/P curve for a mixture of argon and CO_2 (E equals volts/cm and P equals pressure in mm). We have not verified this entire curve but we have shown that varying the pressure or the applied voltage in a chamber operating on the plateau does not change the output pulse. Operation on this plateau gives the fastest rise time and in the case of a chamber that does not have a uniform field gives a constant velocity throughout the chamber. Using a mixture of commercial argon and carbon dioxide and using an ionization chamber containing only metal and ceramic parts, it is found that the pulse size out of the chamber is stable when it is filled and the gas left in without circulation, except for possibly very small leaks. The commercial gases may have impurities that affect the recombination but apparently the volocity of the electrons is still very high. It should be pointed out that by stability one does not mean stability to a degree needed in alpha pulse analysis work; the stability statement is based on the lack of shift of the alpha pile up part of a fission bias curve[1] over a long period of time. The importance of these observations is that the required degree of stability of the chamber itself may be obtained merely by keeping materials that will contaminate the gas out of the chamber and not bothering with gas circulation and filtering.

If it is intended to use the parallel plate chamber as a measure of energy it is important to know what the effect of using finite planes is. Let it be pointed out here that as far as the induced current is concerned voltage dividing rings do not help in the slightest; some of the current that should be induced in the infinite plane is induced in the rings. The rings are useful only in determining the direction of the particles (electrons) motion. We can see that the above is true by examining Equation 1 and realizing that one must ground all of the electrodes but the collection plate when solving for the induced current. As the walls of the pressure tank effectively act as a ground and the exact pulse size is not important in fission rate work a chamber with a cross section as shown in Figure 5 has been adopted. A potential plot is included that permits one to estimate the error. The added capacity over that in the design used by other workers[1] is not important as the noise is not important.

The chambers used were normally run at about 18 lbs/in^2 absolute with a spacing of about 1 cm. The voltage across the chambers was about 1200 volts. A clipper was normally used that cut the pulse back to a triangular pulse of about .3 μs length, Figure 6. The investigation of various pulse shapes was done with alpha pulses by photography. For several cases the fission pulse shapes were checked and turned out to be the same. A summary of several possible pulse shaping methods is given in Figure 7. It should be noted that clipping very short, to

a point where differentiation occurs, gives a pulse the length of the collection time of the electrons; a shorter clipping time, as observed by other workers, does not improve this. A shorter clipping time would improve normal operating resolution somewhat.

The differentiation and clipping scheme of Figure 4 was tested, as shown in Figure 8, on alpha particles. The noise of the arrangement was very bad, due to differentiating to such a low level of voltage, but in general the expected results were obtained as exemplified in Figure 6. The differentiated pulse was about .15 μs long and this could be clipped back to .1 μs; at this point the bandwidth of the amplifiers prevented further study. It is clear however that this is a feasible method of energy measurement and considering that the alpha pile ups are exponential in nature such a method would give one a much higher tolerable alpha background. As the samples used did not require this higher alpha tolerance, the equipment was not modified.

Grid chambers were not used in the fission rate studies. Their primary advantage of giving a pulse size proportional to the charge tranferred through the grid-collector region is well known. They will not be discussed here except to remark that they will be used in the energy studies unless their response time turns out to be too excessively long; in this case, a parallel-plate differentiator-clipper chamber will be used.

Amplifiers. The main amplifier used for these experiments is a standard Radiation Laboratory model designed by Mr. Gerald Essex. Experiments since its design have indicated how it could be improved, but as a production model readily available it is a very adequate amplifier. See Figure 9.

The preamplifiers are again feedback amplifiers as shown in Figure 10. The amplifier shown is typical of one suitable for this purpose. It is worth noting that obtaining the screen voltage through a large resistance to a high voltage provides a good deal of stabilization in the direct current operating point of the tube and as the grid-plate transconductance is fairly well determined by the plate current of the tube this provides a fair amount of stabilization for normal tube aging. Cathod follower outputs are avoided, for a cathode follower with a low cathode resistor has rather poor stabilization or sensistivity. Some discussion of the design of such amplifiers is given in References 3 and 4.

The amplifier system taken as a whole has a sensistivity or stabilizing factor of 15, except of course for the cathode follower outputs of the main amplifier.

Discriminator and Scaler. It was considered desirable to have a discriminator that would respond to a very short pulse and consequently very little pulse energy. The normal circuits used for discriminators did not seem to be satisfactory and thus the blocking oscillator circuit shown in Figure 11 was used. The constants in this particular circuit are not suited for high counting rates although they could be readjusted for such rates.

Standard laboratory scalers were used.

Shielding. Several models of the fission counter were constructed. The first model had the ion chamber, pre-amplifier, and main amplifier mounted in a standard

Bud cabinet that had been well shielded. All ventilation ports were either covered with sheet copper or double layers of fine copper screen. Power supply connections and 110 volts a.c. were brought through a filter box using Sprague Hi-Pass .5 μF filter condensers. With this mounting, arcs may be drawn from an arc vacuum leak detector and no counts are observed. This model gave no observable electrical background counts, however, later models have inductance as well as Hi-Pass filters as a safety measure.

A model was constructed for study of slow neutron fission and the ionization chamber and preamplifier were well shielded but located ten feet from the main amplifier. This model also seems to have a good noise background, but does not compare with the completely shielded model.

The main conclusion to be drawn from these shielding experiments is that if sufficient care with lead-in wire filtering and ground connections is taken it is possible to construct a small laboratory instrument for fission counting that will have a low background. Admittedly, even though the observable background is zero in this equipment, if counting rates of perhaps five counts a day were being obtained, a more isolated installation would be preferred.

Stability. All equipment has been run off saturable reactor voltage regulators. All plate voltage supplies for electronic devices are regulated. Where non-standard equipment has been used, screen stabilization of pentodes has been used.

The amplifiers themselves have a stabilization constant, or sensistivity of fifteen.

The main criteria for deciding that this system is sufficiently stable has been the failure of fission bias curves, particularly the alpha pile up, to change over a period of weeks.

Limitations. The limits on the background are difficult to set although it appears to be zero; without an infinite amount of background information this figure is uncertain. Moreover, the electrical background in Nature is not statistical.

The limits of tolerable alpha background have never really been pushed. The most active sample to date was a curium sample with 5×10^7 alpha counts per minute and this gave a plateau from about 34 to 44 volts on the bias selector. This sample was not clipped as short as it could be. It is felt, as indicated, that by the differentiation - clipper scheme an improvement of more than a factor of 10^3 could be obtained. This has not been attempted for it would involve considerable amplifier redesign. Some of this gain has already been realized by other workers who seem to be clipping to the point of differentiation. This could be done here by using shorter delay lines.

Conclusions. A spontaneous fission counter that is a semi-portable laboratory instrument is fairly easy to construct. The counter reported here can be greatly improved by redesign of the counter electronics circuits. Many of the problems of an energy distribution counter have been partially solved in the course of this work.

References

[1]Rossi and Staub, LA 1003R, LA 1004R or National Nuclear Energy Series, Section V, Vol. II.
[2]Ramo, Simon, Proc. IRE, Vol. 27, pg 584-585, Sept. 1939.
[3]Elmore and Sands, National Nuclear Energy Series, Section V, Vol. I.
[4]Watkins, Dean A., AECU-184(LAMS-834) "A Transient Analysis of the Cathode-Coupled Feedback Loop" March 3, 1949.

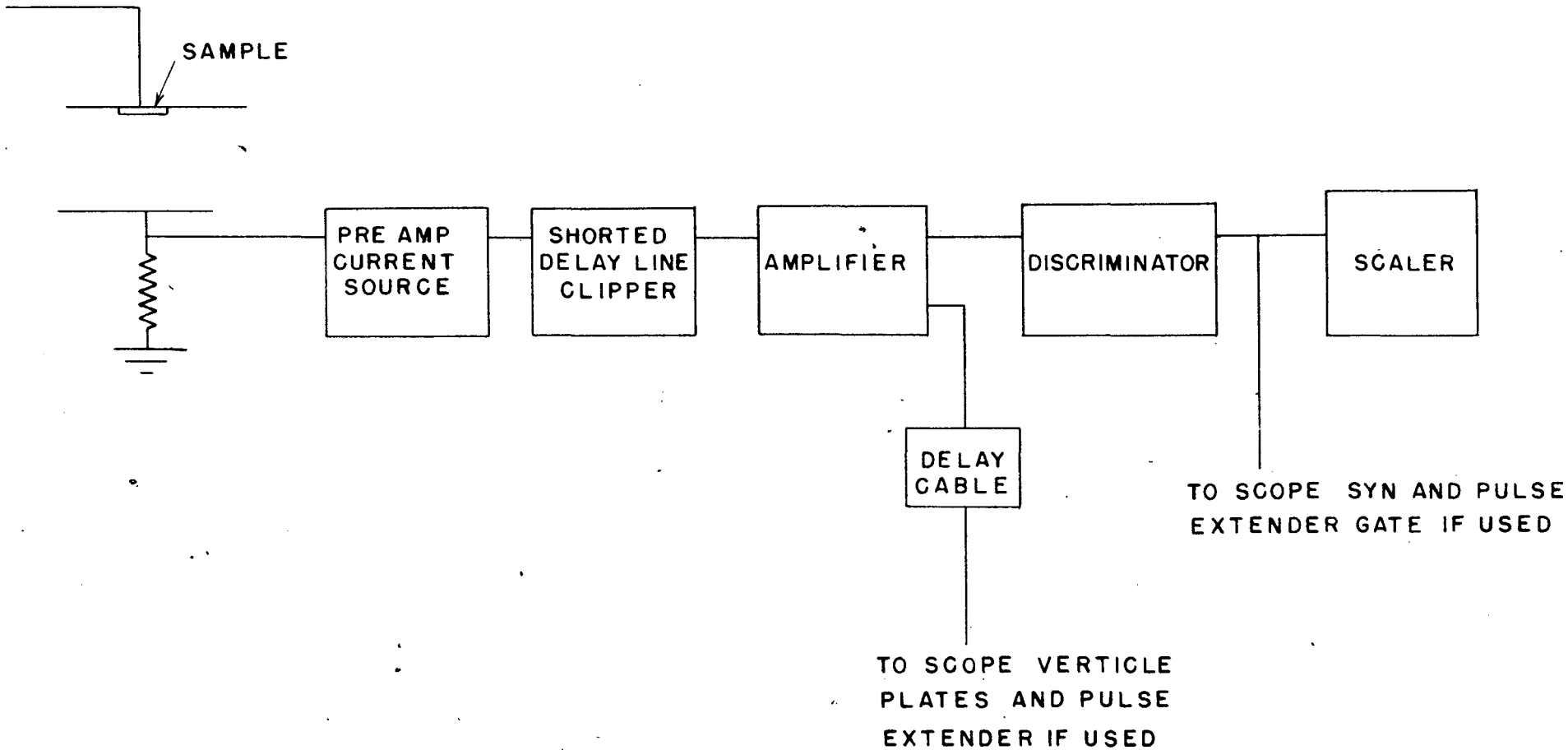
SAMPLE
PRE AMP CURRENT SOURCE
SHORTED DELAY LINE CLIPPER
AMPLIFIER
DISCRIMINATOR
SCALER
DELAY CABLE
TO SCOPE SYN AND PULSE EXTENDER GATE IF USED
TO SCOPE VERTICLE PLATES AND PULSE EXTENDER IF USED

FIG. 1

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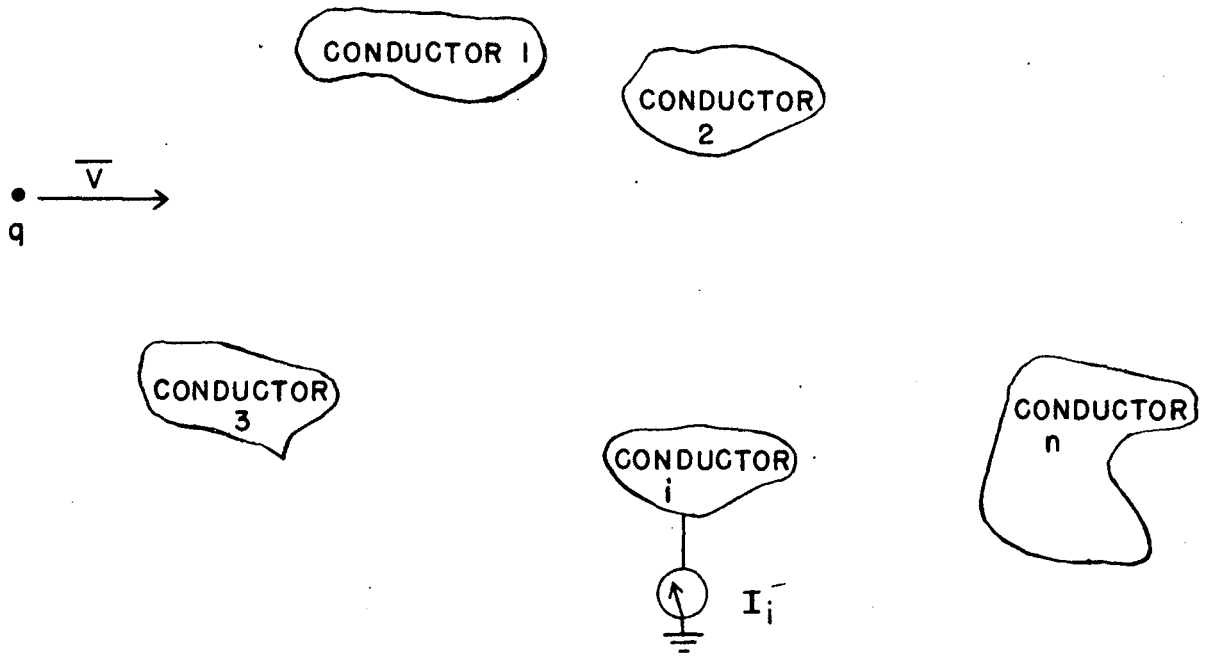
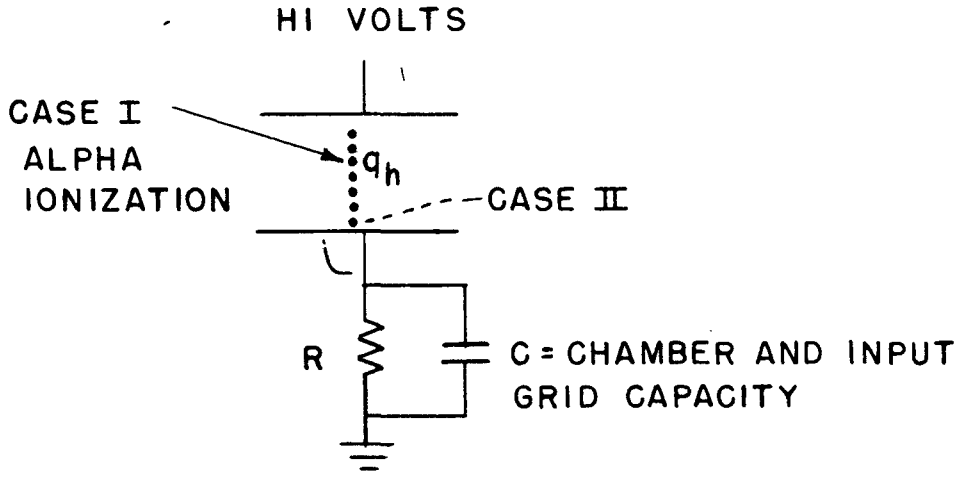


$I_i = g\overline{V} \cdot \overline{Ea}$

WHEN $\overline{Ea}$ = FIELD AT g WITH ALL CONDUCTORS BUT i GROUNDED AND ONE VOLT ON i.

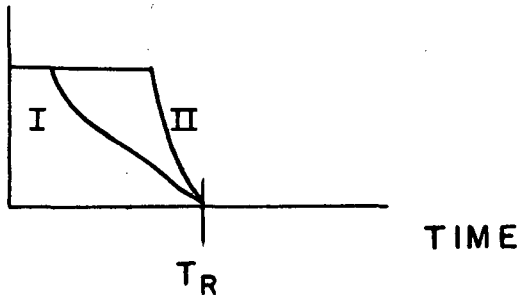
FIG. 2



CURRENT

$$I = \sum_h q_h \, \overline{V} \cdot \overline{E}_a$$

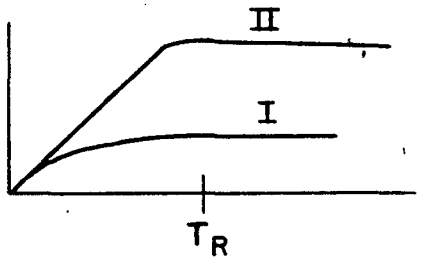
$$= V E_a \sum q_n$$



INDUCED CURRENT VS TIME

VOLTAGE

$$\text{VOLTS} = \int_0^t I \, dt$$

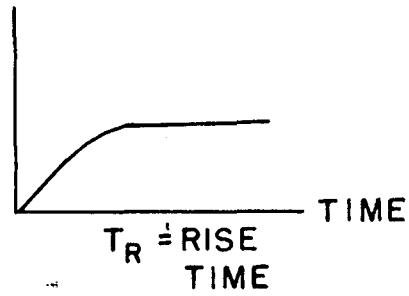


CHAMBER SIGNAL VOLTAGE VS TIME

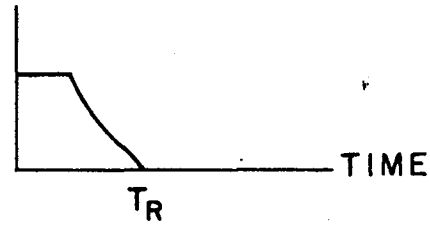
FIG. 3

14505-1

CHAMBER
SIGNAL VOLTAGE
= Vs



$$\frac{dVs}{dt} \sim I$$



$$\text{CLIPPED } \frac{dVs}{dt} = \left[\frac{dVs(t)}{dt} - \frac{dVs(t-T_C)}{dt}\right]$$

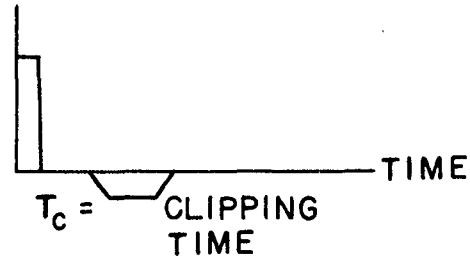
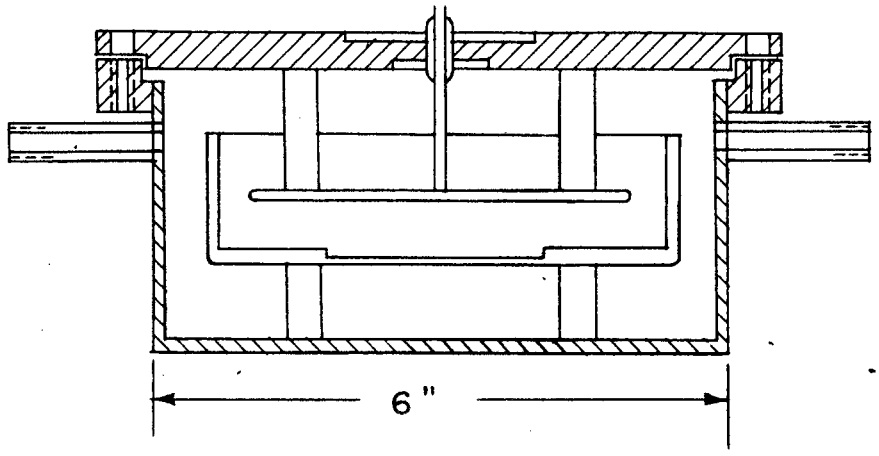


FIG. 4


6"

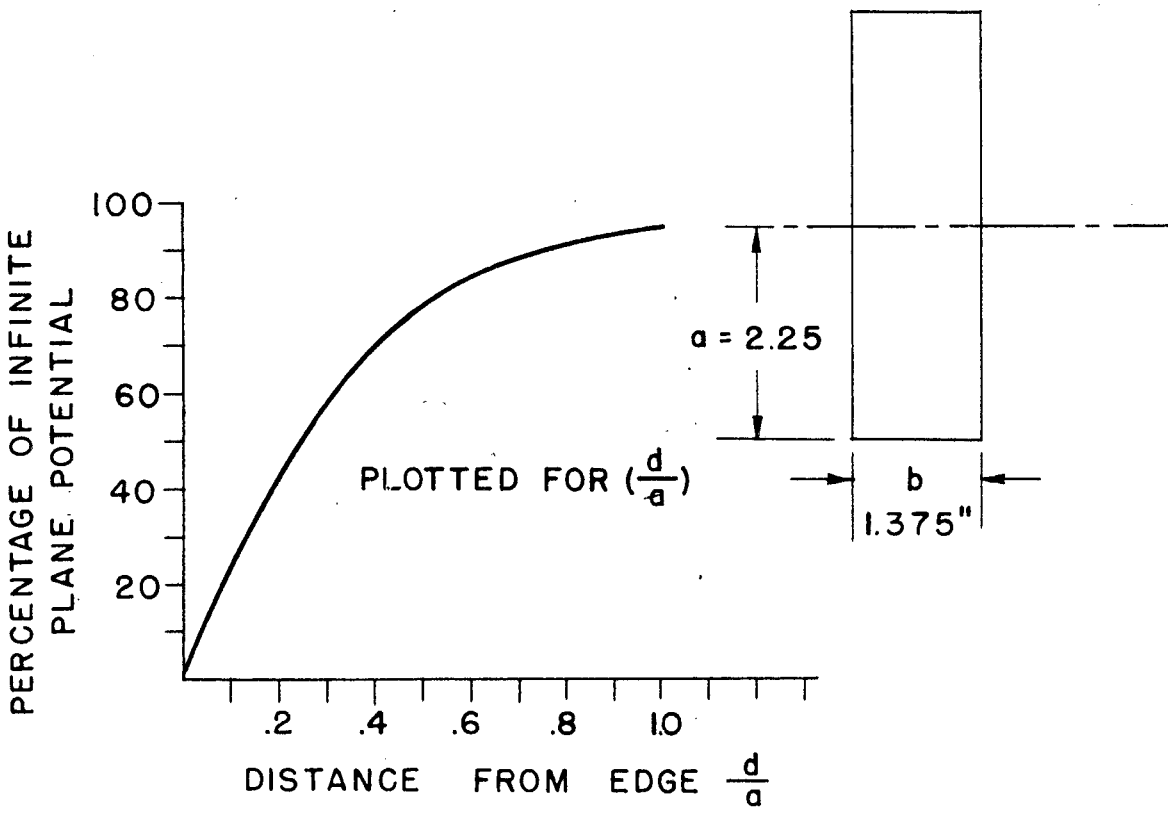
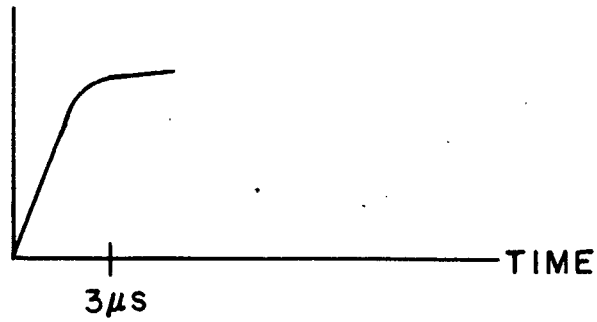

PERCENTAGE OF INFINITE PLANE POTENTIAL
100
80
60
40
20
.2
.4
.6
.8
1.0
DISTANCE FROM EDGE d/a
PLOTTED FOR (d/a)
a = 2.25
b
1.375"

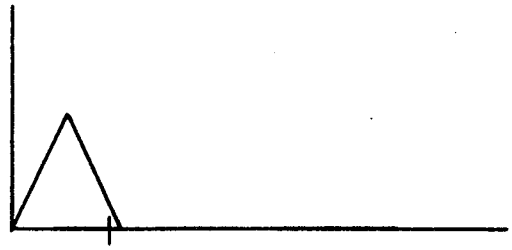
FIG. 5

14506-1

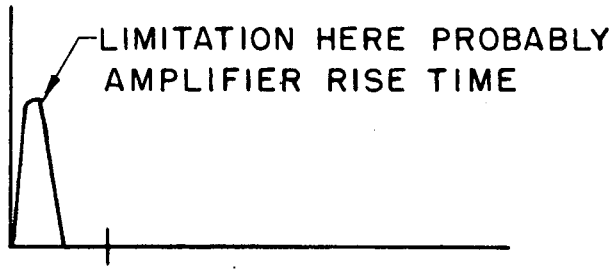
UNCLIPPED PULSE



NORMAL CLIPPING



DIFFERENTIATED



DIFFERENTIATED
AND CLIPPED

APPROXIMATE OSCILOSCOPE PATTERNS

FIG. 6

The following is intended as a summary of the properties of delay lines, differentiators and integrators for application to nuclear physics. All cases considered are simple, passive networks.

The definitions of differentiation and integration are well known. By clipping we mean the difference between the values of a function at time t and time t plus T; it may be compared to differentiation as a difference equation may be compared to a differential equation.

In the table we have made a distinction between those networks which should be driven by a voltage source and those which should be driven by a current source. Proper design of feedback circuits can provide one or the other.

As indicated in the table, we believe a linearly rising voltage is the best applied voltage to study a differentiation circuit with, and that a step voltage is the best driving function for the study of an integration network.

Columns 1-7 contain all of the necessary information; the remaining columns contain information and examples derivable from these.

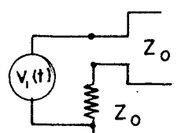
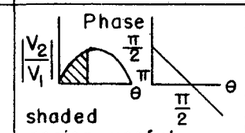
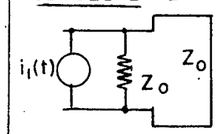
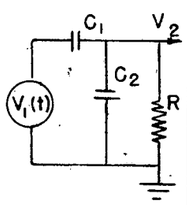
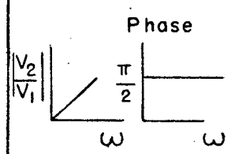
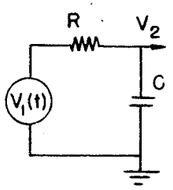
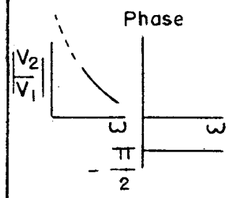
1 CASE	2 USE	3 LIMITS OF USE	4 STEADY STATE GAIN	5 DRIVING SOURCE	6 STEADY STATE FREQ. RES. POWER	7 TRANSIT RESPONSE	8 TRANSIT GAIN AFTER TIME T	9 GAIN IN PRACTICAL CIRCUIT FOR 10% ERROR	10 % ERROR FOR TIME	11 REMARKS
OPEN LINE:  Z_0 = line characteristic impedance	Clipper will differentiate if θ is very small.		$\frac{V_2}{V_1} = \text{Sine}\ \theta \angle\left(\frac{\pi}{2} - \theta\right)$ Where $\theta = \beta l$ β = propagation constant	VOLTAGE SOURCE	 shaded region useful area if clipping time equals pulse rise time	$(V_2\ t)$ $V_2(t) = \frac{V_1(t) - V_1(t-T)}{2}$ T = 2 (transit time of line)	.5	.5	0	
CLOSED LINE  Z_0 = line characteristic impedance	Clipper		$\frac{V_2}{i_1 Z_0} = \text{Sine}\ \theta \angle\left(\frac{\pi}{2} - \theta\right)$ Gain referred to voltage $i_1 Z_0$	Current Source	Same	$V_2(t) = Z_0 \frac{[i_1(t) - i(t-T)]}{2}$	.5	.5	0	
	Differentiation $\frac{d\epsilon^{jwt}}{dt} = jw\epsilon^{jwt}$	a) Good if $\omega R(C_1 + C_2) \ll 1$ b) Time constant $= R(C_1 + C_2)$	$\frac{V_2}{V_1} = \frac{\frac{(C_1+C_2)}{C_1}(\omega RC_1)^2 + j\omega(RC_1)}{1 + (\omega RC_1)^2 \frac{(C_1+C_2)^2}{C_1}}$ $\sim j\omega\ (RC_1)$	Voltage Source		Response to $V_1 = Kt$ is: $V_2 = KRC_1\left[1 - \epsilon^{-\frac{t}{R(C_1+C_2)}}\right]$	KRC_1 When $K = \frac{dV_1}{dt}$	$< .4$	$\epsilon^{-\frac{T}{R(C_1+C_2)}}$	Good for differentiating functions changing more slowly than design function
	Integration $\int \epsilon^{j\omega t} = \frac{1}{j\omega}\epsilon^{j\omega t}$	a) GOOD IF $\frac{T}{R\epsilon} \ll 1$ b) Time constant meaningless but = RC	$\frac{V_2}{V_1} = \frac{1 - j\omega(RC)}{1 + (\omega RC)^2}$ $\sim -\frac{j}{\omega RC}$	Voltage Source		Response to V = Step function $V_2 = V_1(1 - \epsilon^{-\frac{t}{RC}})$ $V_2 \sim V_1\left[\frac{t}{RC} - \frac{t}{RC}\ 2\ \frac{1}{2}\right]$ $\sim V_1\left(\frac{t}{RC}\right)$	$\frac{T}{RC}$	$< .1$	$\sim \frac{T}{(RC)}$	Good for integration times shorter than design time

FIG. 7

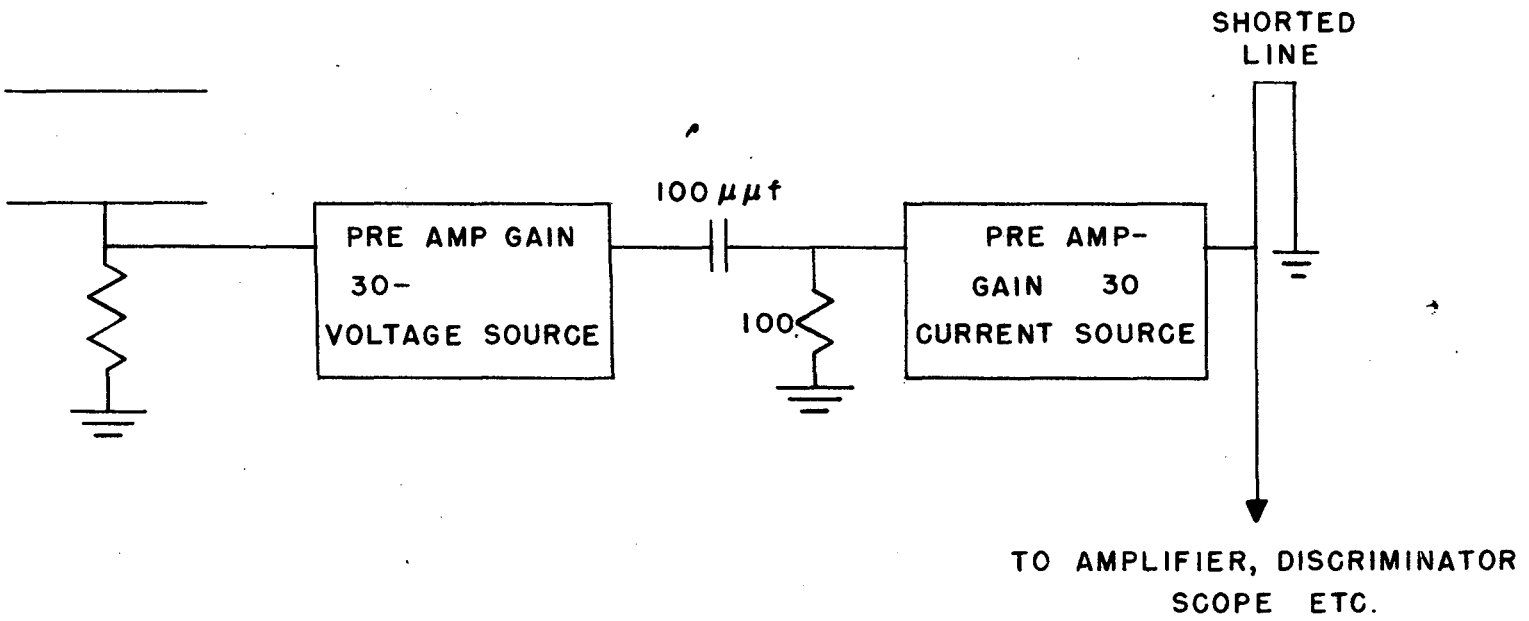

SHORTED
LINE
PRE AMP GAIN
30-
VOLTAGE SOURCE
100 μμf
100
PRE AMP-
GAIN 30
CURRENT SOURCE
TO AMPLIFIER, DISCRIMINATOR
SCOPE ETC.

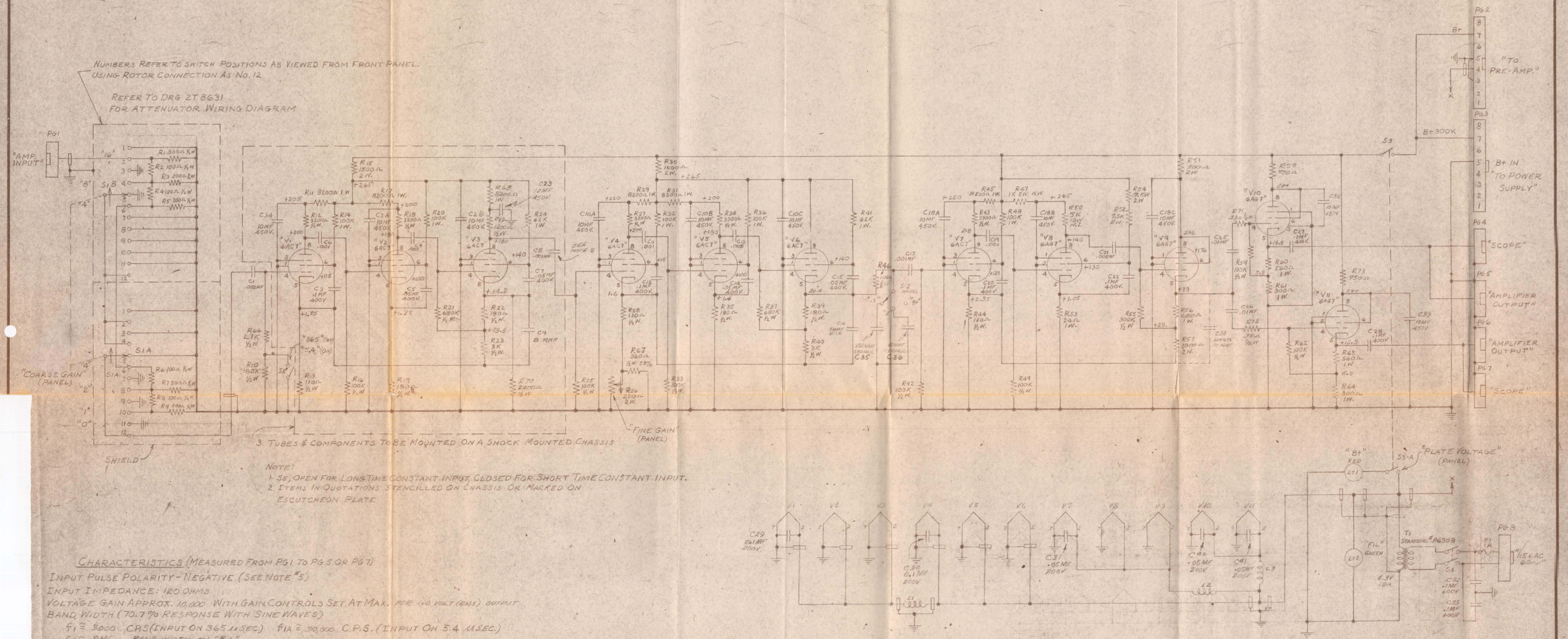
FIG. 8

14502-1

MATERIAL

SHOWN ON 2T8931

CHANGE LETTER	DRAWN BY	CHECK BY	DATE	CHANGE
B	EOG		4/5/48	REDRAWN FROM 2T4404A
C	LDM		7-8-48	H.P.L. FROM 2T4404 (PART)
D	RJL	LDM	7-13-48	MRL ACTS PER M.U.
E	EOG		4-5-49	ADDED C33, 35, 36 & R46
F	LDM	HB	7-2-52	REM. R65 (SH.)



NOTE:
1. S5, OPEN FOR LONG TIME CONSTANT INPUT, CLOSED FOR SHORT TIME CONSTANT INPUT.
2. ITEMS IN QUOTATIONS STENCILLED ON CHASSIS OR MARKED ON ESCUTCHEON PLATE

NOTE:
3. L1, 2, & 3, 23 TURNS #22 ENAM. APPROX. 9/32 DIA. & 15/16" LONG
4. SOCKET VOLTAGES ARE APPROXIMATE
5. CONNECT C8 AS SHOWN FOR NEGATIVE INPUT PULSES. FOR POSITIVE INPUT PULSES CONNECT C8 TO CATHODE OF V3

CHARACTERISTICS (MEASURED FROM PG1 TO PG5 OR PG7)

INPUT PULSE POLARITY - NEGATIVE (SEE NOTE #5)
INPUT IMPEDANCE: 120 OHMS
VOLTAGE GAIN APPROX. 10,000 WITH GAIN CONTROLS SET AT MAX. FOR 1.0 VOLT (RMS) OUTPUT
BAND WIDTH (70.7% RESPONSE WITH SINE WAVES)
$f_1 \cong$ 3000 C.P.S. (INPUT ON 365 μSEC.) $f_{1A} \cong$ 30,000 C.P.S. (INPUT ON 5.4 μSEC.)
$f_2 \cong$ 9MC BAND WIDTH ON "B+"
MAXIMUM PULSE OUTPUT: ≅ 90 VOLTS PEAK (POSITIVE)
RISE TIME (10% TO 90%) ≅ .05 μ SEC. } BANDWIDTH ON B+ MC.
FALL TIME (100% TO 10%) ≅ .15 μ SEC. } FOR 75 VOLT PULSE OUT
B+ POWER = 155 MA AT 300V

AC LINEAR AMP. MODEL III
SCHEMATIC

FIRST USED ON			
ROUGH F FINISH	FINE ff FINISH		
GOOD f FINISH	GRIND G FINISH		
TOLERANCES WHERE NOT OTHERWISE GIVEN	±.010		
DATE REQ'D	MAKE		

ISSUED TO	DATE ISSUED	DELIVER TO	JOB NO.

RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA–BERKELEY

DRAWN BY EOG	CHECK BY	DATE 4-5-48
APPROVED BY H. Pete	DRG. NO. 2T4404F	
SCALE		

"ALBANENE" 195L K. & E. CO., N.Y. REG. U. S. PAT. OFF.

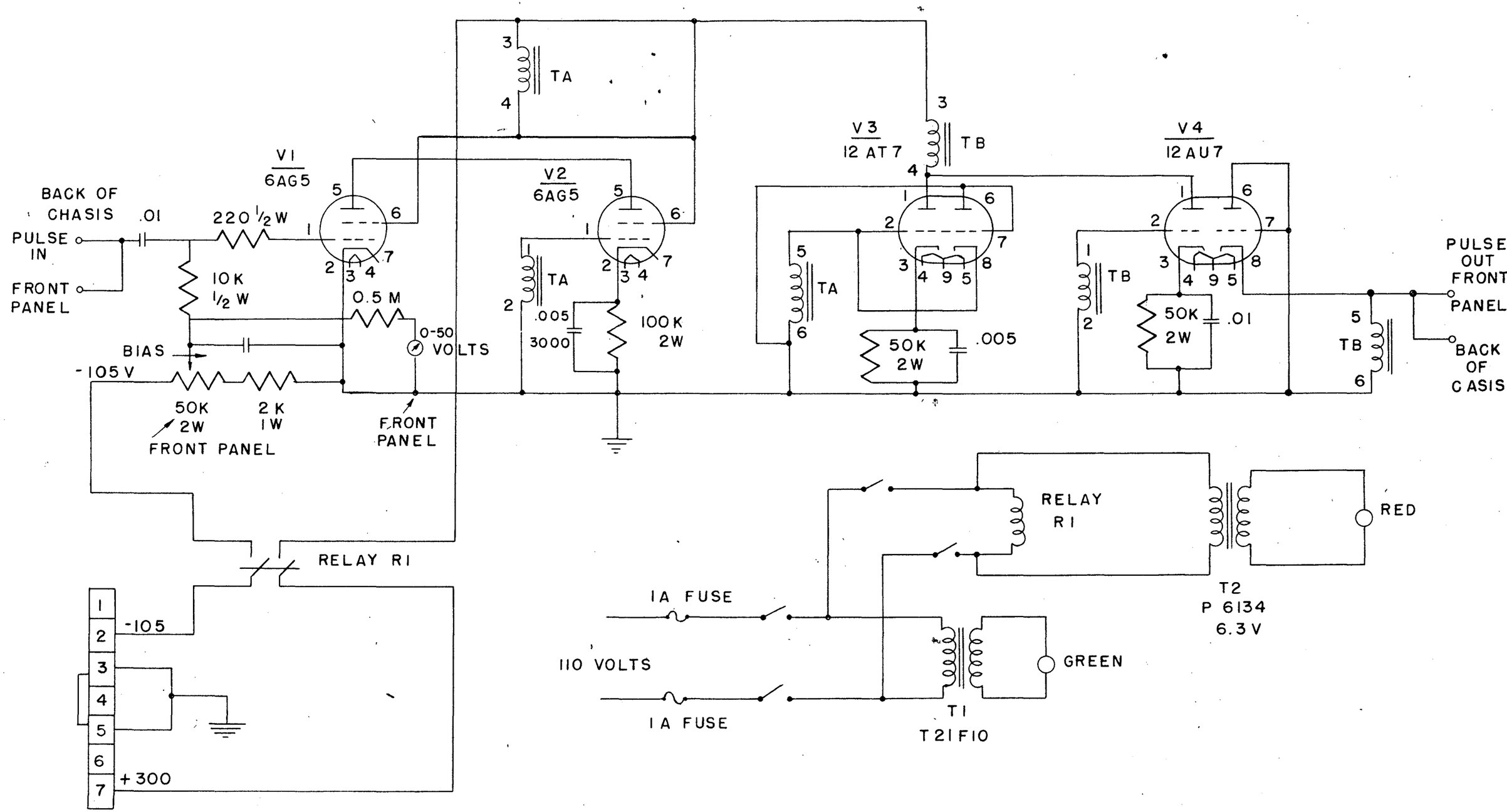
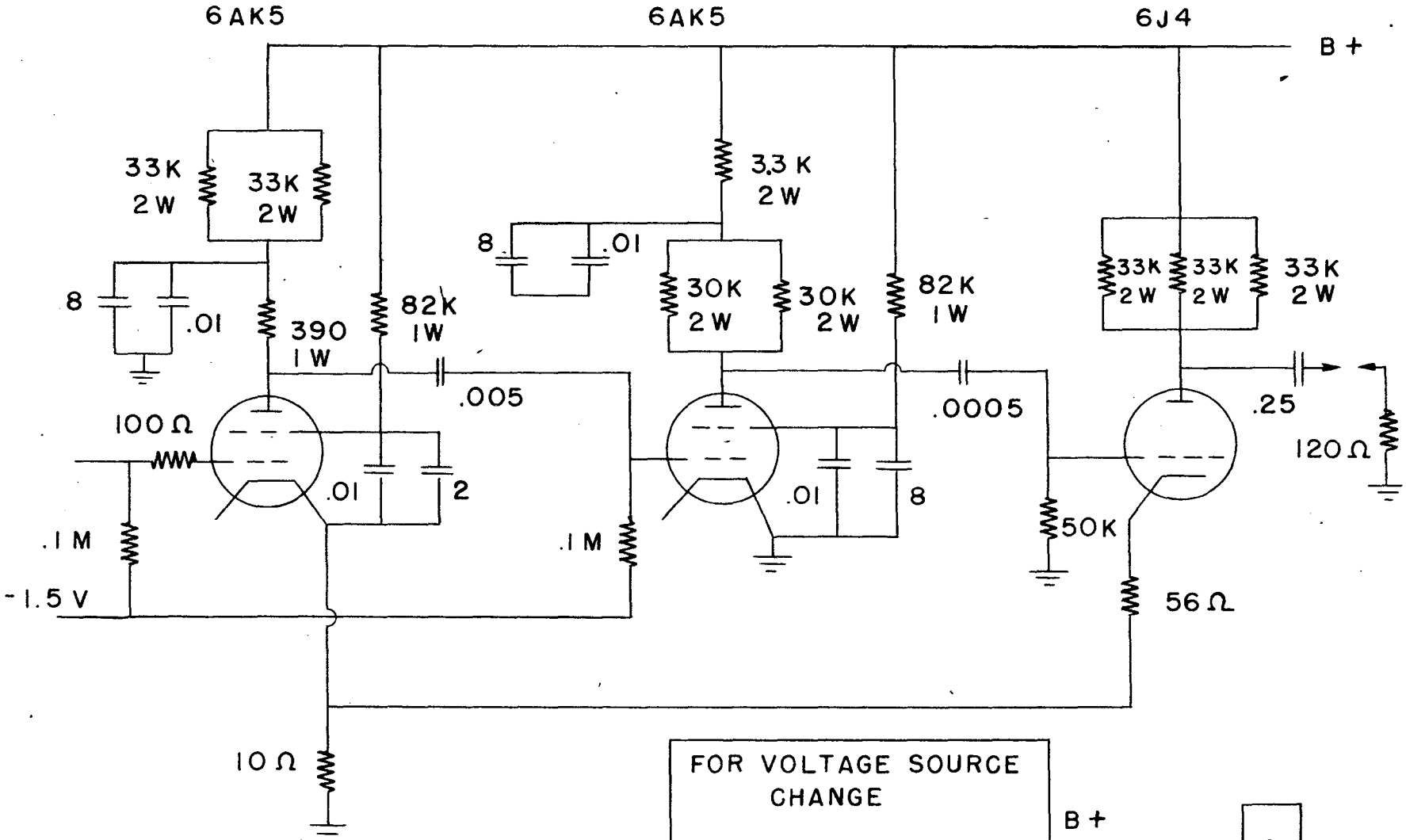


FIG. 11

DISCRIMINATOR

14503-2/

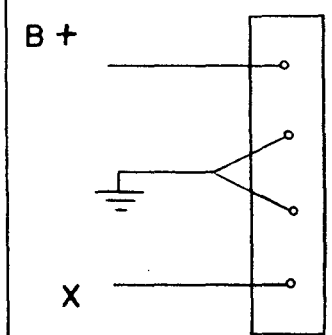


FOR VOLTAGE SOURCE CHANGE

1) 56 Ω TO 100 OHMS

2) 33K IN PLATE OF T3 TO 27K AND BYPASS PLATE TO GROUND.

3) TAKE OUTPUT FROM CATHODE OF T3 •



IONIZATION CHAMBER PRE-AMP

CURRENT SOURCE

FIG. 10

14508-1

D. Bio-Organic Chemistry Group

B. M. Tolbert

Synthetic and Experimental Chemistry

M. Calvin, B. Tolbert, P. Adams, R. Bartsch, A. Fry, I. Gray, H. Hauptmann, D. Hughes S. Ikeda, E. Jorgensen, B. Neivelt, R. Ostwald, R. Selff and Y. Stone

Preparation of Sodium Isobutyrate-1-C^{14}, Sodium Isovalerate-1-C^{14}, and Sodium Isocaproate-1-C^{14}. These three branched chain fatty acids were prepared by the reaction of isopropyl-, isobutyl- and isoamylmagnesium bromides, respectively, with $C^{14}O_2$ using vacuum line techniques. The material as the free acid was purified by steam distillation and converted to the sodium salt by titration with a pH meter. The equivalent weight of the material checked in all cases. The preparations were carried out on a 20 mmole scale, and the specific activity of the sodium isobutyrate was 1.72 μc/mg., of the sodium isovalerate, 3.35 μc/mg., and of the sodium isocaproate, 1.79 μc/mg. The yields were 97.5 percent, 96.0 percent and 95.5 percent, respectively, based on the barium carbonate used to begin the synthesis.

Preparation of Leucine-1-C^{14}. The synthesis of this material has been achieved by the bromination and amination of the corresponding fatty acid. Isocaproic acid-1-C^{14} was brominated and the product aminated using liquid ammonia without isolation of the bromo compound. The leucine was then purified by repeated crystallization. The yield was 43 percent based on $C^{14}O_2$ used to begin the synthesis, and the specific activity was 1.6 μc/mg. Paper chromatography and radioautography of this material showed only one radioactive compound in the final product.

Preparation of Sodium Isocaproate-2-C^{14}. In the last quarterly Report, UCRL 460, a new method for the preparation of alcohols and halides from fatty acids was described. This method was designed to give high yield of very pure materials in the range where traces of ethanol from the use of lithium aluminum hydride could not be easily separated. The procedure is as follows:

$$R\text{-}\overset{*}{C}O_2Na \xrightarrow{C_{16}H_{22}Br} R\overset{*}{C}O_2C_{16}H_3 \xrightarrow[\text{Cu chromite}]{H_2} R\overset{*}{C}H_2OH$$

$$\xrightarrow{PBr_3} R\overset{*}{C}H_2Br$$

This reaction has now been carried out with the high specific activity material described earlier.

Sodium isovalerate-1-C^{14}, 2.09 g., specific activity 3.35 μc/mg., was converted to cetylisovalerate by shaking the dry salt with 5.40 g. cetyl bromide in a sealed tube at 280° C for eleven hours. The cetyl valerate was transferred

to a stainless steel hydrogenation bomb and shaken with 5.5 g. copper chromite and 2500 psi of hydrogen at 250°C for ten hours. The amyl alcohol was pumped out of the bomb and treated with phosphorus tribromide. The isoamyl bromide was washed with water and dried over phosphorus pentoxide. The yield of purified isoamyl bromide-1-C^{14} was 70 percent based on the $C^{14}O_2$ used to begin the synthesis.

It was originally planned to convert this osoamyl bromide to the 2-labeled acid by converting it to the Grignard and carbonating this material. Trial runs showed the yields to be not better than 40 percent in this step, so the nitrile was tried.

$$R\overset{*}{C}H_2Br \xrightarrow{KCN} R\text{-}\overset{*}{C}H_2CN \xrightarrow[2.\ H^+]{1.\ OH^-} R\overset{*}{C}H_2CO_2H$$

$$\xrightarrow{NaOH} R\overset{*}{C}H_2CO_2Na$$

On low activity runs, some formate (up to 20 percent) was found in the isocaproate, but this was destroyed by treating a solution of the salt with mercuric sulfate with good recovery of the acid. In the high specific activity run this step was not necessary.

The isoamyl bromide from the above preparation was condensed with 1.65 g. potassium cyanide by refluxing in alcohol 24 hours in the presence of a very small amount of potassium iodide. A large excess of silver sulfate and 25 ml of water were added to the reaction flask, and the solution distilled until all alcohol had been removed and the temperature of the distillate remained at 100°C for about 2 ml of distillate. Investigation of inactive runs showed that the nitrile is distilled almost quantiatively under these conditions.

The distillate was allowed to reflux 24 hours with 15 g. potassium hydroxide, then acidified and steam distilled. The steam distillate was titrated with 1N sodium hydroxide, filtered and dried. The yield was 0.949 g. of sodium isocaproate-2-C^{14} with a specific activity of 2.97 μc/mg. or a yield of 39 percent based on $C^{14}O_2$. The equivalent weight was 139.19 (theor. 138.15).

Anal. Calcd. for $C_6H_{11}O_2Na$: C, 52.16; H, 8.03. Found: C, 51.06; H, 7.96.

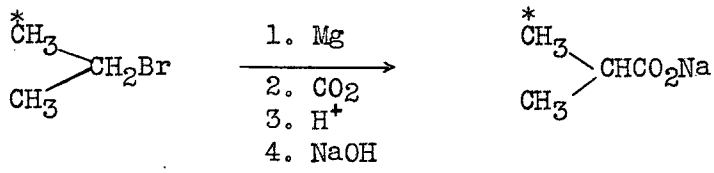
Preparation of Isopropyl Bromide-1-C^{14}. This material, an important intermediate in the preparation of branched chain fatty acids and amino acids, has been prepared in 50 percent yield by the following series of reaction:

$$\overset{*}{C}O_2 \longrightarrow \overset{*}{C}H_3I \xrightarrow[2.\ C_{17}H_{35}CO_2H]{1.\ CH_3\overset{O}{\overset{\|}{C}}\text{-}H} CH_3CH_2OH\overset{*}{C}H_3 \xrightarrow{PBr_3}$$

$$CH_3CH_2Br\overset{*}{C}H_3$$

Methyl iodide (2.84 g., 20 mmole) was treated in dry repurified hexyl ether (50 ml) on the vacuum line with 0.49 g. of magnesium. After the Grignard was formed 1.2 cc. of acetaldehyde dissolved in 30 ml hexyl ether was added slowly over three-quarters of an hour at -20°C. The solution was stirred 15 minutes more and then heated to 60° for 15 minutes. Low boiling material was then pumped off and 5.97 g. of stearic acid added. After a series of distillations, the alcohol was isolated and treated with 4-5 cc of phosphorus tribromide for 1-3/4 hours at reflux. The isopropyl bromide produced was washed with water and dried over phosphorus pentoxide. Thus, 10.2 mmoles of isopropyl bromide was prepared in 51 percent yield based on methyl iodide. The density and index of refraction checked the identity of this product.

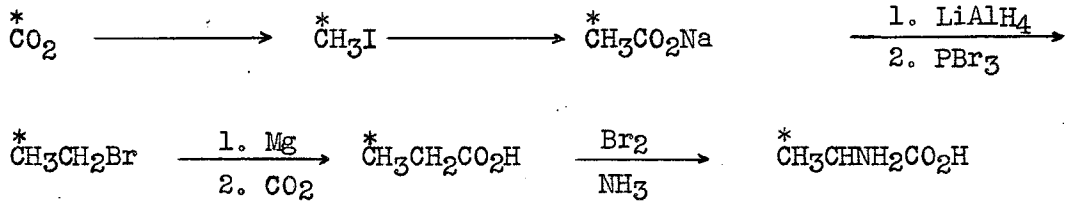
Preparation of Sodium Isobutyrate-3-C^{14}. This material was prepared as follows:



Isopropyl bromide-1-C^{14} (1.25 g.) prepared as described above was converted to the Grignard reagent and carbonated by the same procedure used for making methylene-labeled acetic acid. The acid was steam distilled, and converted to the dry sodium salt. The yield was 0.538 g., specific activity 1.50 μc/mg., or a yield of 48 percent from the isopropyl bromide or 16.8 percent based on the $C^{14}O_2$ used to begin the synthesis. The equivalent weight was 108.0 (theor. 110.0). This yield could probably be improved by going through the nitrile as described for the α-labeled isocaproate.

Preparation of Alanine-3-C^{14}. Two methods have been studied for the synthesis of this compound. The first failed to give a single radioactive product, but the second method gave a pure product.

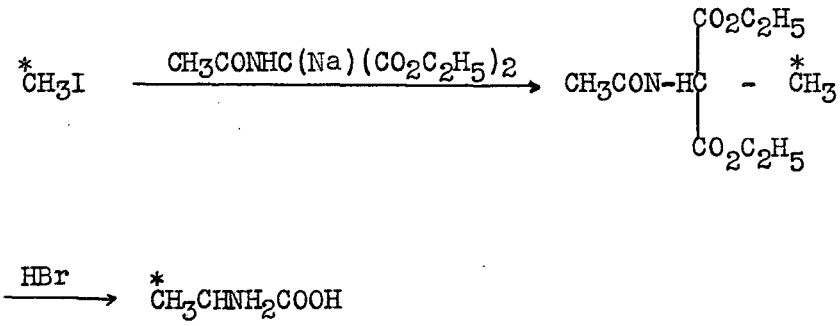
The successful method was as follows:



Twelve millimoles of sodium propionate-3-C^{14} containing 0.8 μc/mg. was converted to propionic acid-3-C^{14} by treatment with anhydrous hydrogen chloride in the usual manner. It was then converted to bromopropionic acid-3-C^{14} with bromine, using phosphorus and iodine as catalysts. After hydration of the bromopropionyl bromide it was converted to crude alanine by treatment with ammonia and ammonium carbonate. The purification was achieved by passage through a column of Dowex 50 resin (anion exchanger), elution with ammonium hydroxide and subsequent sublimation in high

vacuum. The yield of alanine-3-C^{14} was 77 percent with a specific activity of 0.87 μc/mg. The purity was established by paper chromatography.

The unsuccessful attempt to make alanine-3-C^{14} was as follows:

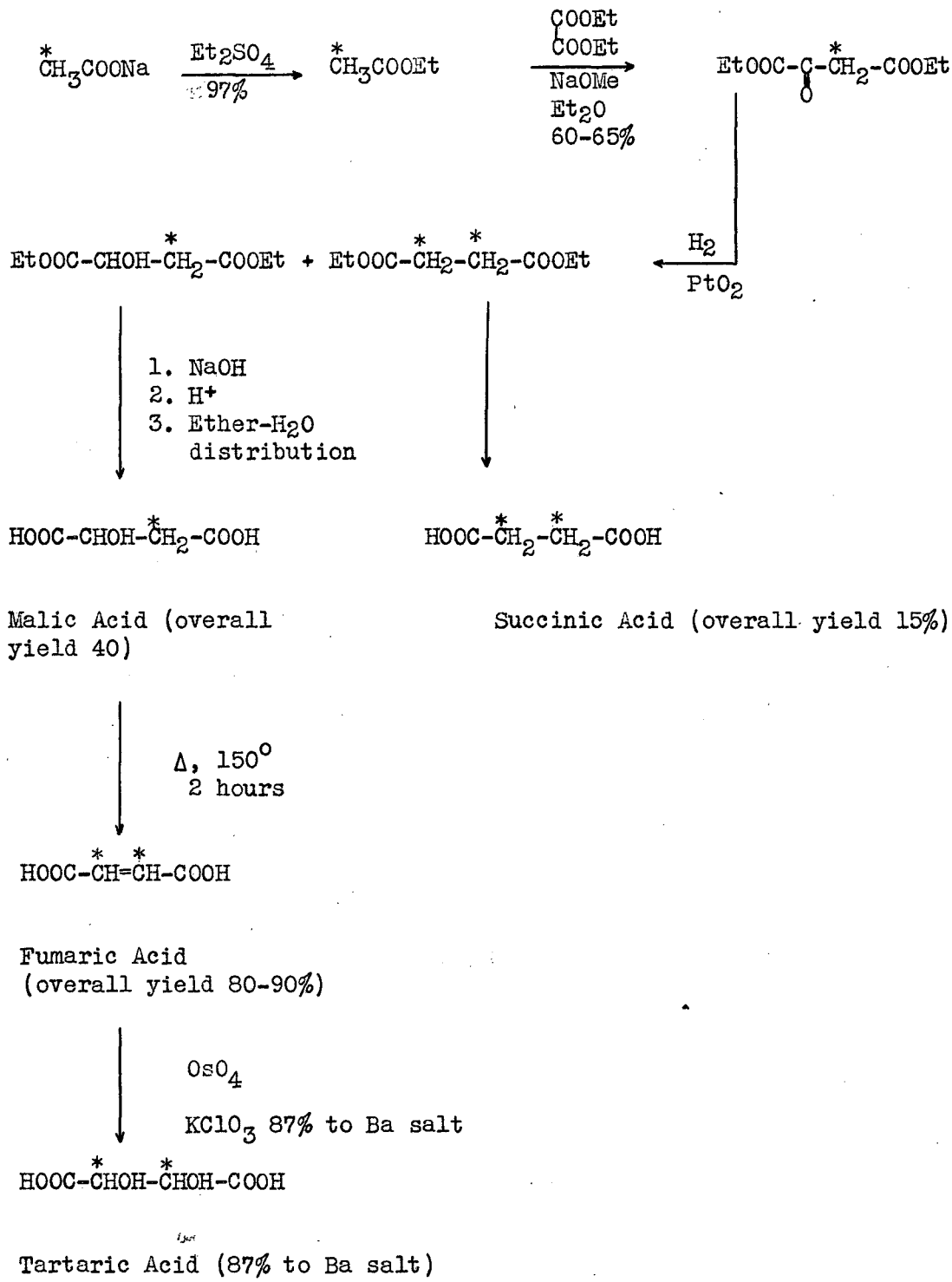


The condensation was carried out in anhydrous tertiary butanol with potassium. After evaporation of the solvent, the crude condensation product was recrystallized from hexone yielding 75-80 percent of product with the correct specific activities and melting points. On two subsequent high specific activity preparations the product could only be obtained as a yellow oil. The hydrolysis and decarboxylation were carried out with 48 percent hydrogen bromide, the acid was distilled off and the crude product was purified by passage through a column of Dowex 50 (anion exchange resin), elution with ammonium hydroxide and a high vacuum sublimation.

This alanine-3-C^{14}, obtained in yields of 65-70 percent, proved to be contaminated with considerable amounts of inactive glycine (from unreacted acetomidomalonate) and about 10 percent of an active, ninhydrin-negative compound. This was established by paper chromatography. The active contaminate is most likely N-methyl glycine (sarcosine). It could not be separated from the alanine by a Dowex A (cation exchange resin) nor by oxidation with periodate in alkaline solution. It was expected that such oxidation would convert the sarcosine to methylamine and leave pure alanine behind. Instead, only small amounts of inactive methylamine could be obtained and about 80 percent of the alanine was destroyed by this process. The remaining portion proved to still be contaminated.

Separation of the alanine from the active contaminant but not from the inactive glycine was achieved by fractional elution from a Dowex 50 column. The elution was carried out with 0.2N hydrochloric acid. Consecutive fractions were collected automatically, tested individually for activity, and the active fractions were tested on paper strips by paper chromatography with phenol.

Preparation of Dicarboxylic Plant Acids. As described in previous quarterly reports, the synthesis of malic, succinic, fumaric and tartaric acids labeled in the 2-3 carbon atoms has been undertaken. In these syntheses methyl-labeled sodium acetate is converted to ethyl acetate, condensed with methyl oxalate, and the ethyl oxalacetate hydrogenated to a mixture of malic and succinic acids. The malic acid thus prepared is converted to fumaric and tartaric acid:


*CH3COONa
Et2SO4
97%
*CH3COOEt
COOEt
COOEt
NaOMe
Et2O
60-65%
EtOOC-C-*CH2-COOEt
O
H2
PtO2
EtOOC-CHOH-*CH2-COOEt + EtOOC-*CH2-*CH2-COOEt
1. NaOH
2. H+
3. Ether-H2O
distribution
HOOC-CHOH-*CH2-COOH
HOOC-*CH2-*CH2-COOH
Malic Acid (overall yield 40)
Succinic Acid (overall yield 15%)
Δ, 150°
2 hours
HOOC-*CH=*CH-COOH
Fumaric Acid
(overall yield 80-90%)
OsO4
KClO3 87% to Ba salt
HOOC-*CHOH-*CHOH-COOH
Tartaric Acid (87% to Ba salt)

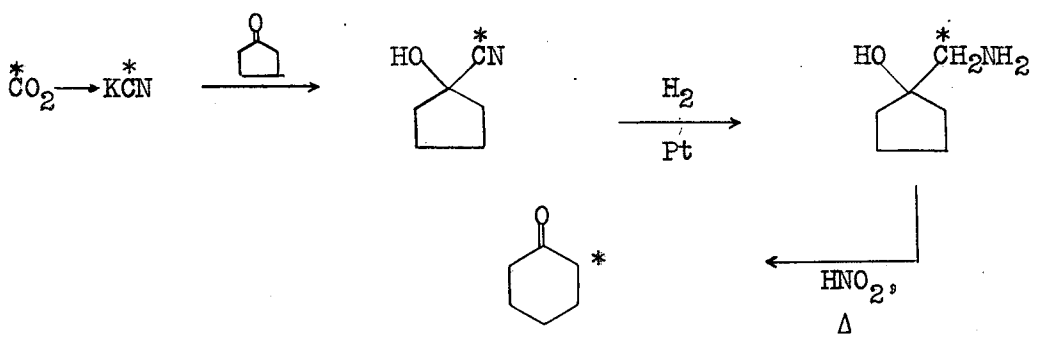
Malic and Succinic Acids. Methyl-labeled sodium acetate (20 mmoles) is heated under reflux for three hours at 160-170°C with diethyl sulfate (72 mmoles). The ethyl acetate formed is distilled into a flask containing 50 ml of anhydrous ether, sodium methoxide (40 mmoles) and diethyl oxalate (30 mmoles). This is heated overnight under dried reflux, neutralized with cold 50 percent sulfuric acid and filtered directly into the hydrogenation vessel through anhydrous sodium sulfate. The ether is removed at room temperature, 50 ml of absolute ethanol and 500 mg of platinum oxide added and the solution hydrogenated at atmospheric pressure.

The platinum is removed by filtration, an equivalent amount of dilute sodium hydroxide added and the esters saponified by stirring overnight at room temperature. The solution is then neutralized with sulfuric acid and a slight excess of the calculated calcium chloride added to remove unreacted oxalic acid. The filtrate is acidified with sulfuric acid and steam distilled to recover unreacted acetic acid. The aqueous residue is concentrated and continuously extracted with ether for two days. The crude mixture of malic and succinic acids obtained on removal of the ether is separated by distribution between ether and water and subsequent recrystallization of the enriched fractions from ethyl acetate-n-hexane. Inactive malic and succinic acids are added as carriers to obtain pure second crops of lesser activity.

Fumaric Acid. Malic acid is placed in a cold finger type sublimation vessel which is partially evacuated. After heating on an oil bath at 150°C for two hours, isopropyl alcohol and dry ice are added to the cold finger and the vessel evacuated to about 20 microns pressure. Sublimation is complete in about two hours; a product melting at the reported 286-287° was obtained in 80-90 percent yield of theoretical.

Tartaric Acid. The sublimed fumaric acid (5 mmoles) is washed into a flask with hot water. To this is added potassium chlorate (6.5 mmoles) and 0.1 ml of 1 percent aqueous osmium tetroxide and heated in the closed flask for ten hours at 50°. The osmium tetroxide is removed by benzene extraction, the solution neutralized with sodium hydroxide and excess barium chloride (saturated solution) added. The solution is refrigerated overnight, the crystals formed being collected by filtration, washed with cold water and dried. The yield of barium tartrate is 87 percent.

Preparation of Cyclohexanone-2-C^{14} and Ring-Labeled Intermediates. In the last quarterly report, UCRL 460, a procedure for making ring-labeled compounds via the cyanhydrin ring expansion method was described.



The numerous transfer involved in this preparation made the overall yield quite low and one high specific activity run failed completely to produce cyclohexanone.

An attempt has been made to modify this procedure to give more reliable results. Toward this end, all except essential transfers of material have been eliminated. Thus, the formation of the cyanhydrin, the reduction of the nitrile group and the treatment with nitrous acid are all carried out in the same hydrogenation bottle.

Cyanhydrin formation is an equilibrium reaction and the equilibrium is not too favorable toward the cyanhydrin formation. Prelog and Kobelt (Helv. Chim. Acta, 32, 1187 (1949)) have recently found that a few drops of tri-n-propylamine shifts the equilibrium toward cyanhydrin fomation and this amine has been used in the last several runs.

Reduction of the cyanhydrin to the amino alcohol proceeds smoothly with slightly more than the theoretical uptake of hydrogen. The reduction is made in an alcoholic solution in the presence of platinum from platinum oxide.

Treatment of the amino alcohol with nitrous acid results in a brown-colored reaction mixture. This appears to be the result of decomposition and the formation of this color can be reduced by the addition of ether to the reaction mixture before allowing it to warm up on the steam bath.

The ether phase is then separated from the aqueous phase and washed with potassium bicarbonate solution and dried. The ether is removed by flash distillation and the residual yellow-brown liquid distilled.

Distillation of the product has presented a major problem. Two runs have been distilled under reduced pressure using a simple distillation unit and a receiver cooled with a mixture of dry ice and isopropyl alcohol (-80°). All the material volatile at 80° and 0.7 mm mercury was collected. The second run gave a volume of distillate of 0.6 ml and the third run 1.0 ml. This corresponds to 29 percent and 49 percent yield based on cyanide, respectively, assuming the distillate contains only the desired product. Additional runs are in progress with further improved procedures.

Preparation of Diethylaminoethanol-1-C^{14}. Procaine is the diethylaminoethanol ester of p-aminobenzoic acid. *In vivo* it undergoes rapid hydrolysis and the p-aminobenzoic acid is directly excreted as hippuric acid. The fate of diethylaminoethanol is not known; only about 30 percent has been accounted for in non-tracer studies. Because of the physiological importance of this compound it was decided to synthesize this material labeled in the one-position of the chain as follows:

$$\overset{*}{C}O_2 \longrightarrow CH_3\overset{*}{C}O_2Na \xrightarrow{(CH_3)_2SO_4} CH_3\overset{*}{C}O_2C_2H_5 \xrightarrow[Cl_2]{P_4,\ I_2}$$

$$ClCH_2\overset{*}{C}O_2C_2H_5 \xrightarrow{(C_2H_5)NH} (C_2H_2)_2NCH_2\overset{*}{C}O_2C_2H_5 \xrightarrow{LiAlH_4}$$

$$(C_2H_5)_2NCH_2\overset{*}{C}H_2OH$$

One low activity run has been completed to date with a yield of 35 percent. It is expected this value can be considerably improved.

Isotope Effect in the Decarboxylation of Substituted Malonic Acids. During the past quarter the work in this field has been confined to preparation of intermediates for synthesis of these substituted compounds. A small scale preparation of α-naphthylmethylchloroacetic acid was described in the last quarterly report, but attemps to increase the scale of this reaction have been unsuccessful, as the product is quite impure. This impurity has now been identified as α(α-naphthyl)acrylic acid. This identity has been established by neutralization equivalents, carbon-hydrogen analysis and catalytic hydrogenation to the known α-naphthylmethyl acetic acid. The unsaturated acid does not add bromine in carbon tetrachloride at room temperature.

Attempts to replace the chlorine with cyanide in the above chloro acid have been unsuccessful to date. In the presence of water the chloro acid is always hydrolyzed to the corresponding hydroxy acid. With potassium cyanide in absolute alcohol, α(α-naphthyl)α-ethoxy propionic acid, M.P. 144-145°, was obtained as shown by neutralization equivalent, carbon-hydrogen analysis and ethoxyl analysis. With potassium cyanide in dioxane an oil was obtained which has not yet been identified.

An attempt is also in progress to prepare diphenylmalonic acid, which is also reported to decarboxylate very readily; the free acid has never been isolated. The ethyl ester of diphenylcyanoacetic acid has been prepared by heating the ethyl ester of diphenylchloroacetic acid with $Hg(CN)_2$. This ester was prepared by treating benzilic acid with dry HCl in absolute ethanol and also by treating the acid chloride of diphenylchloroacetic acid with ethanol. The above acid chloride was prepared by treating benzilic acid with PCl_5. To date it has not been possible to crystallize this ester. Work is in progress on both of the above syntheses.

Biological Chemistry

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M. Kirk, J. Krone, B. Krueckel, M. Meinke and J. Weaver

Metabolism of Propionic Acid-C^{14} In Vitro. Work is being continued on the metabolism of sodium propionate by mouse liver slices. Three additional experiments have been performed under conditions varying somewhat from those described in the last quarterly report. When the slices were incubated with sodium propionate-2-C^{14}, approximately one-fourth as much active carbon dioxide was evolved as when carboxyl-labeled propionate was used, and slightly more activity remained in the water soluble fraction. The chromatograms of the ether and water soluble components, however, showed the same active products for both alpha and carboxyl runs.

In an attempt to compare the metabolism of normal and tumor-bearing animals, livers of myelo-cytoma bearing mice were incubated with carboxyl-labeled sodium propionate. No detectable difference in the distribution of radioactivity in any fractions of the active material thus produced were observed between these and normal livers.

A series of such metabolism experiments was run for short incubation intervals (15, 30, 45 and 90 minutes) to determine whether a sequence of product formation could be found. Previous experiments had been run for two and four hours. Results of this series are as yet incomplete and will be reported later.

One of the major radioactive products formed in these incubation experiments is alanine. The ninhydrin method of Van Slyke, et. al. was used to degrade such alanine formed from experiments using either alpha or carboxyl-labeled sodium propionate. Activity of both the carbon dioxide and the acetaldehyde was determined. The distribution of the label in the alanine is listed below.

	-COOH	$\sum \alpha + \beta$
$CH_3CH_2\overset{*}{C}OOH$	99%	2%
$CH_3\overset{*}{C}H_2COOH$	15%	85%

The ether soluble fraction from these experiments, when chromatographed, showed two major and three minor active compounds. The two major compounds have been shown to be neither malic, succinic or fumaric acids. Additional work on these and other unidentified products is continuing.

Metabolism of Sodium Isobutyrate-1-C^{14} and Sodium Isocaproate-1-C^{14} in Rats. Recent in vitro work has indicated that isobutyric acid is degraded to the half aldehyde of methylmalonic acid and that this compound may then release one mole of carbon dioxide and form propionaldehyde. Alternatively, it is thought that isocaproic acid is beta-oxidized to isobutyric acid. The purpose of this work was to study the

metabolism of these compounds in the living animal by means of radioactive tracers.

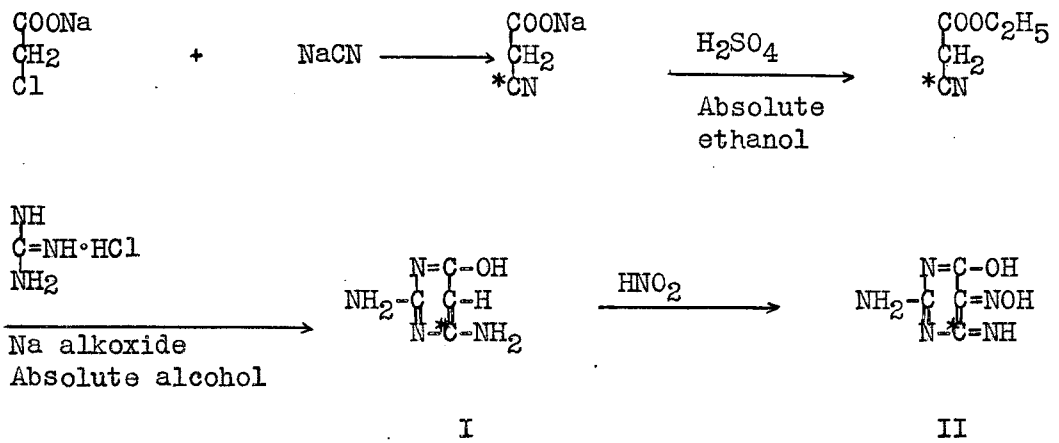
The isobutyric and isocaproic acids were labeled in the carboxyl group. The compound in question was injected intraperitoneally into a 200 g. rat. The rat was placed in a metabolism cage and the carbon dioxide excreted in the breath collected at intervals. For both compounds 85 percent of the injected activity was excreted in the breath in five hours.

In the experiment with the sodium isocaproate, which could be beta-oxidized to give labeled acetic acid, more activity was found in the urine, fat and protein than in the case of sodium isobutyrate, where more activity was found in the glycogen. This would be expected as the later could yield only labeled carbon dioxide or labeled propionic acid, and thus these facts are in accord with existing theories. There was a definite difference in the initial rate of excretion of the carbon dioxide in the breath between the animals injected with the two compounds, that of the isocaproate being the slower initially. This might indicate that there are in the degradation of the isocaproate to carbon dioxide more competing mechanisms.

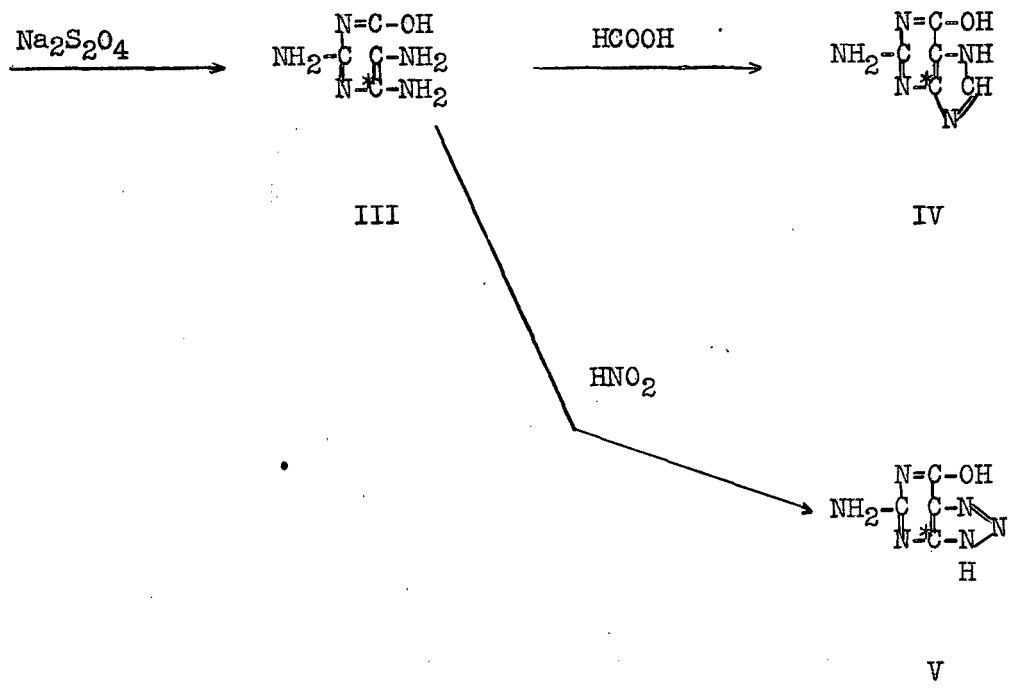
Additional work is underway to clear up these points by the use of liver slice technique. In addition, alpha-labeled isocaproate and methyl-labeled isobutyrate are being used with liver slices in an attempt to determine what pathway is followed in the synthesis of leucine (if possible).

Purines and Nucleic Acids Labeled with C^{14}. The desirability of synthesizing and studying the metabolism of several purines, including adenine, guanine and guanazolo (5-amino-7-hydroxy-1-H-v-triazolo-(d)-pyrimidine) for metabolic and inhibition studies in normal and tumor bearing animals has been discussed in the previous quarterly report.

During the period covered in this report, the main synthetic effort has been a study of the synthetic steps used to prepare guanine and guanazolo. The reactions involved are:



(reaction continued on following page)



By the proposed synthetic scheme, guanine and guanazolo may be readily labeled with C^{14} in any desired position. It is planned to prepare the compounds first using radioactive cyanide, and the resulting compounds will be labeled in the indicated position.

The preparation of ethyl cyanoacetate from chloroacetic acid and sodium cyanide was discussed in the previous report.

The effect on yield of a number of variables in the condensation of ethyl cyanoacetate and guanidine hydrochloride to yield I was investigated. The variables included solvent (methanol, ethanol and n-butanol) and the quantities of guanidine hydrochloride and sodium. The yield was not critical upon excesses or relative amounts of guanidine hydrochloride or sodium, or on the alcohol used. Methanol has been chosen as the solvent since the yield appeared to be slightly larger than with ethanol or butanol.

The pH at which nitrosation of I to yield II occurred was studied, and in a sodium acetate-acetic acid buffer nitrosation occurred at a pH of 5 or less to yield crude II from ethyl cyanoacetate in an overall yield of 70-75 percent.

II can be reduced to III in 75 percent yield with sodium hydrosulfite ($Na_2S_2O_4$). Treatment of III with formic acid yielded crude IV in 90 percent yield. Thus, the overall yield of crude guanine from ethyl cyanoacetate is approximately 45 percent.

Several methods have been studied for the conversion of III to V including

those described by Roblin, et. al. (J. Am. Chem. Soc., 67, 270 (1945)) and by Cavalieri, et. al (J. Am. Chem. Soc., 70, 3875 (1948)). By slight modifications in the former method, mainly in methods of purification, yields of once recrystallized guanazolo of approximately 80 percent have been obtained. This represents a considerable improvement in yield over that reported by these authors. The overall yield of guanazolo from ethyl cyanoacetate is approximately 40 percent. No analysis has been obtained of the product, and the yield is based on the assumption that it is obtained as the anhydrous compound.

Preliminary experiments indicate that 4,6-diamino-5-phenylazo-pyrimidine, an intermediate in the preparation of adenine (see previous report) may be smoothly reduced by the action of zinc dust in glacial acetic acid. These experiments indicate that the crude reduction product, 4,5,6-triaminopyrimidine sulfate, may be obtained in a yield of approximately 70 percent. The reduction by this method is easier to carry out than that described by Cavalieri et. al (J. Am. Chem. Soc., 71, 533 (1949)) and the yield is comparable. It is planned to begin the syntheses of these compounds with radioactive carbon shortly.

Metabolism of Methyl-labeled Choline in the Chicken. The ability of animals to utilize choline and homocystine in place of methionine is now generally known. This fact has been used in an attempt to follow the metabolism of choline chloride and to determine whether the materials for the formation of the egg come via the body tissues or directly from the food being ingested.

Two chickens, one laying and one non-laying, were maintained on a basal diet with the required methionine replaced by the necessary amount of choline and homocystine. Since the laying hen needs more energy and food, it will require more choline. The problem was to see if the additional amount of choline went directly to the egg or was incorporated into the body tissues.

Into the crop of each of the chickens 90 mg of choline chloride containing 70 μc of C^{14} was introduced. The chickens were then placed in a metabolism cage and the carbon dioxide excreted in the breath collected. The breath samples were only taken for six hours after administration of the activity, and during this time less than 0.1 percent of the administered activity was excreted. The animals were sacrificed on the fourth day, and the liver, kidney and spleen removed and the carcasses saved. The activity in the eggs and the organs is being determined.

Other Experiments. Work has continued on a number of other projects, but the details will be reported in later reports or in summaries by other groups. These projects include:

1. The preparation and determination of biological activity of a number of purine and pyrimidine isoteres.

2. The study of the rate of metabolism to $C^{14}O_2$ of simple organic compounds.

3. The metabolism of C^{14}-labeled stilbamidine in mice.

Photosynthesis Chemistry

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M. Goodman, H. Hirsch, C. Ouellet, L. Schou, W. Stepka, P. Warrington and J. Weigl

The investigation of the nature of carbon dioxide reduction during photosynthesis by green plants in this laboratory has fostered the development of methods which have elucidated many of the chemical processes involved. In addition to further development of methods and extension of the knowledge of normal photosynthesis it is now practical by these methods to study the metabolism of plants under abnormal conditions and that of related non-green photosynthetic organisms. Among the non-green photosynthetic organisms being studied is the red photosynthetic bacterium Rhodospirillum rubrum. Abnormal metabolism conditions are represented by the green algae Scenedesmus which can utilize hydrogen gas and form water instead of forming oxygen gas from water or it can fix carbon dioxide using the reaction of hydrogen and oxygen gases as energy source. These processes have not been investigated nor compared with those in normal photosynthesis.

Photoreduction, the Hydrogen-Oxygen-Carbon Dioxide Dark Reaction and Photosynthesis. It has been shown in the literature that algae (e.g. Scenedesmus), after being allowed to remain in an atmosphere of hydrogen gas in the dark acquire the ability to reduce carbon dioxide by the two following processes.

1. Photoreduction (a light induced reaction)

$$2\,H_2 + CO_2 \xrightarrow{\text{low light intensity}} (CH_2O) + H_2O \qquad (1)$$

(no oxygen is evolved in this reaction)

2. The hydrogen-oxygen-carbon dioxide reaction (a dark reaction)

$$2\,H_2 + O_2 + XCO_2 \xrightarrow{\text{dark}} \text{products} \qquad (2)$$

(This latter process is presumed to occur as a result of the "knallgas" reaction.)

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O + \text{heat} \qquad (3)$$

(Pressure-time curves for this reaction indicate consumption of hydrogen and oxygen according to reaction (3), although others have sometimes observed that the reaction

$$H_2 + O_2 \longrightarrow H_2O_2 \qquad (4)$$

also occurs. At any rate, when carbon dioxide is added to the "knallgas" mixture an enhanced fixation of carbon dioxide takes place.)

In this study rate curves for the appearance of products using the radiogram method have been obtained for the following four cases:

1. Photoreduction at low light intensity (about 790 ergs/cm^2/sec, 45 f.c.).

2. Photosynthesis at low light intensity (about 790 ergs/cm^2/sec, 45 f.c.).

3. The hydrogen-oxygen-carbon dioxide dark reaction.

4. The hydrogen-carbon dioxide dark reaction (same as 3. above except absence of oxygen).

The primary object has been to determine whether the course of carbon dioxide fixation is the same in photoreduction, photosynthesis and the hydrogen-oxygen-carbon dioxide dark reaction. A brief summary of this study is reported below.

Experimental Details. The experiments were carried out in a Warburg-type apparatus. All conditions were identical except for the variables noted later (temperature, 20.7° C; moderate shaking speed; 0.10 cc centrifuged Scenedesmus in 2.9 cc 0.05 M KH_2PO_4 (pH~4.5)). The cell suspensions were placed in the flasks with $Na_2C^{14}O_3$ solution in the side arm. In all experiments the flasks were flushed with hydrogen for one hour and allowed to remain in an atmosphere of hydrogen in the dark for a period of 16-18 hours. At the end of this adaption time (a) the $Na_2C^{14}O_3$ was added from the side arm for the H_2-CO_2 dark series of experiments; (b) oxygen was added to a pressure corresponding to about 0.5 percent of the gas pressure for the H_2-O_2-CO_2 dark series of experiments and the $Na_2C^{14}O_3$ then added after the "knallgas" reaction had started; or (c) the light was turned on and the photoreduction process allowed to proceed until the pressure had leveled off after which the $Na_2C^{14}O_3$ was added. For photosynthesis experiments, algae were shaken in the light for one hour and the $Na_2C^{14}O_3$ added. Five to six flasks were run in a series. At the end of a given time the total contents of a flask was removed, centrifuged in the dark, the supernatant liquid discarded and the cells killed in boiling 80 percent ethanol. Since samples were taken over a course of 300 minutes, any reactions occurring during the sampling time (3-4 minutes) were assumed to be negligible. One-half of the total soluble extract for each sample was chromatographed (phenol-water, butanol-water-propionic acid), and the resultant radiogram counted in the usual manner.

Summary of Results. Total radioactivity fixed vs time was plotted for each series of experiments. In each case the plot was linear with time. Slopes were about 9000 cpm/0.1 cc cells/min. for photoreduction; 5000 cpm/0.1 cc cells/min. for photosynthesis; 900 cpm/0.1 cc cells/min. for the H_2-O_2-CO_2 dark reaction; and about 150 cpm/0.1 cc cells/min. for the H_2-CO_2 (O_2 absent) dark reaction.

In addition, the fraction soluble in 80 percent ethanol leveled off for both the photosynthesis and photoreduction at about 40-50 percent soluble whereas in the other two cases percentage radioactivity in these solutes paralleled the total radioactivity, the amount insoluble being no greater than 10-15 percent.

It should be noted that the slope figures above show an increased value for photoreduction over photosynthesis which would appear to be above that due to experimental error. It might conceivably be due to a shift in internal pH due to different reaction conditions.

A second series of plots was made based on the radioactivity present in each of the compounds identified on the chromatograms. These data were plotted as fraction of total activity (or percent of total activity) present in each compound vs time for each of the four cases. Compounds were counted separately and arbitrarily grouped for plotting as phosphates (total), sucrose, three carbon amino acids, four carbon and five carbon acids and amino acids, and malic acid. For the light induced reactions (photoreduction and photosynthesis) the phosphates rose rapidly with time and passed through a maximum. For the H_2-O_2-CO_2 dark reaction, phosphates also passed through a maximum but the maximum here corresponded only to about a third of the fraction present in the other two cases.

Radioactive sucrose was present in all four cases. In photoreduction it rose essentially linearly with time. In photosynthesis it rose rapidly and leveled off. For the H_2-OC-CO_2 dark reaction and the H_2-CO_2 dark reaction it reached only a few percent.

The time-fraction curve for malic acid was essentially similar for photosynthesis, photoreduction and the H_2-O_2-CO_2 reaction. In each case it reached an initial high value corresponding to about 30 percent, then decreased rapidly leveling off at 10-15 percent. The similarity in the three cases for malic acid regardless of the presence or absence of light indicates a similar function of malic acid for the mechanism in all three cases, although it does not prove this.

A further similarity for photosynthesis, photoreduction and the H_2-O_2-CO_2 dark reaction is shown by the time-fraction curve for four carbon and five carbon acids and amino acids. These compounds reach a high value initially, pass through a minimum and then increase or level off.

A third series of plots was made in order to determine the appearance of radioactivity with time in the separate phosphates. For photosynthesis, phosphoglyceric acid, hexose monophosphate and hexose diphosphate pass through a maximum, phosphoglyceric acid always being present in greater amount than hexose monophosphate which, in turn, is greater than hexose diphosphate. A similar plot could not be made for the other cases with the exception of the H_2-O_2-CO_2 dark reaction since the phosphate spots were ill defined. However, in the H_2-O_2-CO_2 dark reaction the phosphoglyceric acid radioactivity distribution passed through a maximum.

Photosynthetic Bacteria. In an extension of the study of the comparative biochemistry of photosynthesis, the red photosynthetic bacterium *Rhodospirillum rubrum* has been cultured in both yeast extract and malic acid. It is known to absorb carbon dioxide in the light with concomitant oxidation of some organic substrate in its medium, but the nature of the carbon dioxide reduction intermediates as well as that of the substrate oxidation products are unknown.

Work has, therefore, been undertaken to elucidate the nature of these compounds using the techniques developed in this laboratory. Synthetic C^{14}-labeled malic acid has been fed as substrate and the intermediates formed during oxidation studied using paper chromatography. $C^{14}O_2$ has also been fed and its reduction products studied in the same way. The latter experiment was performed using molecular hydrogen as the substrate but the results are as yet not available.

Non-photosynthetic experiments with $C^{14}O_2$ fixation have demonstrated the operation of reversible decarboxylation reactions consistent with the existence of a tricarboxylic acid cycle and is identical to dark fixations in algae and higher plants.

Low Temperature Experiments. One of the major difficulties in the elucidation of the path of carbon in photosynthesis is the uncertainty as to whether a given compound is directly and uniquely connected with photosynthesis or if, on the other hand, the compound in question is more closely related to respiration. Since photosynthesis cannot be studied independently of respiration in the intact organism, it is desirable in the study of the path of carbon in photosynthesis to devise a means whereby the complicating effects of respiration are reduced as much as possible.

From what is known about the influence of temperature on enzymatic and photochemical processes it is reasonable to assume that the photosynthetic reactions immediate to the primary photochemical step will be affected less by low temperatures than will the strictly enzymatic reactions of respiration. That is, one may expect the early steps in the path of carbon to be driven forward by a mass law effect of the accumulated reducing power produced in the primary photochemical act. According to this reasoning, conditions of high light intensity (to generate reducing power) and low temperature should lead to an accumulation of the compounds involved in the early steps of photosynthesis. Previous work in this laboratory has led to the elaboration of a scheme which attempts to explain the route of carbon dioxide assimilation by green plants. Among the compounds involved phosphoglyceric acid occupies a key position. Therefore, if this compound (or its conversion products) accumulates under the proposed conditions, the case for its direct participation in photosynthesis would be further strengthened.

Experiments have been performed to test the time-course of carbon dioxide fixation by Scenedesmus D_3 at 2°C when illuminated with light of 2500 f.c. at each surface of the experimental vessel and to follow by means of paper chromatography in conjunction with radioautography the incorporation of labeled carbon into the various compounds.

One hundred milliliters of algae suspension containing 1 ml of packed cells were adapted for thirty minutes in a jacketed vessel of special design which permits the circulation of water at the desired temperature around the inner vessel containing the cell suspension. For the experiments described the temperature of the cell suspension was maintained at 2°C. During the adaption period the cells were illuminated by opposed beams of 2500 f.c. each, measured at the surface of the vessel. A gas mixture composed of 1 percent CO_2, 5 percent O_2, 94 percent N_2 was bubbled through the cell suspension.

Following the adaption period the gas bubbler was withdrawn, and approximately 65 μc of labeled carbon as a solution of sodium bicarbonate was introduced. The vessel was immediately stoppered and shaken between the beams of light for the desired period of time. Intervals used were 0.5 min., 1 min., 2 min., 4 min., and 8 min. At the end of the shaking period the cell suspension was rapidly emptied into 500 ml of boiling absolute ethanol. After cooling in running tap water plates were made for a count of the total activity fixed. Extraction was allowed to continue overnight after which the suspension was filtered free of cell debris, the filtrate made to known volume and again plates of the filtrate made to determine the

percentage of soluble activity. The filtrates were subsequently reduced to 4 ml volume and this concentrated extract was then chromatographed and radioautographs made. Owing to the greatly reduced rates of carbon dioxide fixation as a result of the low temperature, exposures in excess of a month are required for radioautographs of suitable density.

The total amount of carbon fixed by 1 ml of packed cells shows a linear relationship with time from 22 x 10^3 cpm for 30 seconds of exposure to $C^{14}O_2$ to 1.9 x 10^6 cpm for 8 minutes of exposure. From the 30-second experiment 93 percent of the activity appears in the soluble extract. The soluble activity drops to 84 percent, 78 percent and 51 percent for the 2 min., 4 min., and 8 min. experiments, respectively. These figures are a clear indication that even at 2°C the algae are able to convert carbon dioxide into insoluble cell material in the presence of light.

Analysis of individual radioactive spots on the chromatograms is continuing, but is, as yet, incomplete.

Malonate Inhibition Experiments. The effect of malonate inhibition of photosynthesis of the algae Scenedesmus has been further studied and several experiments were performed in which length of photosynthesis, light intensity, etc. have been varied. In each case, the previously reported effect has been observed: while total radiocarbon fixed is not appreciably changed, the amount of labeled malic acid is markedly decreased by malonate inhibition.

The glyceric acid from these experiments has been degraded to test the operation of the proposed photosynthetic cycle during inhibition. In oneexperiment where the inhibition reduced the labeled malic to 17 percent of that formed in the control experiment, the distribution of activity in the carboxyl, alpha and beta carbons of the glyceric was 73 percent, 17 percent and 10 percent, respectively, in the control and 62 percent, 25 percent and 13 percent in the inhibition experiment. Thus, it appears that the cycle may operate somewhat faster when the side reaction leading to the formation of malic acid is blocked. Additional experiments and degradations are being performed to verify this result and several other compounds that appear diminished by inhibition are being investigated.

Low Light Intensity Photosynthesis. A rate experiment study has been performed at 20° with 500 f.c. light intensity incident from each side of a 1 cm thick illumination vessel containing 1 g. of Scenedesmus D_3 in 100 ml of distilled water. From initial steady state photosynthesis in 1 percent $C^{12}O_2$ in air, the photosynthesis with $C^{14}O_2$ was continued for 30 seconds, 60 seconds, 2 min., 4 min., and 8 min. Linear incorporation of C^{14} was observed as well as a sigmoid curve representing C^{14} fixed in insoluble material (protein, polysaccharides, etc.). The relative amounts of each compound synthesized is being determined.

Phosphoglyceric Acid. This compound identified earlier in this laboratory has been separated by paper chromatography into two isomers, the identity of which is under investigation. The isomer appearing earliest in photosynthesis is tentatively considered 2-phosphoglycerate while that appearing next is considered 3-phosphoglycerate. The major evidence for this conclusion is the relative amounts of each at longer photosynthesis times at which 3-phosphoglycerate strongly predominates. The known biological equilibrium contains over 80 percent of the 3-isomer.

Phosphopyruvic Acid. A reinvestigation of the intermediates of very short photosynthesis has been undertaken. An important product has been identified as phosphopyruvic acid. In the low temperature-high light intensity experiments already described phosphopyruvate was observed to form only after the 2-phosphoglycerate and 3-phosphoglycerate. It is felt that $C^{14}O_2$ forms 2-phosphoglycerate and not phosphopyruvate in the first carbon dioxide fixation step of photsynthesis.

Identification consisted of a correspondence of the known hydrolysis rate of phosphopyruvate in acid with that of the activity in the radioactive spot under investigation. As the compound hydrolyzed, the activity disappeared when determined by direct plating since pyruvic acid is volatile. The hydrolysate co-crystallized quantitatively with pyruvic acid dinitrophenylhydrozone.

The Role of Glycolic Acid in Photosynthesis. Glycolic acid oxidation in plants has been demonstrated by other workers, but the glycolic acid itself has not definitely been identified in plant extracts; the oxidative enzyme system ubiquitous in green tissues rapidly destroys glycolic acid. We have observed as much as 30 percent of the C^{14} fixed by algae as glycolic acid by use of paper chromatographs and radiograms of plant extracts. The conditions for optimum glycolic acid formation are: high light intensity, aerobicity and lack of carbon dioxide following photosynthesis with $C^{14}O_2$. Since these conditions are also those for photo-oxidation, Professor James Franck suggested that glycolic acid then may be a photo-oxidation product of the C_2-CO_2 acceptor molecule of photosynthesis. Experiments were then performed in 1 percent oxygen in which condition photo-oxidation was reported by Franck to be minimal. Glycolic acid was observed in small amounts (1-3 percent) in these experiments and thus remains a possible intermediate in the cycle for regeneration of the carbon dioxide acceptor molecule.

Identification of Intermediates of Photosynthesis. Glyoxylic Acid. The isolation and identification of glyoxylic acid is in progress. Since glycolic acid appears in all photosynthesis experiments as well as glycine, it is reasonable to suggest that glyoxylic acid will be found. Periodate oxidation of photosynthesized glyceric acid has been shown to yield glyoxylic acid as the dinitrophenylhydrozone. With a sample of labeled glyoxylic acid it will be possible to determine its chromatographic coordinates for comparison with those of unknown compounds.

Paper Chromatorgraphy of Phosphorylated Compounds. Phosphate-containing compounds can now be detected on paper chromatographs using the spray test developed originally in this laboratory and improved by Hanes and Isherwood. The paper chromatogram is sprayed with a solution containing ammonium molybdate and perchloric acid. The dried paper is heated for nine minutes at 80°C and then exposed to hydrogen sulfide. A blue color shows the location of phosphate. This test will detect 2 μg phosphorus as inorganic phosphate and 15 μg phosphorus as phosphoglyceric acid.

Authentic samples of compounds are being co-chromatographed with unknown radioactive products in order to determine identity. The chromatogram is sprayed to locate the phosphate compound and compared with the radiogram. 3-Phosphoglyceric acid was added to an extract from a 60 second sugar beet leaf photosynthesis and the mixture chromatographed. An exact correspondence of the 3-phosphoglyceric acid spot was found with one of the major radioactive areas. Experiments using

this procedure are now in progress with other known phosphate compounds and the major unknown phosphorylated intermediates.

Separation of Phosphate Esters by Ion Exchange Resins. Strong base type anion exchange resin (Dowex A1) in the neutral chloride form is being studied for the development of separation methods for the phosphorylated intermediates of photosynthesis. Previously it has been possible to separate inorganic phosphate, fructose-1,6-diphosphate and the hexose monophosphates. From this work such resin separations appeared promising for separation of phosphates in high yields and purities.

It has now been possible to separate 3-phosphoglycerate from fructose-1,6-diphosphate in one operation with quantitative recovery of both constituents by the following procedure: A solution of 6.8 mg (680 μg P) each of barium 3-phosphoglycerate and barium fructose-1,6-diphosphate was absorbed on a 35 cm x 6 mm column of 300 mesh Dowex A1 resin and washed thoroughly with water. The column was eluted with a solution containing 0.2 N Cl^-, 0.05 N H^+ and 0.15 N Na^+ at a flow rate of 0.098 cm/min. or 1.08 cm^3/min. 3-Phosphoglycerate emerged from 18-22.4 ml and fructose diphosphate emerged from 28-35.4 ml in quantitative yields. No phosphorus was detectable in the eluate from 22.4-28 ml.

Identification of Phosphate Esters by Infrared Absorption Spectra. A survey of the possible methods of identifying phosphate esters has been extended to include infrared absorption. Preliminary results are reported for authentic phosphoglyceric acid, fructose diphosphate and radioactive phosphoglycerate isolated from algae which had photosynthesized for five seconds in $C^{14}O_2$.

Barium 3-phosphoglycerate (prepared by Prof. C. Neuberg)

Solid	960, <u>1015</u>, <u>1070</u>, 1130 cm^{-1}

Phosphoglyceric acid (prepared by W. Stepka)

Solid	955, <u>1020</u>, <u>1080</u>, 1140 cm^{-1}
Solution	740, 790, 815, 1020, 1080, 1130, 1220 cm^{-1}

Phosphoglyceric acid isolated from algae by Prof. Calvin and mixed with an equal amount of that prepared by Prof. Neuberg.

Solid	950, <u>1020</u>, <u>1075</u>, 1130 cm^{-1}
Solution	740, 700, 865, <u>1020</u>, 1075, <u>1130</u>, <u>1230</u> cm^{-1}

Barium fructose-1,6-diphosphate

Solid	960, <u>1050</u>, 1120 (?) <u>1280</u> cm^{-1}
Solution	750, 865, <u>930</u>, <u>1050</u>, 1070, 1190 cm^{-1}

Spectra of solid samples were determined with a Perkin-Elmer instrument, while those of solutions were determined with a Baird instrument. Underlined maxima are those which differ markedly in the two compounds. The quantities required are 150 μg for solid samples and 3-5 mg for solution samples.

II QUARTERLY PROGRESS REPORT. Project 48B

W. M. Latimer, Director

A. Metals and High Temperature Thermodynamics.

L. Brewer, L. A. Bromley, D. Mastick, Raleigh McKisson
G. Elliott, L. Templeton and Alexander Lindsay

Thermodynamics of CN and N_2 Gases. The detailed report of this completed work has been written up and a more concise report is being written for a journal publication. A recheck of the C_2 heat of formation is being made.

Gaseous Aluminum Oxide Species. This work has been completed with the determination of the Al vapor pressure and the demonstration of the oxide species Al_2O and AlO in the gas in equilibrium with Al_2O_3. The thermodynamic properties of these species have been determined. No gaseous hydroxide was found. A detailed report of this work has been completed and a more concise report is being written for a journal publication.

Gaseous Oxide Species of Transition Metals. The work with NiO has been completed with the demonstration that NiO vaporizes by decomposition to the gaseous elements rather than to undecomposed molecules as reported in the literature. Similar consideration of the MnO and FeO systems indicates similar behavior and experiments are in progress to set upper limits to the stability of the undecomposed molecules. In the progress of this work, the vapor pressure of iron has been determined and found to check well with the values given in the literature. No evidence was found for gaseous iron hydroxides.

Gaseous Oxide and Hydroxides Species of Mo and W. There is definite evidence for gaseous hydroxides in these systems. Work is continuing in the attempt to determine the exact species and their thermodynamic properties.

Reflection Coefficients of Gaseous Molecules. A molecular beam of iron atoms was allowed to impinge upon a platinum plate. Virtually all of the iron stuck, but about 1 percent of the atoms were reflected. A similar experiment with carbon vapor indicated a larger percent of reflection. These data combined with previous vapor pressure data for graphite confirm the previously obtained heat of sublimation of graphite.

Liquid Metal Systems. The new high temperature calorimeter is complete and is in operation. The high temperature camera is also in operation for study of ternary metal systems.

Refractory Studies. Virtually all of the boride phases found in the Ti, Zr, Cb, Ta, Ce, Th, and U systems have been identified and their structures worked out. Ce and Th were very similar with cubic MB_6 and tetragonal MB_4 phases. UB_4 was isomorphous with ThB_4 but a phase UB_2 with the hexagonal AlB_2 structure was also found. Ta_2B with the Mo_2B structure and TaB_2 with the AlB_2 structure were found. A TaB phase was also found, but the structure is not worked out. CbB_2 also had the AlB_2 structure and CbB was isomorphous with TaB, but Cb_2B which appears to disproportionate upon cooling was not isomorphous with Ta_2B. The Ti and Zr systems

both had an MB_2 phase of AlB_2 structure with a lower phase. A report which summarized the data obtained on melting behavior and other properties of these borides is being written up.

Thermal Conductivity of Gases. Attempts were made to find a satisfactory method of measuring the pressure changes of a gas when it is subjected to sudden temperature changes. A change was made in the apparatus to reduce vibration and thus to aid in the measurement of pressure changes.

Heat Transfer in Forced Convection Film Boiling. An apparatus has been designed and is under construction.

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B. Basic Chemistry, including Metal Chelates

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

Lanthanum Chemistry. The effect of ionic strength variance on the dissociation of TTA is being studied further in acetate-acetic acid buffer, in an attempt to decrease the uncertainty factor in the accurate determination of the complexing constants of lanthanum. Further investigation of the first complexing constants of lanthanum by inorganic anions is underway.

The Exchange of I^{131} Between Iodine and Iodate Ion. This work is being written for publication.

The Thermodynamics of Rhenium. Calorimetric runs on the heat of manganous-permanganate couple are in progress and calculations involving this value, it is hoped, will lead to a value for the potential of the couple.

ReO_2 produced by the vacuum decomposition of NH_4ReO_4 was found to be quite free from other rhenium oxides. An x-ray analysis agreed with the monoclinic structure previously reported by Zachariasen.

DECLASSIFIED

Ore Reduction

E. F. Orlemann, M. Lusby, and Sterling Sorenson

Microamperometric Titration of Uranyl Ion with Chromous Ion. Numerous difficulties were experienced in trial runs on the micro scale. Since some of these may be inherent in the analysis and others in the micro scale, it was decided to investigate the tiration on a macro scale, and, if successful, reduce to micro.

Some titrations have been completed, but with about a 20 percent error. An effort is being made to reduce this error. Oxidation of Cr^{++} and contamination of Pt anode are the main difficulties.

Fluorimetric Studies of U(VI). In the fluorimetric determination of U(VI), the ion has been fused into a sodium fluoride-sodium potassium carbonate system in a suitable container at a temperature near the sudion point of the flux mixture. Platinum crucible covers have been used for the containers with resulting quenching of the fluorescence by some impurity in the platinum, or by platinum itself, being dissolved in the flux during the heating period. The amount of quenching has been found to be directly a function of the time and temperature to which the samples have been heated. On analysis of the flux in which quenching has been known to occur, the Spectrographic Group has been unable to determine the offending element(s) due to extremely small amounts present. In order to overcome these difficulties the samples are now prepared in dishes fabricated from 99.99+ purity gold and are heated for a fixed time in a controlled temperature muffle furnace. Previously heating in a Meeker burner had been tried, with unsatisfactory results. From recent experiments it is apparent that quenching is no longer a factor in this work.

Phosphate Complexes of U(VI). A study of effect of the phosphate radicals on the phase equilibrium:

$$UO_2^{++}(aq) + 2\ TTA\ (benzene) = 2\ H^+\ (aq) + UO_2K_2\ (benzene)$$

is being undertaken. Preliminary experiments are underway in which it is hoped the concentrations at which phosphate ions will effect this equilibrium will be bracketed.

D. Engineering Development of Plutonium Separation

T. Vermeulen, T. E. Hicks, Howard Crandall, Barney Rubin,
Milton Davis, Hugh Lehman, Alexander Kaminski, Homer Rea and Albert Lane

A one-stage mixersettler prototype has been constructed and tests have been performed to determine whether bearing and seal design is satisfactory.

The Pulse Column. A 1/2 in. diameter pulse column has been operated in a manner to obtain preliminary data on the extraction behavior of uranium with different solvents. Solvents used were cyclo-hexanone, hexone (methylisobutyl ketone), and pentaether (dibutoxy-tetraethylene-glycol). Disappointing results were obtained with cyclohexanone in that HTU's of 12 inches or greater were obtained under the conditions used, as compared to HTU's of 3 inches or better as reported by Hanford using hexone.

A run using hexone as solvent was made in order to determine whether the very favorable results reported by Hanford could be duplicated, although their optimum results were not obtained, it is felt on the basis of visual observation of column behavior that the differences in performance between this column and the Hanford columns may be attributed to differences in the physical properties of cyclohexanone and hexone, and not necessarily to the column itself.

Several modifications have been made in the feed and overflow systems to permit reproducible operation, since it is felt that some of the poor behavior possibly could be attributed to this cause.

Investigation of column behavior with pentaether is now underway, and preliminary results indicate that HTU's of six inches or less may be obtained.

Incidental to these observationshave been the determinations of the density and optical density vs concentration curves for uranyl nitrate in cyclohexanone and pentaether.

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