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HIGH SPECIFIC RADIOACTIVITIES OF COBALT, PLATINUM AND IRIDIUM FROM PHOTONUCLEAR REACTIONS

by

Darleane Christian

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

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Dean of Graduate College

Iowa State College
1951

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TABLE OF CONTENTS

INTRODUCTION 1

REVIEW OF LITERATURE 5

INSTRUMENTS EMPLOYED 24

- Synchrotron 24
- Beta Counters 24
- Windowless Gas Flow Type Geiger-Mueller Counter ... 25
- Electrodeposition Apparatus 25
- Filtering Apparatus 26

MATERIALS 28

- Preparation of Complexes 28
- Special Chemicals 28
- Ion Exchange Resins 29

EXPERIMENTAL INVESTIGATIONS 30

- Backscattering in the Windowless Counter 30
  - Introduction 30
  - Experimental procedure 32
  - Results and discussion 35
- Cobalt-58 and Cobalt-58m 40
  - Choice of complex 40
  - Chemical procedure 41
  - Experimental procedure 47
  - Results 53
- X-Ray Irradiation of Platinum 67
  - Objectives 67
  - Procedures 68
  - Calculations and results 74

SUMMARY 105

LITERATURE CITED 107

ACKNOWLEDGMENTS 112

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LIST OF FIGURES

Figure 1. Backscattering Curves for the Windowless Counter 37

Figure 2. Self-Absorption Curve for Co^{58m} 52

Figure 3. Short Component from 1.0 Hour Irradiation of Cobalt 54

Figure 4. Long Component from 30.1 Hour Irradiation of Cobalt 55

Figure 5. Platinum Fraction from 1.5 Hour Irradiation of $PtCl_4.xH_2O$ 76

Figure 6. Self-Absorption and Self-Scattering Correction Factors for 0.7 Mev E_{β}-max. of 18h Pt 77

Figure 7. Iridium Fraction from 1.5 Hour Irradiation of $PtCl_4.xH_2O$ 84

Figure 8. Aluminum Absorption Curve for 19h Ir^{194} 20 Hours after End of Irradiation 86

Figure 9. 140m Iridium Component from Irradiation of $PtCl_4.xH_2O$ 88

Figure 10. Aluminum Absorption Curve of Combined 140m and 19h Iridium Activities 3 Hours after End of Irradiation 89

Figure 11. Iridium Activities from 0.25 Hour Irradiation of $PtCl_4.xH_2O$ 93

LIST OF TABLES

Table 1. Platinum Isotopes 14

Table 2. Pt^{191} 15

Table 3. Pt^{193} 16

Table 4. $Pt^{195m(?)}$ 17

Table 5. Pt^{197} 18

Table 6. Characteristics of Beta-emitters 33

Table 7. Amount of Cobalt in Electrodeposition Samples 45

Table 8a. Self-absorption Data for Co^{58m} Samples 50

Table 8b. Determinations of R_2/R_1 61

Table 9. Co^{58m} Yield Determinations 65a

Table 10. Yields of Activities Produced in Irradiations Of $PtCl_4 \cdot xH_2O$ 78

Table 11. Resin Separations 94

Table 12. Butyl Acetate Extractions 96

Table 13. $(NH_4)_2PtCl_6$ Precipitations 97

Table 14. $[Pt(NH_3)_4]PtCl_4$ Precipitations 100

Table 15. Separation of Activity from 9.4 g of $[Pt(NH_3)_4]Cl_2$ 102

INTRODUCTION

The attainment of high specific activities is an important requirement for the detection and utilization of radioactivities produced by photonuclear reactions. In those nuclear transformations in which an element different from the target element is produced, suitable chemical procedures for separation of the radioactive element from the irradiated element can usually be devised. However, finding rapid and efficient chemical methods for separating isotopes of the target element formed in the (γ,n) reaction presents a more difficult problem.

The Szilard-Chalmers reaction, in which the radioactive atom is ejected from a compound containing the element to be transformed, has been used extensively in obtaining high specific activities from neutron bombardments. A similar process can be used to obtain high specific activities from photonuclear reactions if appropriate complexes are irradiated with x-rays. Some of the requirements which must be fulfilled in order for the process to be successful are: (1) the radioactive atom must be ejected from its position in the complex molecule, (2) it must not exchange rapidly with the inactive atoms in other molecules, (3) the recombination of active atoms with any fragments to reform the original complex must be negligible, (4) the complex itself must not undergo appreciable decomposition during the irradiation, and (5) some method for separating the active atoms from the target compound must be available.

In order to facilitate the study of the properties of cobalt and platinum activities produced in the synchrotron by (γ,n) reactions, an attempt was made to find complexes of these elements which would undergo Szilard-Chalmers type reactions. Since both of these elements form easily prepared non-equilibrium complexes, it was believed that suitable complexes could be found.

A high specific activity of cobalt was desired in order to determine if the 8.8h metastable state of Co^{58}, recently reported by Strauch, could be produced by a (γ,n) reaction on cobalt, and to determine its rate of formation relative to the 72d Co^{58} and to a C^{11} standard. Since Co^{59} is the only naturally occuring isotope of cobalt, a (γ,n) reaction can give only the activities of Co^{58}. A (γ,p) reaction on cobalt produces the stable Fe^{58}. Thus, if a separation of the trace amount of active cobalt atoms from the bulk of a suitable complex could be accomplished, a high specific activity of Co^{58} and Co^{58m} would be available for study. Since the energies of the Co^{58m} K and L conversion electrons are only 17.0 and 24.1 Kev, self-absorption in the sample would make their detection impossible unless the activity could be concentrated in some way and counted in a windowless counter. In the case of platinum, the problem is more difficult since there is the possibility of forming several radioactive platinum isotopes by (γ,n) reactions. Also, iridium and osmium isotopes may be formed by other photonuclear reactions. Therefore, a portion of the following study is devoted to the investigation of the activities actually formed when $PtCl_4 \cdot xH_2O$ is irradiated in the 68 Mev maximum energy synchrotron. Iridium was of special interest since (γ,p) or (γ,pn) reactions on Pt^{196} and Pt^{198} would give Ir^{195}, Ir^{196} and Ir^{197} to which no activities were assigned when this research was begun. The well known 19h Ir^{194} would also be formed by (γ,p) on Pt^{195} or (γ,pn) on Pt^{196}. It was hoped that some new activities could be detected, their mass numbers assigned, the energies of the emitted radiations estimated and the relative rates of formation determined. After chemical separation of any osmium or iridium activities formed, the platinum isotopes could be studied and their relative yields determined.

A Szilard-Chalmers process using certain platinum complexes was also investigated. An attempt was made to obtain some information about the efficiency of the process and the final state of the active atoms. Devising a suitable method for separation of the activity is more difficult than with cobalt since the final valence state of the active atoms cannot be as readily predicted. Both Pt^{II} and Pt^{IV} are quite stable while Co^{II} is much more stable than Co^{III}.

In most of the above investigations it becomes necessary to compare the absolute disintegration rates of the various activities. In these calculations, corrections for self-absorption, absorption and backscattering must be made. Many of these corrections had to be determined experimentally while others could be obtained from previously published work on absolute beta counting. Since little work has been published concerning the windowless gas flow Geiger-Mueller counter, some backscattering experiments were performed using this counter.

REVIEW OF LITERATURE

The Szilard-Chalmers effect was first reported by L. Szilard and T. Chalmers (1) in 1934. A sample of ethyl iodide containing a trace of free iodine was irradiated with slow neutrons. A large fraction of the radioactivity produced by the neutron capture was found in a new chemical form which was separated from the ethyl iodide by extraction with an aqueous solution of a reducing agent. In this manner these workers obtained a radioiodine sample with a higher specific activity than that of the ethyl iodide. Since then a great many other organic halides have been similarly investigated. S. Kikuchi, K. Fushima and H. Aoki (2) have measured the energies of the gamma-rays emitted by chlorine, bromine and iodine following neutron capture. From these, the recoil energies of the halogen atoms have been calculated to be ample to cause rupture of the carbon halogen bonds. However, in these studies it has been found that only about 50 per cent of the active atoms can be extracted from the target material; the rest apparently are retained in the organic phase. W. Libby (3) has formulated a theory of the retention mechanism in organic halides. He assumes that the gamma-ray emitted after neutron capture imparts a high enough energy to the recoil halogen atom to assure its quick removal from the molecule from which it has just been ejected, so that it cannot recombine with this fragment. In passing through the organic halide, the recoil atom may collide with another haolgen and be left with too little energy to escape from the molecular fragments formed by the collision. J. Franck and E. Rabinowitsch (4) first postulated this idea of a "reaction cage". Thus recombination may occur to form molecules of the original type. There is also a smaller probability for the formation of other types of organic halides.

Successful Szilard-Chalmers reactions have also been carried out with metal organic compounds and metal complex salts. Of particular interest here are those of platinum and cobalt which have been investigated. J. Steigman (5) has proposed the criterion of optical activity as a sufficient, but not necessary condition to be satisfied in choosing suitable complexes, since this should eliminate the possibility of exchange. Among the inorganic complexes whose optical isomers have been resolved and, therefore, satisfy this criterion are: the oxalato, the ethylenediamine and the dipyridyl complexes. Platinum and cobalt have complexes belonging to one or more of these groups.

Steigman used aqueous solutions of the nitrates of the ethylenediamine complexes of platinum, cobalt, iridium, rhodium and ruthenium to obtain high specific activities of these elements from (n,γ) reactions. In the case of platinum, the activity formed was separated by precipitation of platinum metal with zinc dust and a little hydrochloric acid after the addition of 10-20 mg of platinum chloride carrier. This sample contained 44 times as much activity as the complex sample. However, the counting rates were not corrected for differences in self-absorption which must have been important here. The Co^{60} activity (5.3y) formed in neutron irradiation of the cobalt complex was separated by extraction of cobalt(II) thiocyanate by ether and amyl alcohol, and precipitated as cobalt sulfide for counting. The ratio of concentrate activity to the activity of the complex salt was found to be 10.

S. Chatterjee and P. Ray (6) have concentrated 90 per cent of the Co^{60} activity formed in neutron bombardment of $[Co(CN)_6]^{\equiv}$, containing a trace of cobalt(II), by precipitation of the cobalt(II) with α-nitroso-β-napthol. P. Sue and G. Kayas (7, 8) have studied the efficiency of the Szilard-Chalmers process in hexaamminecobalt(III) nitrate, tris(ethylenediamine)cobalt(III) nitrate and bis(diethylenetriamine)cobalt(III) nitrate to test the hypothesis that the volume of the coordinated groups and the structure of the complex ion, itself, may be important in the success of a Szilard-Chalmers reaction. They proposed that although very large groups and complicated structures should be highly effective in preventing exchange, they may actually decrease the probability that the central atom will be ejected from the complex. They found 86 per cent of the activity ejected from the hexaammine-, 75 per cent from the tris(ethylenediamine)- and only 10 per cent from the bis(diethylenetriamine)cobalt(III) nitrate.

Few such reactions have been used to concentrate activity formed by (γ, n) reactions. W. Barkas and co-workers (9) have reported concentration of Br^{78}, Br^{80m} and Br^{80} by irradiation of liquid ethyl bromide with x-rays, produced by bombardment of lithium with protons. A concentration factor of around 10 per cent was obtained by aqueous extraction of bromide ion. O. G. Holmes and E. J. McCallum (10) reported the use of the copper salicylaldehyde-o-phenylenediimine chelate complex to concentrate the Cu^{63} activity formed by irradiation in the 18 Mev maximum energy betatron of the University of Saskatchewan. They irradiated both the solid complex and pyridine solutions of the complex. When the solid was irradiated, washed with water and copper sulfide precipitated from the filtrate, 95 per cent of the activity was retained in the complex. If the solid was dissolved in pyridine after irradiation, copper carrier added, the complex precipitated with 15 per cent acetic acid, and the carrier removed as copper sulfide, only 45 per cent of the activity was found in the complex. When a 0.053 M pyridine solution of the complex was irradiated only 18 per cent retention was observed. By adding varying amounts of copper carrier to the solution to be irradiated, the retention in the complex was reduced to 9 per cent. Similar results were obtained by R. Duffield and M. Calvin (11) in neutron bombardments of this complex. Holmes and McCallum calculated the maximum recoil imparted to the Cu^{62} nucleus by the photonuclear process to be about 0.1 Mev which is more than enough to break chemical bonds.

No record has been found in the literature of a Szilard-Chalmers type process being used to concentrate cobalt or platinum activities formed by (γ,n) reactions. By the following calculation (12, p. 262) it can be shown that the recoil energy of the active atoms formed in such processes is sufficient to break chemical bonds, most of which are of the order of 1-5 ev, and that one could, therefore, expect the active atoms to be ejected from the irradiated complexes.

$$E_M = (E_\gamma + Q)m / M + m = E_M(m/M) \qquad (1)$$

where E_γ is the energy of the incident gamma-rays, Q is the energy released in the nuclear reaction or the threshold of the reaction, m is the mass of the neutron and M is the mass of the recoil atom. This equation neglects the small momentum imparted to the atom by the impinging gamma-ray. (W. Libby (3) has derived an exact equation for the recoil energy.) From the available data on photoneutron yields as functions of energy, Katz and co-workers (13) have noted that the cross sections have peaks, on the average, about 6 Mev above the threshold for the reaction and the resonance peaks have a half-width of 5-6 Mev. Therefore, most of the reactions will occur between 3 and 9 Mev above threshold which means that the recoil energies are 0.05-0.15 Mev for cobalt and 0.015-0.045 Mev for platinum. If the active atoms ejected in the photonuclear process do not replace inactive atoms in the complex, do not recombine with fragments of the complex, and do not exchange, a concentration of the activity should be observed.

There has been no previous report of the formation of any of the isotopes of cobalt by a photonuclear reaction on cobalt, probably because a (γ,n) reaction gives only the 72d Co^{58} or the 8.8 hour Co^{58m} and (γ,2n) gives the 270d Co^{57}. Little of the 72d or 270d cobalt would be formed in the usual irradiation times, and the 8.8h Co^{58m} cannot be readily detected with the ordinary mica window Geiger-Mueller counter. Unless these activities can be separated chemically from the target cobalt, there will be little chance of detecting them because of the very low specific activities which will be formed.

The 72d Co^{58} was reported by J. J. Livingood and G. T. Seaborg (14) in 1938. Its half-life was measured as 72d and the activity definitely assigned by them to Co^{58} in 1941 (15). It was produced by the following reactions: Mn(α,n), Ni(n,p), Fe(d,n), Fe(p,α) and probably by Fe(α,np). They also reported that the activity emitted a 0.6 Mev gamma-ray and positrons having a maximum energy of 0.4 Mev. L. G. Elliott and M. Deutsch (16,17) have studied the disintegration scheme by examination of a Co^{58} source in the magnetic lens spectrometer, and found a gamma-ray of 0.810 ± 0.015 Mev. By beta-ray spectrometer measurements it was shown to emit positrons with a maximum energy of 0.470 ± 0.015 Mev. They reported that Co^{58} decays to a state of Fe^{58} 0.805 Mev above the ground state and that this state decays by emission of a gamma-ray. Ninety per cent of the Co^{58} disintegrations were found to occur by K electron capture while the other 10 per cent are by the 0.47 Mev positrons. Each positron emitted is accompanied by a 0.805 Mev gamma-ray. W. M. Good, D. Peaslee and M. Deutsch (18) have found the positron branching ratio for Co^{58} to be 0.145 ± 0.005 positrons per disintegration.

K. Strauch (19) first reported identification of Co^{58m}. He observed that it decays with an 8.8h half-life by emission of a 24.9 ± 1.0 Kev gamma-ray, and determined the ratio of the K to L conversion coefficients to be 1.9 ± 0.2. Strauch believes this transition is of the type $\Lambda = 4$. The relative cross section for the formation of Co^{58m} to Co^{58} when manganese is bombarded with alpha particles was calculated to be 1.7 from data he obtained by observation of growth of the continuous positron spectrum of the 72d activity. The 8.8h activity was also found in cobalt fractions from nickel and cobalt bombarded with 18 Mev deuterons and fast neutrons, and from deuterons on copper.

In the following investigation the nuclear isomers of Co^{58} have been separated and their relative rates of formation for the photonuclear process calculated. E. Segre, R. Halford and G. T. Seaborg (20) first reported chemical separations of nuclear isomers. They separated the 18m daughter of Br^{80} from the 4.4d upper level of Br^{80}. Tertiary butyl bromide containing Br^{80} was synthesized and shaken with a methanol-water solution. The tertiary butyl bromide was separated by extraction with benzene, bromide carrier was added to the water layer and the bromide was precipitated with silver ion. The 18m daughter of 4.4h Br^{80} was found in this precipitate from the aqueous phase.

D. De Vault and Libby (21) observed similar results with bromoform. G. T. Seaborg, G. Friedlander and J. Kennedy (22) studied the isomeric transitions in Zn^{69}, Te^{127} and Te^{129} using the Zn and Te diethyl compounds. They were able to separate the Te^{127} and Te^{129} isomers in which a conversion electron is emitted although energies of only 9.2 and 6.6 kcal are imparted to the recoil tellurium atoms. The Zn^{69} isomers, in which the transition gamma-rays are largely unconverted, but which give an energy of 40 kcal to the recoil zinc atoms could not be separated. Therefore, they concluded that the isomer separation process occurs due to the high state of electronic excitation resulting from the loss of a conversion electron, rather than from the recoil energy imparted to the atoms. E. Cooper (23) has shown theoretically that decay by K-capture or internal conversion can cause separation of a daughter activity from the original complex. These processes result in a vacancy in the K or L electron shells. During the filling of such a vacancy a large positive charge can be accumulated by Auger processes. A molecule containing an atom which can undergo an isomeric transition is considered as being at the minimum of its potential energy curve. After the isomeric transition process the original atomic configuration of the molecule may no longer represent the minimum potential energy of the molecule and on vibration dissociation will occur.

Table 1 shows the known platinum activities and their mass assignments and the stable isotopes of platinum as given by the United States National Bureau of Standards (24, p. 225)

Table 1. Platinum Isotopes

190*	191	192*	193	194*	195m	195*	196*	197*	198*	199
0.012	3d K	0.78	4.33d K	32.8	80m I.T.	33.7	25.4	18h β^-	7.2	29m β^-

*Stable isotopes, abundance given in per cent.

Of these, the only activities which would be expected from photonuclear reactions on platinum are Pt^{197}, Pt^{193} and metastable states of the stable isotopes, formed as a result of (γ, n) or possibly (γ, γ') reactions. Pt^{191} might be formed in very low yield. Tables 2, 3, 4 and 5 summarize the present knowledge about these activities.

The mass assignment of the 80m platinum to Pt^{195m}, however, does not appear to be definitely established. R. Sherr, K. T. Bainbridge and H. H. Anderson (25) suggested its assignment to a metastable state of Pt^{196} or Pt^{197} on the basis of its production by fast, but not slow neutron bombardment of platinum, by deuterons on platinum and by fast neutron bombardment of mercury, but not by alphas on osmium or by

Table 2. Pt^{191}

$T_{\frac{1}{2}}$ 3.0d	G. Wilkinson	1948	(26)
Radiations			
K e^- = 0.5 γ 0.57 1.7 K,L x-rays	G. Wilkinson	1948	(26)
Formation			
Ir(d, 2n) Pt(n, 2n) Pt (d, p) small amount	G. Wilkinson	1948	(26)
Basis of Mass Assignment			
Daughter of 1 d Au^{191} No Ir daughter of $T_{\frac{1}{2}}$ more than a few minutes Not produced by (n,γ)	G. Wilkinson	1948	(26)

Table 3. Pt^{193}

Half-life			
$T_{\frac{1}{2}}$ = 4.33d	G. Wilkinson	1949	(26)
3.5	N. Hole	1948	(27)
4.0d	C. E. Mandeville and others	1948	(28)
2.8d	R. S. Krishnan and E. A. Nahum	1941	(29)
3.3d	E. M. McMillan	1937	(30)
Radiations			
K	G. Wilkinson	1949	(26)
e^- = 0.115	C. E. Mandeville and others	1948	(28)
	G. Wilkinson	1949	(26)
0.112	N. Hole	1948	(27)
γ = 0.126	N. Hole	1948	(27)
0.18, 1.5	G. Wilkinson	1949	(26)
K, L x-rays	G. Wilkinson	1949	(26)
	C. E. Mandeville and others	1948	(28)
(K x-ray)/(L x-ray) ~ .5	G. Wilkinson	1949	(26)
$\gamma\gamma$ or γ x coincidences	C. E. Mandeville and others	1948	(28)
Formation			
Pt(n,γ)	C. E. Mandeville and others	1948	(28)
	G. Wilkinson	1949	(26)
	E. M. McMillan	1937	(30)
	L. Seren	1947	(31)
not by (n,γ)	N. Hole	1948	(27)
Pt(fast n)	N. Hole	1948	(27)
Pt(d,p)	R. S. Krishnan and E. A. Nahum	1941	(29)
Ir(d,2n)	G. Wilkinson	1949	(26)
Ir(α,pn)	G. Wilkinson	1949	(26)
Basis of Mass Assignment			
Daughter of 16h Au^{193}	G. Wilkinson	1949	(26)
No Ir daughter of $t_{\frac{1}{2}}$ more than a few minutes		1949	(26)
Not formed by decay of Ir^{194}		1949	(26)

Table 4. $Pt^{195m(?)}$

Half-life			
$T_{\frac{1}{2}}$ = 80m	R. Sherr and others	1941	(25)
78m	N. Hole	1948	(27)
87m	D. L. Mock and others	1948	(32)
Radiations			
I. T.			
$\gamma = 0.337$	N. Hole	1948	(27)
$\alpha = \infty$			
K/L = 1.3			
Formation			
Pt(d,p)	R. Sherr and others	1941	(25)
Pt(fast n)	R. Sherr and others	1941	(25)
Pt(γ,n)	D. L. Mock and others	1948	(32)
Hg(n,α)	R. Sherr and others	1941	(25)
Basis of Mass Assignment			
Not produced by Pt(n,γ)	R. Sherr and others	1941	(25)
No active daughter (?)	N. Hole	1948	(27)
Not produced by α's on Os or d's on Ir	R. Sherr and others	1941	(25)

Table 5. Pt^{197}

Half-life			
$T_{\frac{1}{2}}$ = 18h	G. Wilkinson	1949	(26)
19h	E. M. McMillan and others	1937	(30)
	R. Sherr and others	1941	(25)
Radiations			
β^- = 0.65	R. Sherr and others	1941	(25)
0.72	R. S. Krishnan and E. A. Nahum	1941	(29)
Formation			
Pt(n,γ)	E. M. McMillan and others	1937	(30)
	L. Seren and others	1947	(31)
Pt(d,p)	R. S. Krishnan and E. A. Nahum	1941	(29)
Pt(n,2n)	R. Sherr and others	1941	(25)
Pt(γ,n)	H. Waffler and O. Hirzel	1948	(33)
Hg(n,α)	R. Sherr and others	1941	(25)
Basis of Mass Assignment			
No active daughter	R. S. Krishnan and E. A. Nahum	1941	(29)

deuterons on iridium. Hole (27) reported the cross section ratio of a 3.45d activity to the 78m activity produced in fast neutron irradiations of platinum to be about 15. Hole stated that he looked for daughters to both of these activities with "no result". He gave no indication of the method he used and it is difficult to understand how the formation of the 18h Pt^{197} daughter could have been definitely ruled out since this isotope was formed in high abundance in the irradiations. On the basis of Hole's report, the United States National Bureau of Standards (24) has, tentatively, assigned an 80m activity to Pt^{195}. It was probably assigned to Pt^{195} rather than Pt^{196} because metastable states of even-even isotopes are believed to be highly improbable (34).

Wilkinson (26) has assigned a 4.33d activity to Pt^{193} and a 3.0d activity to Pt^{191}. He made a careful study of the properties and formation of these two isotopes and the assignments seem to be quite definitely established. He found no iridium daughters of half-lives greater than a few minutes to either the 4.33d Pt^{193} or the 3.0d Pt^{191}. However, the K/L x-ray ratio of 0.5 observed for the 4.33d activity is abnormally low, and may indicate decay by L electron capture in addition to K capture, or gamma-ray conversion in the L shell. A 3.3d activity which McMillan and co-workers (30) detected in 1937 from slow neutron irradiation of platinum and suggested might be isomeric with the 18h Pt^{197}, was probably the 4.33d Pt^{193}. The 3.45d activity which Hole produced in fast, but not slow, neutron irradiation of platinum can also be identified as Pt^{193}. He found that it emitted a 0.126 Mev gamma-ray and reported a K/L ratio of 0.23. Since it would be expected that the yield of Pt^{193} would be much higher in fast than in slow neutron irradiations, its intensity must have been below Hole's limit of detection in slow neutron irradiations. Other investigators (28, 30) have reported the formation of similar activities in slow neutron irradiations of platinum. Recently, J. M. Cork and co-workers (35) have reported activities of 17.4h, 3.4d and 83d in platinum irradiated in the pile.

There seems to be something of a paradox in the above results. Although Wilkinson found no daughter to the 4.33d Pt^{193}, the low K/L ratio and the high conversion coefficient indicate an internal transition. On the basis of this evidence and the 3-4d half-life, M. Goldhaber and A. W. Sunyar (36) have classified a platinum isotope having these characteristics as an M4 type of internal transition. If such an isomeric transition actually does take place to a daughter Pt^{193}, decaying by electron capture with a very long or very short half-life, Wilkinson would not have detected it. The presence of an isomeric transition in Pt^{193} would appear to be a possibility which should be investigated further.

There are a few reports in the literature of the formation of platinum activities by (γ,n) reactions. D. L. Mock and others (32) have reported the formation of an 87m platinum activity when platinum is irradiated in the 20 Mev betatron, and H. Waffler and O. Hirzel (33) produced the 18h Pt^{197} by irradiation of platinum with the gamma-rays from lithium. They report the relative cross section for the formation of the 18h platinum to be approximately 200 if the reaction Cu^{63} (γ,n) Cu^{62} (9.88m) is taken as 100.

At the time this investigation was begun, the only reported activities of iridium were the 10.7d Ir^{190}, the 1.42m and 70d Ir^{192} and the 19h Ir^{194} (24). Of these, only the 19h would be expected to be formed in high intensity from photonuclear reactions on platinum, although a very low intensity of the 70d might be observed. Decays of 19.0h, 20.7h and 19.5h (37, 31, 38) by emission of negative betas of 2.1 Mev (37, 38) and 0.48 Mev (39), and by gamma-rays of 1.35-1.65 (40, 39, 37) and 0.38 Mev (37) have been observed. Recently, in irradiation of platinum with x-rays, Butement (41, 42) reported a 66m activity which he tentatively assigned to Ir^{195}, or more likely to Ir^{197} on the basis of its yield relative to the 18h iridium. However, with stronger samples from (n,p) reactions on platinum he has observed a half-life of 120-150m (43) rather than 66m.

There are some reports on recent investigations of the relative yields of x-ray induced nuclear reactions. H. L. Perlman and G. Friedlander (44, 45) determined the yields of many (γ,n) and a few (γ,p), (γ,2n) and (γ,2p) reactions relative to the reaction, N^{14} (γ,n) N^{13} as one. The yields were determined by irradiation of various elements with the x-rays produced in a tungsten target by 50 and 100 Mev electrons. The yield ratios are nearly the same at both energies. For the (γ,n) reaction on Ni^{58}, the yield is 6.3 while for (γ,n) on Cu^{63}, it is about 33.0 at 100 Mev. For (γ,p) reactions, values seem to vary between 4 and 8 with no upward trend as is observed with (γ,n) reactions. Price and Kerst (46) have also investigated the neutron yields of some (γ,n) processes induced by using betatron bremsstrahlung with maximum energies of 18 and 22 Mev. They have prepared a smooth curve of the photoneutron yields versus atomic number and have obtained fair agreement with the theoretical yield curve predicted by M. Goldhaber and E. Teller (47), and with the yields reported by Friedlander and Perlman, Waffler and Hirzel and McElhinney and co-workers.

In the following investigations, absolute beta disintegration rates were frequently compared and the results of previously reported backscattering, self-absorption and self-scattering experiments for the conventional end-window Geiger-Mueller tube were used (48, 49). No such data were available for the gas flow counter, although recently W. L. Graf, C. L. Comar and I. H. Whitney (50) have compared the aluminum absorption and self-absorption curves of various beta-emitters in the windowless Geiger-Mueller type gas flow counter, the thin end-window counter and the windowless proportional counter. They found that the effects of absorption and self-absorption are of considerably greater magnitude in the windowless counters. This indicates that a much larger proportion of very low energy betas was being measured. When they determined the values for the internal counters using the counting rate at 5.9 mg/cm^2 sample thickness as the N_o value, the curves became identical with those for the end-window counter. The windowless counters were found to be 30 times more sensitive than the end-window counter for 0.167 Mev betas and 10 times more sensitive for 0.53 Mev betas.

INSTRUMENTS EMPLOYED

Synchrotron

The Iowa State College synchrotron which exhibits a continuous spectrum (51) from zero to a maximum energy of 68 ± 5 Mev was used for all irradiations. The samples to be irradiated were contained in test tubes of 1 cm diameter. The test tube was held in a specially constructed lucite holder which was carefully aligned in the x-ray beam. Only one sample at a time was irradiated and all irradiations were at the maximum energy of the synchrotron. The intensity of the beam was monitored by an ionization chamber and plotted by a recording milliammeter. All of the samples used for yield determinations were irradiated at a nearly constant beam intensity.

Beta Counters

Standard end-window Geiger-Mueller counter tubes manufactured by the Victoreen Instrument Company and Radiation Counter Laboratories were used to measure the platinum, iridium, carbon and chlorine activities. The thickness of the mica windows ranged from 1.9 to 2.2 mg/cm^2. The counters were mounted in lead or heavy iron housings to minimize the background counting rates. Background and Co^{60} standard sample counts were taken with all measurements.

Windowless Gas Flow Type Geiger-Mueller Counter

In order to count the low energy radiation from Co^{58m} it was necessary to use a windowless gas flow type Geiger-Mueller counter. A one place gas flow counter made by the N. Wood Company was used. This counter operated at about 1300 volts. "Q" gas obtained from the Nuclear Instrument and Chemical Corporation was passed through the counter at a constant rate. A Co^{60} electroplated standard was counted before and after all experimental samples. Conventional scale of 64 scalers made by the Instrument Development Laboratory and the Nuclear Instrument and Chemical Corporation were used in conjunction with all the Geiger-Mueller counters.

Electrodeposition Apparatus

The cobalt counting samples were electroplated using a Sargent-Slomin electro-analyzer with a rotating anode. For these anodes, 3/16 inch diameter graphite sample electrodes used to produce the arc in emission spectroscopic analyses were employed. These electrodes could be changed so that there was no danger of radioactive contamination from a previous experiment. A micro electroanalysis cell, manufactured by Tracerlab, Incorporated especially for use in electroplating radioactivity for counting samples, was used to hold the solutions. This cell consists of a metal frame on the bottom of which a platinum disc 2.55 cm in diameter, which serves as the cathode, is placed. A rubber gasket and glass chimney are held securely on top of this. The cell has a maximum capacity of 50 ml. When the electrolysis has been completed the liquid can be poured off, the chimney and gasket removed and the electroplated sample weighed and counted.

Filtering Apparatus

The conventional filtering techniques are not convenient for the preparation of radiochemical assays. They are often slow and it is difficult to obtain evenly deposited precipitates which can be removed quantitatively from the filter for weighing and counting. Therefore, a special filtering apparatus was used in the preparation of samples of platinum, iridium, osmium and chlorine activity. Using this apparatus filtering can be done rapidly, and even deposits of the precipitate over a uniform area are obtained. The samples can be readily washed and removed quantitatively for weighing and counting.

The apparatus was constructed in the following manner. One end of a glass sealing tube 3.0 cm in diameter, containing a coarse fritted glass disc was cut off flush with the fritted disc and ground even with it. To the other end of the tube, which formed the bowl of the filter funnel, 5 cm of 0.6 cm diameter glass tubing was sealed. The filter could then be placed in a suction flask in the usual way. Filter paper discs nearly 3.0 cm in diameter were placed on top of the fritted glass disc. A 2.6 cm diameter glass chimney was held securely over the filter paper by rubber bands attached to glass hooks on the chimney and to others on the tube just below the fritted glass disc. Suction was applied by means of a water aspirator and the solution to be filtered was poured into the chimney. After filtering, the samples were washed with alcohol and ether and the chimney was removed. The filter paper containing the 2.6 cm diameter sample could then be easily lifted off the fritted disc, dried and weighed. Before the preparation of the sample the filter paper was similarly washed, dried and weighed.

MATERIALS

Preparation of Complexes

The $K_3[Co(C_2O_4)_3]\cdot 3H_2O$ used in the following investigations was prepared according to the procedure given by D. M. Yost (52, p. 37). $[Pt(NH_3)_4]Cl_2\cdot H_2O$ and a carrier solution of $PtCl_4^=$ were prepared from directions given by R. N. Keller (53, p. 251). $[Pt(NH_3)_2Cl_4]$ was synthesized according to directions given by J. W. Mellor (54, p. 308). K_2PtCl_4 was prepared by reduction of K_2PtCl_6 with $K_2C_2O_4$ (55, p. 286). Reagent grade chemicals, when available, were used in all of the syntheses. Otherwise CP chemicals were used.

Special Chemicals

Platinum(IV) chloride was obtained from Mallinckrodt Chemical Works. A spectrographic analysis indicated that it contained no iridium, osmium or other contaminants which would produce interfering activities. In one irradiation platinum foil was used and a spectrographic analysis of it gave similar results. The osmium used as carrier was obtained from Mallinckrodt Chemical Works as osmium tetroxide. Iridium, obtained as CP iridium trichloride, from Fisher Scientific Co. was used as carrier.

The hydrazine dihydrochloride used in the cobalt electroplating solutions was tested for iron before use. Several bottles of CP grade were found to contain enough of this contaminant to cause serious errors in the weights of the cobalt samples.

Ion Exchange Resins

Amberlite IRC-50 cation exchange resin manufactured by the Rohm and Haas Company was used in the separation of the cobalt(II) from the cobalt complex. It possesses only one type of active exchange center, a carboxylic acid group. This was converted to the potassium salt before use by treatment with potassium hydroxide. This resin is particularly useful in neutral and alkaline solution. Above a pH of 7.0, almost all the carboxylic acid groups take part in exchange reactions. At this pH, IRC-50 has a weight capacity of 7.8-8.0 meq/g and a volume capacity of 3.6-3.8 meq/ml.

Duolite A-2, manufactured by the Chemical Process Co., and Amberlite IR-4B, obtained from the Rohm and Haas Co., were used in some of the experiments with the platinum complexes. Duolite A-2 is a phenolic resin and Amberlite IR-4B is a weakly basic resin containing a modified amine as the active group. Before use, these were converted to the acetate or oxalate forms by treatment with $NaC_2H_3O_2$ or $K_2C_2O_4$, respectively.

EXPERIMENTAL INVESTIGATIONS

Backscattering in the Windowless Counter

Introduction

It was necessary to use the windowless gas flow type Geiger-Mueller tube to count the 17 and 24 Kev conversion electrons emitted by Co^{58m}. The windowless counter has a counting efficiency of nearly 80 per cent when samples are mounted on platinum while the efficiency of most end-window counters is only about 10 per cent. In general, the determination of absolute disintegration rates from counting rates involves the following equation derived by L. R. Zumwalt (56).

$$(d/m) = (c/m)/ f_W f_A f_B f_H f_S (G/100) \qquad (2)$$

f_W is the factor for the effect of beta-ray absorption by the counter tube window and air in the space between the tube and the source. f_A is the effect of air in scattering beta-particles into the counter. f_B is the factor for the increase of counting rate due to backscattering by the material supporting the source. f_H is the factor for the effect of the source support structure and walls of the housing in scattering beta-particles into the counter tube. f_S is the factor for the effect of the mass of the source in causing both scattering and absorption of beta-particles and G is the geometry. Assuming isotropic emission of radiation, the geometry factor for the windowless counter is 50 per cent since one-half of the electrons would then be directed toward the sensitive volume of the counter and be detected. For the windowless counter, f_W and f_A are one. f_S must be determined experimentally, but will be one in the following experiments where essentially weightless sources are used. f_B and f_H can be incorporated into a single backscattering factor, B, which must be determined experimentally. A knowledge of the magnitude of the backscattering for various energy beta-emitters due to different sample backings is, therefore, necessary if one is to determine absolute disintegration rates in the windowless counter.

Since no backscattering data were found in the literature, the factor had to be determined experimentally. For the end-window counter, the counting rate of a nearly weightless source on a thin film can be used as the value for zero backscatterer. This counting rate can then be compared with the rates resulting from placing backscatterers of various elements directly behind the source. However, in the flow counter, one cannot obtain the counting rate at zero backscatterer in this manner since the sample must always be placed directly on top of the steel base of the counter chamber. The counting rate with various backscatterers can be obtained if the sample is placed on backscatterers of at least "infinite thickness" for the radiation involved. (An "infinite thickness" backscatterer is one which gives the maximum limiting counting rate. Engelkemier and co-workers (49) have shown that a thickness greater than 20 per cent of the beta-particle range gives the maximum or saturation effect.) One-half the absolute disintegration rate of the sample, if known, is used as the value for zero backscatterer. From the variation of the counting rate with atomic number of backscatterer, curves of counting efficiency versus atomic number of backscatterer can be plotted for each beta-emitter investigated. The desired backscattering factor can then be read from these curves.

Experimental procedure

Activities used. Four different beta-emitters were used in the experiments to indicate variations which might be due to the beta-ray energies and possibly to the form of the spectrum. Table 6 gives the pertinent data concerning them.

Materials used as backscatterers. Beryllium, magnesium, aluminum, nickel, copper, silver, tantalum and platinum metals were used as backscatterers. Discs about 2.5 cm

Table 6. Characteristics of Beta-emitters

Activity	$T_{\frac{1}{2}}$	E_{max} of β^- (Mev)	Specific activity (d/m mg)	Chemical form	Source
Ni^{63}	85y	0.067	5.3×10^8 ($50\lambda = 0.01\mu g$)	$NiCl_2$	Oak Ridge Pile Ni(n,γ)
S^{35}	87d	0.17	no carrier ($50\lambda = 0.00\mu g$)	H_2SO_4	Oak Ridge Pile Cl(n,p)
Co^{60}	5.3y	0.31	5×10^7 ($50\lambda = 0.15\mu g$)	$CoCl_2$	Oak Ridge Pile Co(n,γ)
P^{32}	14.3d	1.7	4.2×10^8 ($50\lambda = 0.02\mu g$)	H_3PO_4	U. S. Bureau of Standards S(n,p)

in diameter and thick enough to insure saturation backscattering were used. The surfaces of the metals were different, the platinum being bright while the tantalum was quite dull. All of the discs except the beryllium were cut from commercial foils which were probably fabricated by rolling. The beryllium discs appeared to have been cut by an abrasive wheel from rod. The magnesium discs were etched with dilute HCl to remove the oxide film.

Preparation of samples. In preliminary experiments, 50λ aliquots of the various active solutions were evaporated directly on the metal backscatterers. Two samples of each were prepared and counted. An absolute P^{32} standard was prepared by diluting an aliquot of a National Bureau of Standards sample of known disintegration rate and evaporating 50λ of it on platinum. The absolute disintegration rate of the Co^{60} samples was determined by comparison with the counting rate of an electroplated Co^{60} secondary standard. Its disintegration rate was determined by comparison with a similarly prepared primary Co^{60} standard whose absolute disintegration rate had been calculated by F. J. Hughes from coincidence counting data.

In a second series of experiments, Zapon films of about 30 $\mu g/cm^2$ thickness were supported on top of thin plastic rings 2.5 cm in diameter and 1.0 mm high. A 50λ aliquot of each activity was then evaporated on a film. The ring was placed directly on the various backscatterers so that the sample of activity was on top of the film facing toward the counter and 1.0 mm above the backscatterer.

Results and discussion

By comparison of the P^{32} sample evaporated on platinum with its absolute disintegration rate, as determined from the National Bureau of Standards data, an over-all efficiency for the flow counter of 0.775 counts/disintegration was found. When the absolute disintegration rate of the P^{32} was calculated by comparison with the Co^{60} standard, a value 1.07 times that of the value calculated from the National Bureau of Standards data was obtained. Both B. P. Burtt (57) and T. Novey (58) have reported obtaining values 8 per cent higher for the absolute disintegration rate of P^{32} than the values given by the National Bureau of Standards. They believe the National Bureau of Standards value to be in error by 8 per cent because of self-scattering due to the finite thickness of the Ra D-Ra E standards which they used.

The results from the samples prepared by evaporation of the activities directly on the backscatterer proved erratic for Ni^{63} and S^{35}, but quite satisfactory for Co^{60} and P^{32}. However, it was noted that platinum gave results which appeared high in relation to the tantalum values. This may have been due to differences in the metal surfaces. The erratic results obtained with Ni^{63} and S^{35} may have been due to differences in the metal surfaces, attack of the metals by the very dilute acid solutions with subsequent self-absorption of the activities, or by uneven distribution of activity on the backscatterer. All of these factors would become more important with the lower energy beta-emitters.

The thin film experiment was undertaken to minimize the various surface effects. Also, since the same sample of each activity could be used with the different backscatterers, it was necessary to prepare only one sample of each activity and errors due to pipeting or differences in distribution of the activity were eliminated. Any differences in counting rate could then be due only to the backscatterer. The curves for Co^{60} and $P3^{2}$ were essentially the same as in the preceding experiments in which the activity was evaporated directly on the metal surface. The results obtained from the thin film samples are shown in Figure 1. One-half the absolute disintegration rate of

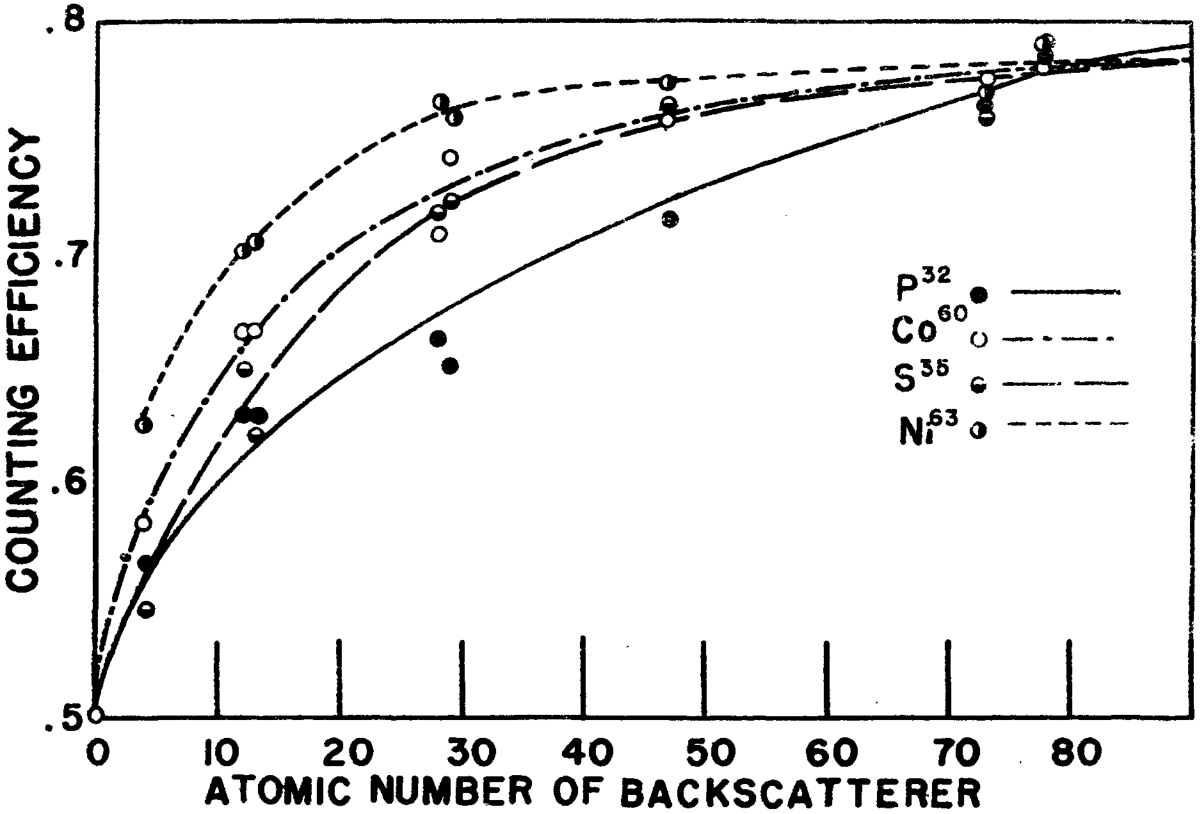

Figure 1 - Backscattering curves for the windowless counter.

Co^{60} and P^{32} was plotted at zero backscatterer. The curves for Ni^{63}, S^{35} and Co^{60} appear to have reached their saturation backscattering value at platinum while the P^{32} curve may still be rising very slowly. Since one-half the absolute disintegration rate was not known for Ni^{63} and S^{35}, their curves were plotted so that the flat portions coincided with that of the Co^{60} curve. Although the shape of the curves is different, the low energy Ni^{63} radiation reaching its maximum value much more rapidly than the higher energy beta-emitters, the saturation backscattering value seems to be independent of the energy of the beta-emitter. Using an end-window Geiger-Mueller tube, L. R. Zumwalt (56) has found that in the beta-energy range 0.3-1.7 Mev, the percentages of backscattering obtained with backings of various atomic number all fell close to the same curve if the counting rates were corrected for absorption in air and in the mica window.

The over-all counting efficiency for the activities on different backscatterers can be read from Figure 1. When samples are mounted on platinum, the counting efficiency seems to be nearly the same for the beta energies investigated. Although a curve for Co^{58m} was not obtained, the values for Ni^{63} and Co^{58m} would be expected to be about the same since most of the betas emitted by the Ni^{63} have energies comparable to the 17 and 24 Kev conversion electrons of Co^{58m}. On the basis of the results shown in Figure I, the backscattering factor was assumed to be the same for the Co^{58m} and Co^{60} samples electroplated on platinum which were compared in the following investigations.

Cobalt-58 and Cobalt-58m

Choice of complex

In order to produce a high specific activity of Co^{58} and Co^{58m} the complex, $K_3[Co(C_2O_4)]\cdot 3H_2O$, was irradiated in the 68 Mev x-ray beam of the synchrotron. This complex was chosen for several reasons. First, it belongs to one of the three main classes of complexes whose optical isomers have been resolved. Therefore, the central cobalt atom would not be expected to undergo exchange. Second, since the cobalt is in the anion,the active atoms, which are ejected from the complex and will probably be present as cobalt(II) ions, can be separated from it by use of a cation exchange resin. This separation method is efficient and rapid, and does not necessitate the addition of inactive cobalt carrier. Third, the preparation of this complex is relatively simple and can be accomplished in a short time.

The rate of formation of Co^{58m} to Co^{58} was determined on the basis of the principle that decay of Co^{58m} to Co^{58} by the emission of conversion electrons would cause dissociation of the complex in which the Co^{58m} was present originally. Therefore, the complex, $[Co(C_2O_4)3]^{\equiv}$, was prepared in solution from the activity separated in the

Szilard-Chalmers process. After a period of time the activity present as cobalt(II) was separated from the complex and the amount of the activities in the complex and in the separated cobalt(II) were determined. From these data it was possible to calculate the relative rates of formation of the two isomers.

The ratio of the rate of formation of Co^{58m} to that of C^{11} was determined by comparison of the absolute disintegration rate of Co^{58m} with that of the C^{11} formed in a portion of the complex during the same irradiation by (γ,n) reactions on the oxalate carbon.

Chemical procedure

Resin Separation. The effectiveness of a cation exchange resin in separating cobalt(II) from the complex anion, $[Co(C_2O_4)3]^{\equiv}$ was determined by performing tracer experiments using Co^{60}. Trace amounts of Co^{60} activity in the form of cobalt(II) were added to solutions containing 0.5 g complex per 20 ml of water. To these, 0.25 g of IRC-50 cation exchange resin in the potassium form were added for each 20 ml of solution. Samples were taken before and after shaking the solution with the resin for varying periods of time. It was found that after 15 minutes only 2-3 per cent more of the activity was removed from the solutions by further treatment with the resin. Therefore, in all of the following separations the resin was shaken with the solutions for only 15 minutes.

The complex solution normally had a pH of about 5.8, but initial pH values of 3.1 up to 5.8 were obtained by the addition of the cobalt tracer in dilute HCl solution. In this range the fractional separation appeared to be independent of the initial pH. In a series of seven experiments, a separation of 96.4 ± 1.7 per cent was obtained when the final pH was between 6.5 and 9.5. At pH values above 9.5, decomposition of the complex was observed and the separation efficiency decreased. The decrease in separation efficiency may be due to the formation of a precipitate of cobalt(III) hydroxide which either carries or exchanges with the active cobalt(II). At final pH values much below 6.5, the capacity of the resin is low due to reversion of the resin to the hydrogen form. The presence of ammonia in the pH range of 6.5-9.0 also reduced the efficiency of the separation.

It was found that quantitative removal of the cobalt(II) activity on the resin could be accomplished in a few minutes by heating the resin with two 10 ml portions of 6 N HCl.

Electrodeposition. All cobalt counting samples were prepared by electroplating the cobalt on platinum discs 2.5 cm in diameter. The deposition was carried out in the apparatus previously described. The completeness of the deposition was tested using Co^{60} as tracer. Using the following procedure it was found that at least 99 per cent of the Co^{60} activity, in solutions having a volume of 5-10 ml and containing 0.5-3.0 mg of cobalt carrier, was removed in 15 minutes with a current of about 1.5 amperes. A solution of $CoCl_2$ from which most of the HCl had been evaporated was taken up in 15 N ammonia and 0.3-0.4 g NH_4Cl and 0.2-0.3 g hydrazine dihydrochloride were added. (The hydrazine dihydrochloride is necessary to prevent formation of cobalt(III). If much cobalt is present it may be necessary to add more hydrazine dihydrochloride.) It was sometimes necessary to add ammonia during the electrolysis so that a strong odor of ammonia could always be detected above the solution.

In the first experiments a rotating platinum anode was used. However, in blank runs an increase in sample weight of about 0.1 mg was noted. Brophy (60) has reported similar high results using platinum anodes and attributed the weight increase to deposition on the cathode of platinum which had been dissolved from the anode, presumably by chlorine evolved during the electrolysis. Our results seem to verify this since when graphite anodes were used no increase in weight was observed in the blank runs. In the following depositions spectrographically pure graphite rods 3/16 inch in diameter were used as rotating anodes. Blanks were again run and no increase in weight was observed. A cobalt(II) carrier solution was prepared by dissolving 0.8071 g of $CoCl_2 \cdot 6H_2O$ in 200 ml of water. If the composition of the salt corresponded to the above formula, the solution should have contained 1 mg/ml of cobalt(II). Using aliquots of this solution, a series of cobalt samples was electroplated, washed with acetone, dried and weighed. The cobalt was dissolved from the platinum discs and the weight determined colorimetrically by the nitroso-R-salt method using the Klett-Summerson photoelectric colorimeter (61). The results obtained by the colorimetric method and by weighing the cobalt samples are compared in Table 7.

Using the colorimetric method the cobalt(II) chloride carrier solution was found to contain 0.95 mg/ml rather than 1.00 mg/ml. One reason for the low results obtained colorimetrically may be that some cobalt was not recovered in the process of dissolving it from the platinum discs. Also, these samples had to be diluted from 50 to 1000 times since the nitroso-R-salt method is used in the region of 5 μg/ml.

<u>Preparation of complex from active cobalt.</u> To determine the relative rate of formation of Co^{58m} to that of Co^{58}, it was necessary to prepare $[Co(C_2O_4)_3]^{\equiv}$ from the active

Table 7. Amount of Cobalt in Electrodeposition Samples

$CoCl_2$ carrier (ml)	Weight (mg)	Error* (%)	Weight# (mg)	Error* (%)	Error** (%)
0.1	0.11	+10.0	0.09	-10.0	-5.3
0.5	0.51	+ 2.0	0.45	-10.0	-5.3
1.0	1.06	+ 6.0	0.95	- 5.0	
2.0	2.05	+ 2.5	1.89	- 5.5	-0.5
4.0	4.05	+ 1.3	3.78	- 5.5	-0.5

* Error if 1.00 ml of cobalt carrier solution equal 1.00 mg.

\# Weight determined by nitroso-R-salt method.

** Error if 1.00 ml of cobalt carrier solution equals 0.95 mg.

cobalt obtained in the Szilard-Chalmers process. Since 1-3 per cent of the complex was found to decompose during irradiation, one could estimate the amount of cobalt to be converted to the complex. The preparation was carried out by addition of a slight excess of all reagents to insure as complete conversion as possible. Instead of precipitating the crystals of the complex it was allowed to remain in solution. A resin separation was then performed to remove any cobalt not converted to the complex.

Co^{60} in trace amounts as cobalt(II) was added to a solution of the complex prepared in this way. A resin separation was performed to determine if the presence of the excess $[C_2O_4]^=$ remaining in the solution after synthesis of the complex would decrease the separation efficiency. The average efficiency for five such separations was 97.5 ± 0.6, about the same as that found previously. After the separation the pH of the solution was adjusted to 4.5 with a small amount of HCl and stored in the dark at room temperature. About 19-20 hours later more Co^{60} was added and another resin separation was performed. A separation of 97 per cent was obtained which is nearly the same as in previous experiments.

Exchange studies. In order to be certain that no exchange between cobalt(II) ion and cobalt in the complex anion occurred during this period of storage in the dark, Co^{60} as cobalt(II) was added to a solution of the complex. The pH was adjusted to 3.5-4.5. After standing in the dark for 19 hours a resin separation was performed. It was found that 98 per cent of the activity was separated from the solution. Apparently then, no exchange occurs at this pH. However, care was taken to keep the solutions acid as decomposition of the complex may occur on long standing at pH values above 6. Experiments similar to the one just described were conducted by allowing the complex to stand at pH values of 6 and 7 and separations of only 82 per cent and 81 per cent respectively were obtained.

Experimental procedure

Relative yield and half-life determinations. For comparison of the Co^{58m} ~~and~~ and C^{11} yields, 1-1.5 g samples of $K_3[Co(C_2O_4)_3]\cdot 3H_2O$ crystals were irradiated for one hour at the maximum energy of the Iowa State College synchrotron. For counting C^{11}, a sample was prepared by spreading a weighed amount of the $K_3[Co(C_2O_4)_3]\cdot 3H_2O$ crystals evenly over a 2.5 cm diameter circle of scotch tape mounted on cardboard. The sample was then covered with scotch tape and the decay followed with an end-window Geiger-Mueller counter for nine to ten half-lives of the C^{11}. The remainder of the complex was dissolved in water and the activity separated as cobalt(II) on IRC-50 cation exchange resin. The activity was eluted from the resin with 6 N HCl and the cobalt electroplated for counting in the gas flow counter. The decay of Co^{58m} was carefully followed to determine its half-life. Very little 72d Co^{58} activity was present in the samples from these short irradiations so a 5 g sample of complex was irradiated for 30.1 hours to obtain enough for a measurement of its half-life.

Co^{60} Standards. The C^{11} counting rate was compared to the counting rate of a Co^{60} primary standard prepared by electroplating Co^{60} with 0.5 mg cobalt carrier on platinum. Its absolute disintegration rate was determined by F. J. Hughes from coincidence measurements. The counting rate of the standard had to be multiplied by the factor, f_W, defined by equation (2), p. 30 to give the beta counting rate corrected for 1.9 mg/cm^2 absorption in air and 2.3 mg/cm^2 in the mica window. This factor was found to be 1.39 by extrapolation of an aluminum absorption curve from which the gamma-ray component had been subtracted. It was also necessary to multiply the beta counting rate of the primary standard by the factor, B, to correct for the backscattering due to its platinum backing. B was determined experimentally to be 0.64 by comparing the counting rates of a nearly weightless

Co^{60} source evaporated on a zapon film with, and without, infinite platinum backscatterer.

The cobalt samples were compared with a secondary Co^{60} standard prepared in a similar manner. Its absolute disintegration rate was determined by comparison with the primary Co^{60} standard. No backscattering corrections were necessary in the flow counter as all the samples were electroplated on platinum (p. 39).

Self-absorption in Co^{58m} samples. In order to calculate the absolute disintegration rate of the Co^{58m} samples, it was necessary to determine the self-absorption corrections for different sample thicknesses. A 4.015 g sample of $K_3[Co(C_2O_4)_3].3H_2O$ was irradiated for one hour in the synchrotron x-ray beam. The cobalt activity separated from the complex was diluted to exactly 200 ml. Samples of 1, 2, 5, 10, 15, 20 and 25 ml were electroplated on 2.5 cm diameter platinum discs for counting. The samples were 2 cm in diameter and had an area of 3.14 cm^2. Samples of 15 ml with 0.6, 1, 1.5, 2.0, 2.7 and 3.5 ml of a carrier solution containing 1 mg/ml of cobalt(II) were also prepared. The results are shown in Table 8a. From the total weight of cobalt in these samples, the concentration of the active solution was calculated to be 0.027 mg/ml. Therefore, the total amount of cobalt resulting from decomposition of the

Table 8a. Self-absorption Data for Co^{58m} Samples

Sample (ml)	Added carrier (mg)	Observed thickness (mg/cm^2)	#Thickness on basis conc. of solution (mg/cm^2)	Activity per ml (cts/min)	Transmission (%)
1.0		0.010	0.009	860	73.0
2.0		0.032	0.017	1245	106.0
2.0		0.029	0.017	1335	113.6
5.0		0.051	0.043	1320	112.3
10.0		0.067	0.086	1217	103.6
15.0		0.130	0.129	1074	91.4
15.0		0.124	0.129	1136	96.6
15.0	0.6	0.318	0.320	835	72.8
15.0	1.0	0.449	0.447	690	58.7
15.0	1.5	0.618	0.606	550	46.8
15.0	2.0	0.786	0.766	479	40.8
15.0	2.7	0.981	0.991	372	31.6
15.0*	3.5	1.190	1.243	290**	24.7
20.0		0.156	0.172	974	82.9
25.0		0.213	0.215	904	76.9

Solution concentration was computed from the total of the observed weights of the samples and the total volume of aliquots (column 1) used in the samples.

* Omitted in calculation of solution concentration

** Corrected for chemical yield

complex during the irradiation was 5.4 mg which corresponds to decomposition of 1.1 per cent of the complex.

A self-absorption curve has been plotted from these results. The counting rate per unit volume was plotted against the thickness of the sample as determined from its actual weight. For one case in which it appeared that the electrolysis was not complete, the counting rate was corrected for chemical yield. From this curve, using 1175 as the counting rate at zero thickness, the counting rates were converted to fractional transmission so that the self-absorption correction could be quickly read for any sample thickness (Figure 2). The dashed line extrapolation to zero and the remainder of the curve show a nearly linear self-absorption of the 17 and 24 Kev conversion electrons, which have ranges of 0.6 and 1.1 mg/cm^2, respectively. When the range of the conversion electrons has been reached the counting rate might be expected to decrease as the reciprocal of the thickness. Such a trend is indicated in Figure 2. The first very steep portion of the curve may be due to absorption of the cobalt Auger electrons emitted following the internal conversion process. These electrons have an energy of approximately 6 Kev. By extrapolation of range-energy curves for beta-particles their range can be estimated to be 0.08 mg/cm^2.

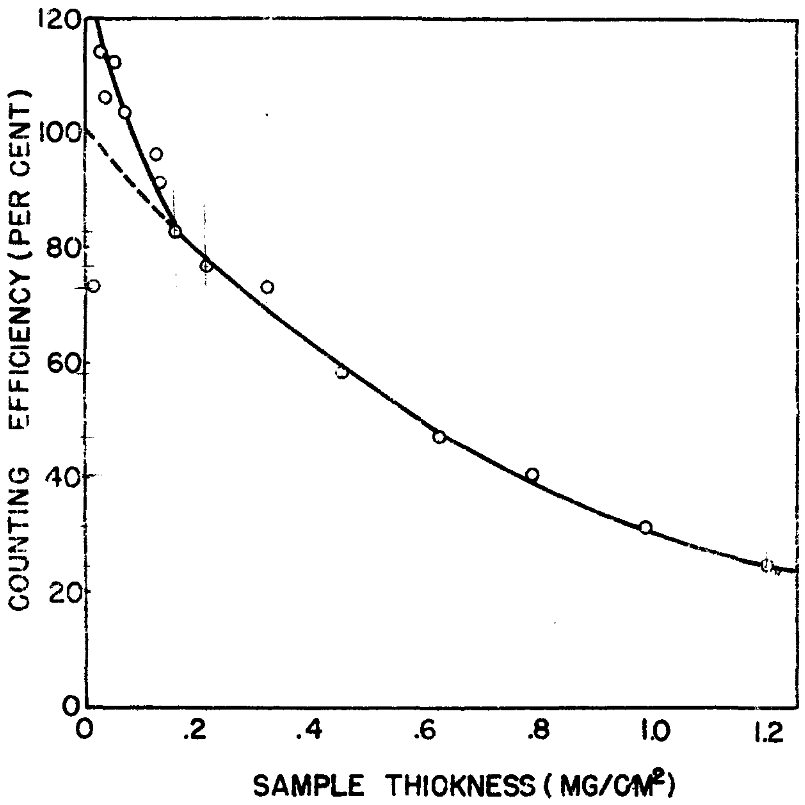

Figure 2. Self-Absorption Curve for Co^{58m}

Relative rate of formation of Co^{58} to Co^{58m}. To determine the relative yields of Co^{58} and Co^{58m} it was necessary to irradiate 4-5 g samples of the complex. Using the cobalt activity separated from the complex, a solution of $[Co(C_2O_4)_3]^{\equiv}$ was prepared. A resin separation removed any cobalt not converted to the complex. The pH was then adjusted to 3.5-4.5 and the complex was stored in the dark for 19-22 hours. At the end of this time another resin separation was performed. Counting samples were prepared from the complex solution and from the cobalt activity eluted from the resin. From the ratio of the counting rates of these samples the rate of formation of Co^{58} to Co^{58m} was calculated.

Results

Activities produced. In the cobalt yield samples a half-life of 9.2 ± 0.2h (Figure 3) was found together with a very low intensity of a longer half-life. By following the long activity produced in a 30.1 hour irradiation, this half-life was found to be 72.0 ± 2.0 days (Figure 4). From magnetic deflection experiments it was found to emit positrons. These two periods were attributed to Co^{58m} and Co^{58}, respectively. No evidence of the formation of the 270d Co^{57} by a $(\gamma,2n)$ reaction was found. A half-life of 20.5m, which is in agreement with previously reported values (24), was found for the C^{11} counted as a yield standard.

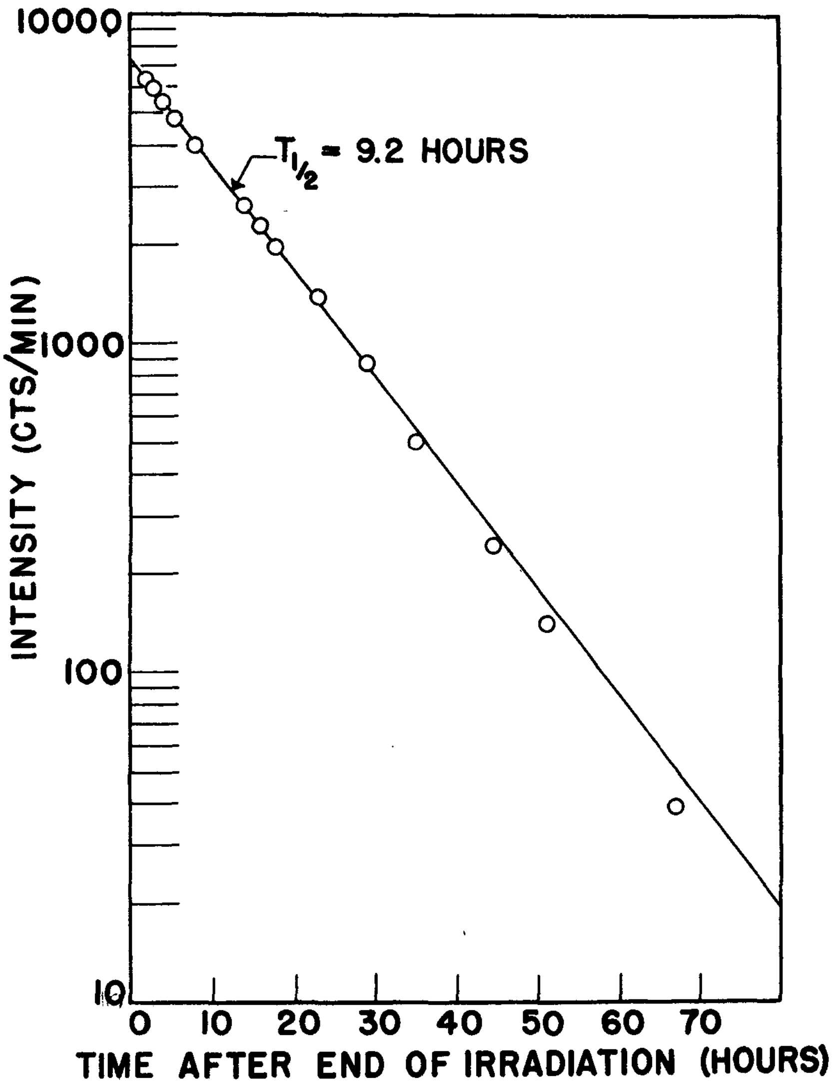

Figure 3. Short Component from 1.0 Hour Irradiation of Cobalt

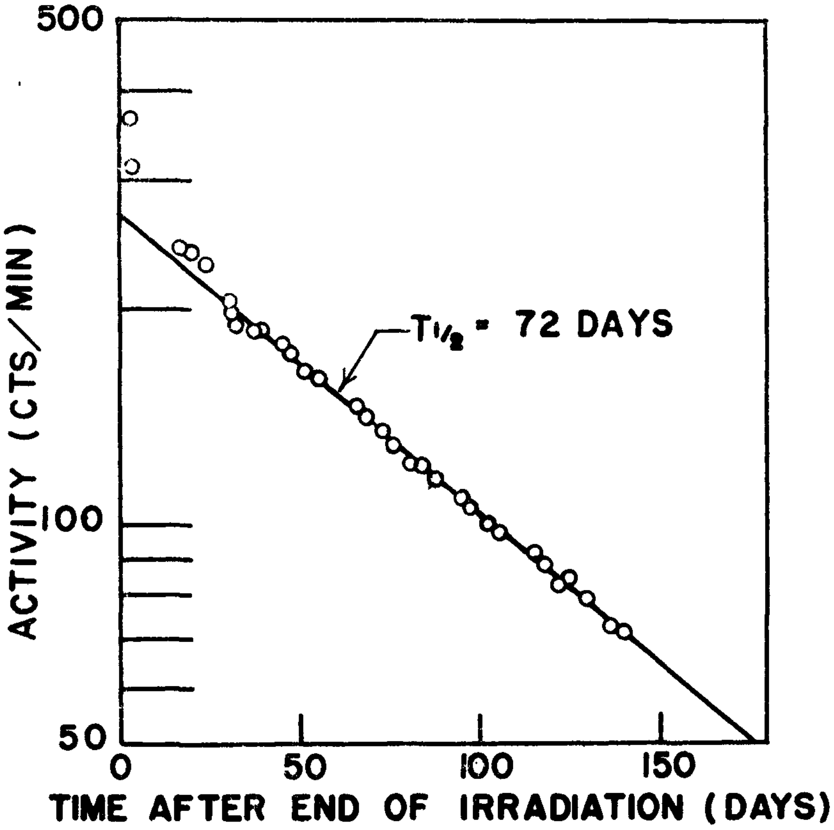

Figure 4. Long Component from 30.1 Hour Irradiation of Cobalt

Calculation of relative rates of formation of Co^{58} isomers. A solution of $[Co(C_2O_4)_3]^{\equiv}$ was prepared from active cobalt as previously described. From the ratio of 72d Co^{58} activity found in the complex to that ejected from the complex by decay of Co^{58m} to Co^{58} in a certain period of time, the ratio of the rate of formation of Co^{58} to that of Co^{58m} has been calculated. Using the standard expressions for radioactive growth and decay the calculation is as follows.

R_1 equals rate of formation of Co^{58m}.

R_2 equals rate of formation of Co^{58}.

N_1 equals number of Co^{58m} atoms.

N_2 equals number of Co^{58} atoms.

N_1^o equals number of Co^{58m} atoms at end of irradiation.

N_2^o equals number of Co^{58} atoms at end of irradiation.

λ_1 equals 0.693/9.2h, disintegration constant for Co^{58m}.

λ_2 equals 0.693/72d, disintegration constant for Co^{58}.

τ equals period of irradiation.

t' equals period from end of irradiation to end of first separation.

t" equals period complex was allowed to stand, the time elapsing between first and second resin separations.

The growth of Co^{58m} atoms during irradiation is given by:

$$\frac{dN_1}{dt} = R_1 - \lambda_1 N_1 \tag{3}$$

Integrating for the period $0 < t < \tau$ for constant beam intensity gives:

$$N_1^{\,o} = \frac{R_1}{\lambda_1}\left(1 - e^{-\lambda_1 \tau}\right) \tag{4}$$

At the time t' after irradiation:

$$\begin{aligned} N_1 &= N_1(t') = N_1^{\,o} e^{-\lambda_1 t'} \\ &= \frac{R_1}{\lambda_1}\left(1 - e^{-\lambda_1 \tau}\right) e^{-\lambda_1 t'} \end{aligned} \tag{5}$$

The growth of Co^{58} atoms during irradiation is given by:

$$\frac{dN_2}{dt} = R_2 + \lambda_1 N_1 - \lambda_2 N_2 \tag{6}$$

Integrating for the period $0 < t < \tau$ gives:

$$N_2^{\,o} = \frac{R_1 + R_2}{\lambda_2}\left(1 - e^{-\lambda_2 \tau}\right) + \frac{R_1}{\lambda_1 - \lambda_2}\left(e^{-\lambda_1 \tau} - e^{-\lambda_2 \tau}\right) \tag{7}$$

At any time t after irradiation:

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2 \tag{8}$$

At the time t' after irradiation:

$$\begin{aligned} N_2 &= N_2(t') = N_2^{\,o} e^{-\lambda_2 t'} + \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^{\,o}\left(e^{-\lambda_1 t'} - e^{-\lambda_2 t'}\right) \\ &= \frac{R_1 + R_2}{\lambda_1}\left(1 - e^{-\lambda_2 \tau}\right) e^{-\lambda_2 t'} + \frac{R_1}{\lambda_1 - \lambda_2}\left(e^{-\lambda_1 \tau} - e^{-\lambda_2 \tau}\right) e^{-\lambda_2 t'} \\ &\quad + \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^{\,o}\left(e^{-\lambda_1 t'} - e^{-\lambda_2 t'}\right) \end{aligned} \tag{9}$$

After the second separation, the N_2 separated from the complex will be only the amount which has formed from decay of the 9.2h Co^{58m} between the first and second separations. Therefore, the number of Co^{58} atoms on the resin, $N_2(r)$, is:

$$N_2(r) = N_1(t')\frac{\lambda_1}{\lambda_1-\lambda_2}e^{-\lambda_2 t''}\left(1-e^{(\lambda_2-\lambda_1)t''}\right) \qquad (10)$$

Or, if $\lambda_2 t''$ is small:

$$N_2(r) \approx N_1(t')(1-e^{-\lambda_1 t''}) \approx N_1^o e^{-\lambda_1 t'}(1-e^{-\lambda_1 t''}) \qquad (11)$$

The number of Co^{58} atoms left in the complex after the second separation, $N_2(c)$, will be equal to the 72d activity present at the end of the first separation times the decay factor plus the 9.2h activity remaining in the complex which will decay to the 72d activity.

$$N_2(c) = N_2(t')(e^{-\lambda_2 t''}) + N_1(t')e^{-\lambda_1 t''} \qquad (12)$$

From the ratio, $N_2(c)/N_2(r)$, and the amount of 72d activity found experimentally in the complex and the resin, R_2/R_1 can be calculated. An example of this calculation for a typical experiment is presented.

$\tau = 1.0$h $\lambda_1\tau = 0.0753$ $\lambda_2\tau = 0.000401$

$t' = 2.1$h $\lambda_1 t' = 0.1581$ $\lambda_2 t' = 0.000842$

$t'' = 21.2$h $\lambda_1 t'' = 1.5964$ $\lambda_2 t'' = 0.00850$

$N_1^o = 0.097R_1$

$N_2^o = 0.033R_1 + R_2$

$N_1(t') = 0.828R_1$

$N_2(t') = 0.1747R_1 + 0.9992R_2$

$N_2(c) = 0.341R_1 \pm 0.991R_2$

$N_2(r) = 0.660R_1$

$N_2(c)/N_2(r) = 0.341R_1 + 0.991R_2/0.660R_1 = 0.517 + 1.502R_2/R_1$

$R_2/R_1 = [N_2(c)/N_2(r) - 0.517]/1.502$

In this experiment the 72d activity separated on the resin, A_r, was 43.9 ± 2.1 cts/min and the 72d activity remaining in the complex, A_c, was 58.8 ± 2.3. (The uncertainities in these measurements are based on the standard deviation due to the statistical fluctation in the counting rates.) The ratio of the 72d activity in the complex to that on the resin is equal to the ratio of the number of atoms of Co^{58} in the complex to the number on the resin, $N_2(c)/N_2(r)$. By counting the samples immediately any 9.2h activity present in them could be detected. In the resin sample 3.8 per cent of the total 9.2h activity was found indicating 3.8 per cent decomposition of the complex either while standing or during the first or second resin separations. A correction was made for this decomposition. The correction proved to be independent of the time at which the decomposition occurred. No self-absorption corrections were necessary as the weights of the complex and resin samples were nearly the same, 0.52 and 0.49 mg/cm^2, respectively. Since resin separations have been found to be 97.5 ± 0.6 per cent efficient a correction was made for the efficiency of the second resin separation. A correction for the efficiency of the first separation in removing any cobalt(II) not converted to complex was not necessary in this experiment as two consecutive resin separations were performed before the standing period. The correction would be $(0.025)^2$ times any unconverted activity and would be negligible. The calculation of $N_2(c)/N_2(r)$ and R_2/R_1 is illustrated below. The results from three determinations of R_2/R_1 are summarized in Table 8b.

$$A_c = 58.8 \pm 2.3 - \frac{2.5 \pm 0.6}{97.5 \pm 0.6}(43.9 \pm 2.1)$$

$$= 57.7 \pm 2.3$$

$$A_r = 43.9 \pm 2.1 + \frac{2.5 \pm 0.6}{97.5 \pm 0.6}(43.9 \pm 2.1)$$

$$= 45.0 \pm 2.1$$

$$A_c/A_r = \frac{57.7 \pm 2.3 + (3.8/96.2)(57.7 \pm 2.3)}{45.0 \pm 2.1 - (3.8/96.2)(57.7 \pm 2.3)}$$

$$= \frac{60.0 \pm 2.3}{42.7 \pm 2.1} = 1.405 \pm 0.069$$

$$R_2/R_1 = \frac{1.405 - 0.517}{1.502} = 0.592 \pm 0.046$$

Table 8b. Determinations of R_2/R_1

τ (hours)	t' (hours)	t'' (hours)	corrected A_c/A_r	R_2/R_1	Sample thickness (mg/cm^2) A_c	A_r	Decomp. (%)
1.0	5.65	19.03	2.46	.72 ±.19	.17	.34	7.3
τ_1=0.65 off 0.13 τ_2=0.27	1.93	21.47	1.35	.69 ±.11	.13	.09	12.4
1.0	2.10	21.20	1.405	.59 ±.05	.52	.49	3.8

In experiments one and two only one separation was performed to remove the unconverted cobalt activity so a correction was made on the basis of 40 ± 5 per cent conversion of cobalt(II) activity to complex. This value was obtained by counting the activity eluted from the resin used in the separations. Self-absorption corrections were also appreciable in experiments one and two. W. L. Graf, C. L. Comar and I. B. Whitney (50) have determined the self-absorption curve for the 0.26 Mev beta of Ca^{45} in a windowless counter. For sample thicknesses under 2 mg/cm^2, the correction may be nearly independent of energy since the radiation being absorbed is probably very soft radiation due to backscattering. As shown in the section on backscattering, the backscattering of nearly weightless beta sources on platinum appears to be independent of the energy of the beta-emitters. The self-absorption corrections applied in experiments one and two were interpolated from the curve for Ca^{45}. They are therefore necessarily quite approximate and may account for some of the variation in the calculated R_2/R_1 values. By weighting the values as $1/\sigma^2$, an average value of 0.61 ± 0.04 was obtained for the ratio of the rate of formation of Co^{58} to that of Co^{58m} for a (γ,n) reaction.

Cameron and Katz (62) have reported measurements of the yields of the isomeric pairs from (γ,n) reactions in

Br^{81}, Zr^{90} and Mo^{92}. In each case the yield of the isomer formed with the smaller spin change in the reaction was favored by a factor of 3:1 to 5:1 which they propose is a fairly general result. In the case of the (γ,n) reaction on Co^{59} the spin change is the same for the formation of either isomer. (K. Strauch (19) believes the spin of Co^{58} to be 5 and that of Co^{58m} to be 2. The ground state of Co^{59} (24, p.54) has a spin of 7/2.) If the relative rate of formation of isomers depends primarily upon the spin change, equal yields would be expected for such a case. The value of 0.61 obtained in these experiments is not incompatible with this hypothesis. However, it also agrees, within experimental error, with the value of 0.59 reported by Strauch for the formation of the isomers by alpha-particle bombardment of manganese. Such agreement would be predicted by the compound nucleus mechanism of photonuclear transformations.

Calculation of the yield of Co^{58m} relative to C^{11}. The yield of Co^{58m} relative to the yield of C^{11} was determined by comparing the absolute disintegration rates of the electroplated Co^{58m} samples with those of the C^{11} samples prepared as previously described. Such a comparison would give the correct value for the yield of Co^{58m} only if nearly all of the radioactive cobalt atoms are ejected from the complex during irradiation. To check the efficiency of the Szilard-Chalmers process in $K_3[Co(C_2O_4)_3]\cdot 3H_2O$, the bulk of the complex was decomposed after the resin separation which removed the activity used in the preparation of the cobalt yield samples. All of the cobalt from the complex was then electroplated on platinum and counted. In several experiments only 2-4 cts/min of 72d activity were found in this sample which usually had a thickness of about 25 mg/cm^2. A counting efficiency of 20 per cent was assumed for a sample of this thickness and on the basis of the total 72d activity separated from the complex and that found in the cobalt from the decomposed complex, it was calculated that only 2-3 per cent of the active atoms remained in the complex. Since the resin separation has been found to be only 96.4 ± 1.7 per cent efficient the Szilard-Chalmers process in synchrotron irradiations of $K_3[Co(C_2O_4)_3]\cdot 3H_2O$ appears to be 100 per cent efficient.

The absolute disintegration rates of Co^{58m} and C^{11} were determined in the following manner. The decay of the samples was followed for seven to eight half-lives and the intensity of each activity at the end of the irradiation was determined by extrapolation of the decay curves. Counting rates were converted to disintegration rates by comparison with the Co^{60} standards counted with exactly the same

Table 9

Co^{58m} Yield Determinations

Irradiation time (hours)	Activity Measured	I_0 (cts/min)	Co^{60} Standard (cts/min)	Co^{60} Standard (dis/min)	Sample Thickness (mg/cm^2)	Wt. Complex Fraction (g)	R (dis/min g complex)	$R_{Co^{58m}}/R_{C^{11}}$ **	Average
1.00	C^{11}	3100	6440	6.793×10^4	15.7	0.0830	5.06×10^5	5.56	5.56
	Co^{58m}	3860	2145	2.90×10^4	0.347	0.2300	4.78×10^5		
1.03	C^{11}	3560	6313	6.815×10^4	15.2	0.0806	6.07×10^5		4.42
	Co^{58m}	6100	2180	2.91×10^3	0.382*	0.3945	4.26×10^5	4.16	
	Co^{58m}	7500	2180	2.91×10^3	0.319	0.3945	4.77×10^5	4.68	
1.00	C^{11}	6110	6330	6.720×10^4	15.0	0.0794	1.05×10^6	6.08	6.08
	Co^{58m}	30400	2180	2.87×10^3	0.442	0.8475	1.13×10^6		
1.00	C^{11}	9000	6414	6.689×10^4	15.4	0.0814	1.47×10^6		4.51
	Co^{58m}	15800	2162	2.86×10^3	0.268	0.3460	1.05×10^4	4.58	
	Co^{58m}	23100	2162	2.86×10^3	0.500	0.8060	1.01×10^4	4.44	
1.00	C^{11}	12500	6696	6.663×10^4	14.8	0.0785	1.96×10^6		5.45
	Co^{58m}	40000	2162	2.85×10^3	0.308	0.5048	1.78×10^6	5.40	
	Co^{58m}	47500	2162	2.85×10^3	0.261	0.5552	1.80×10^6	5.50	
1.00	C^{11}	9200	6113	6.426×10^4	16.3	0.0833	1.49×10^6		5.04
	Co^{58m}	17940	2120	2.74×10^3	0.131	0.2940	1.24×10^6	5.00	
	Co^{58m}	18940	2120	2.74×10^3	0.124	0.2940	1.31×10^6	5.26	
	Co^{58m}	9300	2120	2.74×10^3	0.618*	0.2940	1.21×10^6	4.86	

* Cobalt carrier added.

**Yields in these ratios are based on a target element of one gram-atom of naturally occurring isotopes.

geometry. The counting rate of the Co^{60} primary standard, which was counted with the C^{11} sample, was corrected for absorption and backscattering as described on p. 48. Corrections for backscattering, self-absorption, absorption in air and counter window were applied to the C^{11} and Co^{58m} samples. The combined factor $(f_S)(B)$, defined by equation (2), p. 30, for a C^{11} sample of 0-20 mg/cm^2 covered with 3.5 mg/cm^2 cellophane and counted on the second shelf 16 mm from a regular end-window Geiger-Mueller tube is 0.85 (49, p. 61). f_W for 9.7 mg/cm^2 absorption by the mica counter window, air and the scotch tape covering, which is 5.5 mg/cm^2 thicker than cellophane, was determined to be 1.16 from an aluminum absorption curve of a similar weight C^{11} sample counted with the same geometry. The saturation disintegration rate, which is equal to the rate of formation R, can be found by dividing the disintegration rate at the end of irradiation by $(1-e^{-\lambda\tau})$. This calculation will be valid only if the intensity of the synchrotron beam was constant during the irradiation. In all of the yield determinations this was shown to be the case by a tape recording of current from the ionization chamber used to monitor the beam intensity.

The Co^{58m} samples were corrected for self-absorption using the experimentally determined curve shown in

Figure 2, p. 52. The absolute disintegration rates were determined by comparison with the secondary Co^{60} standard. The Co^{58m} rates of formation were multiplied by six before comparison with those of C^{11} since there were six carbon atoms for every cobalt atom in the complex. The yield ratios were, therefore, calculated on the basis of the naturally occurring isotopic mixture. The results for the yield determinations are given in Table 9. An average value of 5.2 ± 0.7 was obtained for the rate of formation of Co^{58m} to that of C^{11}. If a correction is made for the 96 per cent efficiency of the resin separation this value becomes 5.4. The total saturation yield for Co^{58} and Co^{58m} will be 1.60(5.4) or 8.6 relative to C^{11}. For the reactions Ni^{58} (γ,n) Ni^{57} and Cu^{63} (γ,n) Cu^{62} relative to the reaction C^{12} (γ,n) C^{11}, Perlman and Friedlander (44, 45) have reported values of 2.7 and 14.3 respectively. The value observed for Co^{58} and Co^{58m} seems, therefore, to be in line with their values.

X-Ray Irradiation of Platinum

Objectives

Irradiations of platinum in the x-ray beam of the synchrotron were carried out with three main objectives in mind: (1) the identification and characterization of the osmium, iridium and platinum activities produced by irradiation of $PtCl_4 \cdot xH_2O$, (2) the determination of the yields of all the activities formed relative to that of the Cl^{34} formed by a (γ,n) reaction in Cl^{35} and (3) the attainment of high specific activities of platinum by the Szilard-Chalmers process in some complex compounds of platinum.

Grinberg and Filinov (63) have reported that there is no exchange of the central atom in platinum coordination complexes. Energy considerations have shown that all of the active atoms should be ejected from the platinum complexes. Therefore, if the complex does not decompose upon irradiation and the active atoms do not reform the original complex, high specific activities should be attainable if a suitable separation procedure can be found. Before effective separation procedures could be devised some knowledge about the oxidation state and chemical form of the ejected activity had to be obtained.

Procedures

Separation of osmium, iridium and chlorine from platinum. Standard procedures (64, 65) were used for the separation of osmium and iridium from platinum. Osmium was separated by distillation from concentrated HNO_3 as OsO_4 (64, p. 143). The OsO_4 was collected in 6 N NaOH and OsS_4 was precipitated for counting by passing H_2S into the warm solution. The HNO_3 was removed from the original solution by several evaporations with HCl. Iridium was then precipitated as the hydrated oxide according to the procedure given by Treadwell and Hall (64, p. 145). It was found that in the separation of 5-10 mg of inactive iridium carrier from 4-6 g of active $PtCl_4 \cdot xH_2O$ from which the iridium activity had been removed by several precipitations of IrO_2, platinum activity was carried with the IrO_2 precipitate. If the IrO_2 was dissolved and reprecipitated after the addition of 20-30 mg of platinum carrier, the IrO_2 was obtained free of activity. However, in most of the irradiations, the IrO_2 sample was desired for counting as soon as possible after the end of the irradiation so only one precipitation was performed. After precipitation of IrO_2 the platinum was precipitated as the metal from dilute HCl solution by the addition of powdered magnesium.

The sample of chlorine activity used as a yield standard was prepared immediately from 100-150 mg of the irradiated $PtCl_4 \cdot xH_2O$. The salt was evaporated with a slight excess of Na_2CO_3 and heated until it just fused. The melt was extracted with water, acidified with HNO_3 and AgCl was precipitated with $AgNO_3$.

All of the osmium, iridium, chlorine and platinum samples were filtered using the apparatus described on p. 26. The Whatman no. 50 filter papers used in filtering had been treated with the wash solution to be used, washed with alcohol and ether, dried in the oven at 90° C. and weighed. The samples of activity were similarly washed, dried and weighed to determine the weight of each precipitate. All counting samples were then mounted on cardboard and covered with cellophane or scotch tape.

<u>Preparation of yield and half-life samples.</u> The irradiation of platinum metal was inconvenient since dissolving it in aqua regia was time consuming and the HNO_3 had to be destroyed before the IrO_2 could be precipitated. Therefore, in the yield and half-life studies 4-6 g samples of $PtCl_4 \cdot xH_2O$ were irradiated for about 1.5 hours in order to obtain enough iridium activity for counting. In the investigation of the very short iridium activity, a 1 g sample was irradiated for 15 minutes. If only platinum and chlorine samples were desired, 1 or 2 g samples were irradiated.

If osmium and iridium samples were to be prepared 10 mg of osmium and 5-10 mg of iridium carrier were immediately added to the solution of the dissolved target salt so as to insure exchange between carrier and active atoms. In some of the experiments, 5 mg of phosphorus carrier were added to prevent carrying of any phosphorus activities formed by photonuclear reactions on chlorine (66). All samples were weighed to determine the chemical yield and were mounted for counting as described in the preceding section.

Methods for separation of radioactive platinum from irradiated platinum complexes. There are many chloro- and chloroammine- complex compounds of platinum which may be easily prepared. Among these are the compounds K_2PtCl_4, K_2PtCl_6, $[Pt(NH_3)_2Cl_4]$, $[Pt(NH_3)_4]Cl_2$ which were chosen for study. $[Pt(NH_3)_4]C_2O_4$ which can be readily prepared from $[Pt(NH_3)_4]Cl_2$ was also studied. Methods of separation of these platinum complexes from complexes in which the platinum activity might be present after irradiation were investigated.

The radioactive platinum atoms formed when either solid K_2PtCl_4 or K_2PtCl_6 are irradiated may be present in a different oxidation state than the platinum atoms in the target compound. By addition of platinum(IV) carrier to a solution of the K_2PtCl_4 and precipitation of $(NH_4)_2PtCl_6$ by the addition of NH_4Cl, active atoms present as $PtCl_6^=$ should be removed. There is also the possibility of carrying other complexes present in micro amounts and even some of the dissolved target compound with the precipitate. After addition of $PtCl_4^=$ holdback carrier to a solution of irradiated K_2PtCl_6, precipitation of $(NH_4)_2PtCl_6$ should remove $PtCl_6^=$ and leave activity present as $PtCl_4^=$ in the solution. Again, micro amounts of other complexes and some $PtCl_4^=$ might carry with the precipitate. If the precipitation were incomplete some $PtCl_6^=$ might remain with the $PtCl_4^=$, but this could be determined from the weights of the samples and their specific activities.

Separation of activity present as chloroammine-, chloro- or other complex anions after irradiation of solid $[Pt(NH_3)_2Cl_4]$ was attempted by adsorption on anion exchange resin. Duolite A-2 and IR-4B resins in either the oxalate or acetate forms were found to remove $PtCl_6^=$ from solution. The platinum could be recovered from the resins by treatment with 6 N HCl. Preliminary experiments showed that shaking the yellow-orange solution of $[Pt(NH_3)_2Cl_4]$ with Duolite A-2 resin in the acetate form resulted in some decolorization of the solution. Slow ionization of the complex followed by adsorption on the resin probably occurred. It was expected that any platinum activity present in the form of an anion together with some platinum from the complex might be separated from the bulk of the complex in this manner.

Similar resin separations were performed on solutions of irradiated $[Pt(NH_3)_4]Cl_2$ and $[Pt(NH_3)_4]C_2O_4$. A large excess of resin over the amount necessary to adsorb the total milliequivalents of chloride or oxalate ion present was added so the resin might be expected to adsorb other anions from the solution even though chloride ion might be preferentially adsorbed. $[Pt(NH_3)_4]C_2O_4$ was prepared by shaking solutions of $[Pt(NH_3)_4]Cl_2$ with IR-4B resin in the oxalate form. $[Pt(NH_3)_4]C_2O_4$ is less soluble than $[Pt(NH_3)_4]Cl_2$ and could easily be crystallized when acetone was added to the solutions which had been shaken with the resin.

Extraction experiments showed that $Pt(NH_3)_4^{++}$ does not extract into butyl acetate from a 6 N HCl solution. Since H_2PtCl_6 cannot be extracted into butyl acetate while H_2PtCl_4 can (65), activity present as $PtCl_4^{=}$ or possibly other platinum(II)chloro- or chloroammine- complexes could be separated by butyl acetate extractions. Interference from iridium activities would be eliminated since iridium does not extract into butyl acetate.

Precipitation methods were also used to try to separate activity from the complexes. Addition of $PtCl_4^=$ to a solution containing $Pt(NH_3)_4^{++}$ immediately precipitates Magnus' green salt, $[Pt(NH_3)_4]PtCl_4$ (55). Addition of $PtCl_6^=$ results in the formation of $[Pt(NH_3)_4]PtCl_6$ which decomposes slowly at room temperature and rapidly on boiling to Magnus' green salt. The first method of precipitation might carry activity present as $PtCl_4^=$ if exchange between the $PtCl_4^=$ in the solution and in the precipitate occurs rapidly. The second method would be expected to be more effective in removing activity present as $PtCl_6^=$ or $PtCl_4^=$ since the precipitation is slow and conditions would be more favorable for exchange between the active and carrier platinum atoms. Either precipitation method might carry fractional amounts of activity present in the form of other complexes.

If the platinum activity is present in micro quantities as a chloroammine complex only slightly different from the irradiated complex, such as $[Pt(NH_3)_2Cl_2]$ which forms when $[Pt(NH_3)_4]Cl_2$ is heated with HCl (55), complete separation of the activity from the complex by any of the methods just described may be impossible. In this event some gelatinous precipitate such as $Fe(OH)_3$ might be effective in scavenging the activity.

Calculations and results

18h platinum activity. In the calculation of the yield of the 18h Pt^{197} (Figure 5) formed in the irradiations of $PtCl_4 \cdot xH_2O$, corrections for self-absorption and scattering due to the thickness of the samples were necessary. For sample thicknesses less than 15 mg/cm^2, the correction factor for conversion of the observed counting rate to the absolute disintegration rate for a 0.6 Mev beta-emitter are given by Engelkemeir and others (49). (The 18h Pt^{197} emits a beta having a maximum energy of 0.7.) Most of the platinum samples prepared in these studies were thicker than 15 mg/cm^2 and it was necessary to determine the corrections experimentally. The counting rate per unit weight was determined by precipitation of samples of irradiated platinum of 19.3, 24.7, 38.5, 57.8, 77.0 and 86.5 mg/cm^2. It was not necessary to add platinum carrier to any of the samples. A curve of counting rate per unit weight versus sample thickness was plotted and matched to that given by Engelkemeir and co-workers (49, p. 60). From this curve (Figure 6) the correction factor $(f_S)(B)$ for samples between 0 and 90 mg/cm^2 thickness mounted on cardboard, covered with 3.5 mg/cm^2 cellophane and counted 20 mm from the Geiger-Mueller tube can be read. If the sample is covered with 9.95 mg/cm^2 scotch tape instead of cellophane, the correction factor must be divided by 0.845. This value was found by comparison of the counting rates of samples covered with scotch tape and with cellophane. The correction $f_W f_A$ for 4.3 mg/cm^2 absorption in air and mica counter window was found to be 1.22 from an aluminum absorption curve of the 18h activity.

The yields of all activities detected except the 7m and 70d iridium activities were determined relative to the 18h platinum activity (Table 10). From the average value of the yield of Cl^{34} relative to 18h Pt^{197}, the yields of all the activities relative to that of Cl^{34} can be calculated. Yields were determined on the basis of the naturally occurring isotopic mixture rather than of a parent isotope since some of the activities can be formed from photonuclear reactions on more than one isotope and the parent isotopes of some of the activities were not known. The results from all of the yield determinations are tabulated in Table 10. The Co^{60} primary standard was counted with each sample of activity. Its counting rate was corrected for absorption and backscattering as on p. 48. Since Cl^{34} has a maximum beta energy of 5.1 Mev, no corrections for the 4.5 mg/cm^2 absorption due to air and the mica counter window were made. The combined correction $(f_S)(B)$ for Cl^{34} was taken from data given by Engelkemeir and co-workers (49, p. 61) for a 2.5 Mev beta-emitter.

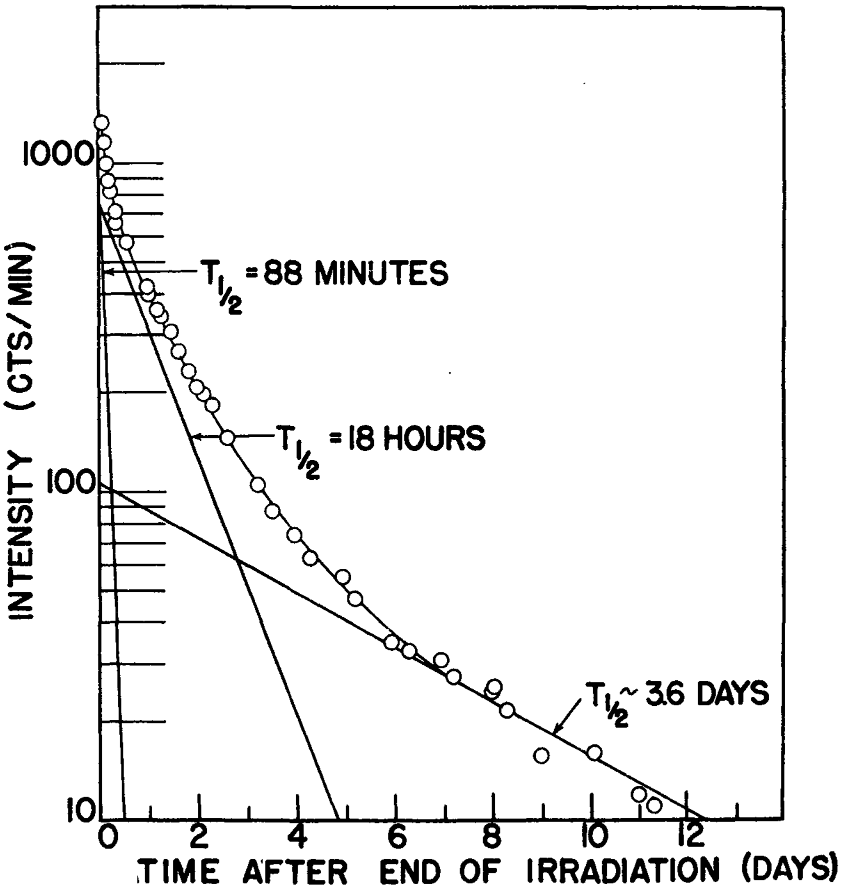

Figure 5. Platinum Fraction from 1.5 Hour Irradiation of $PtCl_4 \cdot xH_2O$

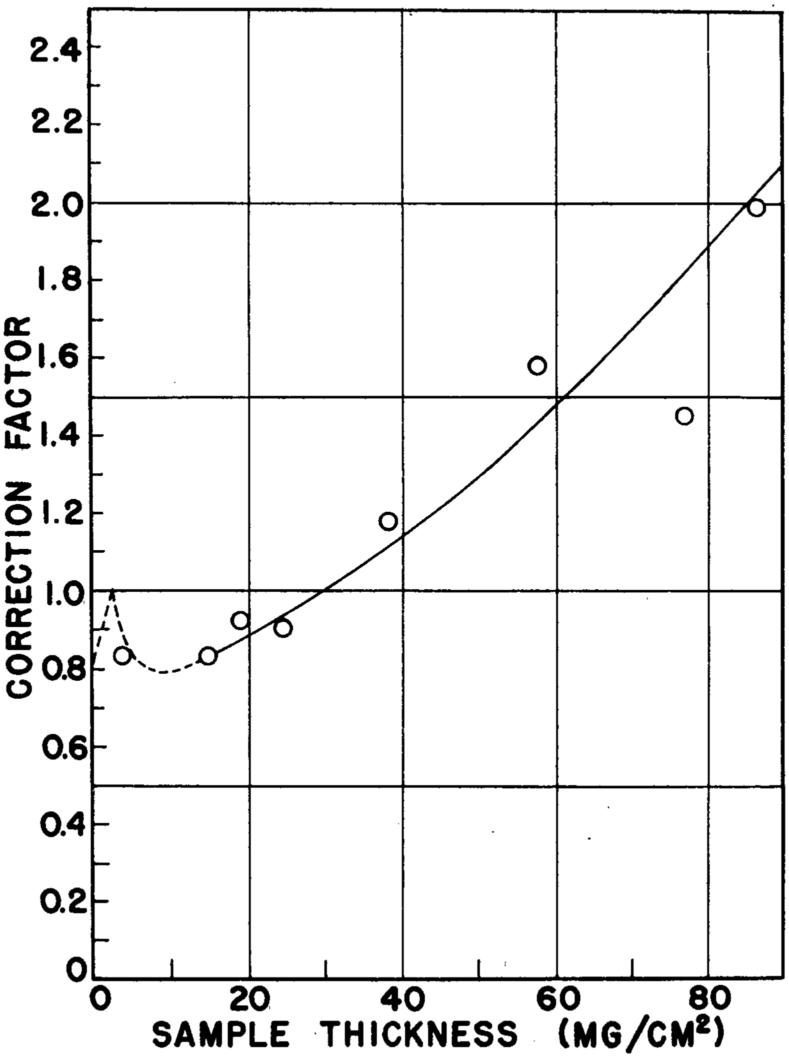

Figure 6. Self-Absorption and Self-Scattering Correction Factors for 0.7 Mev E_{β}-max. of 18h Pt

Experimental points shown by ○

Dashed curve taken from Engelkemeir and co-workers.

Table 10. Yields of Activities Produced in Irradiations of $PtCl_4 \cdot xH_2O$

Irradiation time (hours)	Activity Measured	I_0 (cts/min)	Co^{60} Standard (cts/min)	Co^{60} Standard (dis/min)	Sample Thickness (mg/cm^2)	Wt. Platinum Fraction (g)	Wt. Cl in AgCl Sample (g)	R (dis/min mol Pt)	Yields Relative to 18h Pt^{197}#	Iridium Ratios
Experiment 1 9.6	Ir_{19h}	1440		6.126 x 10^4	24.5	1.044		6.91 x 10^6	0.060	
	Pt_{18h}	2750	3117		33.4	0.177		1.15 x 10^8		
	Pt_{4d}	415			33.4	0.177		3.44 x 10^8	2.99	
Experiment 2 1.68 (intermittent irradiation)	$Ir_{2.3h}$	2080	3728	6.111 x 10^4	2.0	1.421		1.43 x 10^7	0.026	$Ir_{19h}/Ir_{2.3h}$ = 1.91
	Ir_{19h}	670	3728		2.0	1.421		2.73 x 10^7	0.050	
	Pt_{88m}	1245	3173		26.0	0.138		8.74 x 10^7	0.161	
	Pt_{18h}	810	3173		26.0	0.138		5.44 x 10^8		
	Pt_{4d}	88	3173		26.0	0.138		1.09 x 10^9	2.01	
Experiment 3 1.75	Cl_{33m}	660	4352	6.087 x 10^4	22.6		0.030	9.05 x 10^{6*}	0.087	
	Cl_{33m}	2900	4352		91.7		0.120	8.95 x 10^{6*}		
	Pt_{88}	495	3173		75.1	0.398		1.69 x 10^7	.164	
	Pt_{18h}	280	3173		75.1	0.398		1.03 x 10^8		
	Pt_{4d}	31			75.1	0.398		2.79 x 10^8	2.71	
Experiment 4 1.5	Cl_{33m}	3010	4352	6.076 x 10^4	37.0		0.019	2.64 x 10^{7*}	0.086	$Ir_{19h}/Ir_{2.3h}$ = 1.75
	$Ir_{2.3h}$	1615	3709		2.9	1.763		9.38 x 10^6	0.030	
	Ir_{19h}	523	3709		2.9	1.763		1.64 x 10^7	0.053	
	Pt_{18h}	490	4352		20.6	0.109		2.76 x 10^8		
	Pt_{18h}	925	4352		39.8	0.211		3.39 x 10^8		
	Pt_{4d}	106	4352		39.8	0.211		9.16 x 10^8	2.98	
Experiment 5 1.5	Cl_{33m}	1450	4352	6.066 x 10^4	32.4		0.042	1.44 x 10^{7*}	0.092	$Ir_{19h}/Ir_{2.3h}$ = 1.99
	$Ir_{2.3h}$	980	3728		2.3	2.056		4.44 x 10^6	0.028	
	Ir_{19h}	325	3728		2.3	2.056		8.82 x 10^6	0.057	
	Pt_{88m}	430	3201		27.1	0.143		2.86 x 10^7	0.183	
	Pt_{18h}	220	3201		27.1	0.143		1.56 x 10^8		
Experiment 6 3.25	Cl_{33m}	1460	4468	6.034 x 10^4	32.8		0.043	1.20 x 10^{7*}	0.127	$Ir_{19h}/Ir_{2.3h}$ = 1.77
	$Ir_{2.3}$	1030	3747		3.9	2.035		2.71 x 10^6	0.029	
	Ir_{19h}	355	3747		3.9	2.035		4.79 x 10^6	0.051	
	Pt_{88m}	375	3129		28.0	0.148		1.62 x 10^7	0.172	
	Pt_{18h}	250	3129		24.7	0.131		9.42 x 10^7		
Experiment 7 5	$Ir_{2.3h}$	4200	3715	6.027 x 10^4	11.3			9.44 x 10^{4**}		$Ir_{19h}/Ir_{2.3h}$ = 1.80
	Ir_{19h}	1700	3715		11.3			1.70 x 10^{5**}		
	Ir_{70d}	20	3715		11.3			1.76 x 10^{5**}		Ir_{70d}/Ir_{19h} = 1.04
Experiment 8 5	Ir_{19h}	2260	3633	5.985 x 10^4	4.9	2.01		2.08 x 10^7		Ir_{70d}/Ir_{19h} = 0.77
	Ir_{70d}	18	3633		4.9	2.01		1.60 x 10^7		
Experiment 9 .25	Ir_{7m}	660	6954	5.929 x 10^4	1.1			7.7 x 10^{3**}		$Ir_{7m}/Ir_{2.3h}$ = 0.27
	$Ir_{2.3h}$	230			1.1			2.86 x 10^{4**}		

* (dis/min mol Cl)

**(dis/min in sample)

\# Yields in these ratios are based on a target element of one gram-atom of naturally occurring isotopes.

4d platinum activity. In the platinum yield samples a low intensity of a 3.5-4.0d activity (Figure 5) was present. The activity can probably be attributed to Pt^{193} together with a very low intensity of Pt^{191}. The corrections applied to the counting rate of the 4d activity were rather uncertain. $f_W f_A$ for 4.3 mg/cm^2 absorption due to counter window and air was found to be 1.33 by assuming a linear absorption of the 0.11 Mev conversion electron and a range of 17 mg/cm^2 in aluminum. The factor $(B)(f_S)$ was found by extrapolation and interpolation of graphs given by Engelkemeir and co-workers (49, p. 61-64) for 0.2 and 0.4 Mev beta-emitters. (The correction for a 0.11 Mev conversion electron might be expected to be similar to that for a 0.33 Mev beta.) The average yield of the 4d activity was found to be 2.67 (Table 10) relative to 18h Pt^{197} or 27.8 relative to Cl^{34}.

88m platinum activity. An 88m platinum activity (Figure 5) was also found in the platinum yield samples. It is probably the same activity assigned by the Bureau of Standards to Pt^{195m}. Cox and Laslett of the Physics Department of Iowa State College measured the energy of the K and L conversion electrons with a crystal spectrometer and obtained good agreement with the values of 0.32 and 0.26 Mev previously reported for this activity.

(B)(f_S) for the 0.26 and 0.32 Mev conversion electrons emitted by this activity was assumed to be nearly the same as that for the 0.7 Mev beta of 18h Pt^{197} and and was read from Figure 6. $f_W f_A$ for 4.3 mg/cm^2 was determined to be 1.04 by assuming a linear absorption of the conversion electrons. The average yield of the 88m activity can be seen from Table 10 to be 0.170 relative to the 18h Pt^{197} or 1.77 relative to Cl^{34}.

Since there seemed to be some doubt about the mass assignment of this activity, an experiment was performed to determine whether the 88m platinum activity could be produced by a photonuclear reaction on the stable Au^{197} of 100 per cent abundance. If the activity is a metastable state of Pt^{196} it should be formed by a (γ,p) reaction in Au^{197} or, if it is a metastable state of Pt^{195} it should be formed by a (γ,pn) reaction in Au^{197}. The yields of these two types of photonuclear reactions have been reported by Perlman (45) and Moses and Martin (67) to be of nearly the same magnitude. As can be seen from Table 10 (γ,p) reactions in platinum are in all cases at least 0.02 of the yield of the (γ,n) reactions. Therefore, if the 88m activity is a metastable state of either of the above platinum isotopes it would be expected that it would be produced in a yield at least 0.01 that of the 5.6d Au^{196}.

A 1.2 g sample of powdered gold was irradiated for 80 minutes in the x-ray beam of the synchrotron. The sample was dissolved in aqua regia, platinum carrier was added and two samples of $(NH_4)_2PtCl_6$ were precipitated for counting by the addition of NH_4Cl. A 132 mg sample of gold was precipitated from the filtrate and counted. Only 80 cts/min were found in the first $(NH_4)_2PtCl_6$ sample when it was counted 1.5 hours after the end of the irradiation. From a few scattered points at the beginning of the decay curve, it appeared that there might have been 15 cts/min of a short activity present at that time. Extrapolation of these points using an 88m half-life gave an intensity of no more than 40 cts/min of short activity at the end of the irradiation. The remainder of the activity decayed with a half-life of 5.6 days and could be attributed to Au^{196} which carried with the precipitate. It had an intensity of 70 cts/min at the end of the irradiation. The second sample of $(NH_4)_2PtCl_6$ contained only 5 cts/min. The 132 mg gold sample had an intensity of 480 cts/min of 5.6d Au^{196}. If the 40 cts/min in the first precipitate were due to 88m platinum activity the yield relative to that of 5.6d Au^{196} was less than 0.00003. From these results it appears highly improbable that the 88m platinum activity is a metastable state of either Pt^{195} or Pt^{196}.

If the 88m activity is an isomer of Pt^{197} it should decay to 18h Pt^{197} by the emission of conversion electrons. This process would result in the chemical decomposition of a complex containing the 88m activity and 18h Pt^{197} atoms formed by decay of the 88m platinum activity would be found outside the complex. If 18h Pt^{197} could be separated from the complex, it would indicate that it was the daughter of the 88m platinum activity and the mass assignment for the 88m activity could be made. To try to establish this relationship, $[Pt(NH_3)_4]Cl_2$ was irradiated in the x-ray beam of the synchrotron. The activity found outside the complex as a result of the Szilard-Chalmers process was removed by immediate precipitation of $[Pt(NH_3)_4]PtCl_4$. Then, after allowing the complex to stand for various periods of time the growth of 18h Pt^{197}, formed outside the complex by decay of 88m activity remaining in the complex was looked for by counting samples of $[Pt(NH_3)_4]PtCl_4$ precipitated from the solution of the complex. From the data obtained in this experiment it was not possible to determine whether or not an 18h daughter activity was formed. The results of the experiment will be discussed in detail in a later section.

Osmium activities. In the 1.5 hour irradiations of 4-5 g samples of $PtCl_4 \cdot xH_2O$, only 5-10 cts/min were found in the osmium samples. Any very short activities would not have been detected as the samples were not counted until 1-2 hours after the end of the irradiations.

<u>19h iridium activity.</u> The 19h period of Ir^{194} was found in the iridium yield samples (Figure 7). Its yield was found to be 0.054 relative to 18h Pt^{197} and 0.56 relative to Cl^{34}. In experiments 2, 4 and 5 (Table 10) where the IrO_2 precipitate was not purified by dissolving and reprecipitating it, a correction was made in the 19h Ir^{194} counting rate for the amount of 18h Pt^{197} carried in the sample. The amount of 18h platinum which carried was found to be 12.3 per cent of the total 18-19h activity observed in the iridium sample. This value was determined in experiments 5, 6 and 7 by redissolving the IrO_2, adding platinum carrier and reprecipitating IrO_2. The platinum carrier was precipitated and counted with the IrO_2 sample. In these three experiments 12.4, 12.5 and 12.1 per cent of the activity originally present in the IrO_2 sample was found with the platinum carrier sample. An aluminum absorption curve showed that the activity was the 0.7 Mev beta of Pt^{197} and not that of the 2.1 Mev beta of Ir^{194}. If the IrO_2 was again dissolved and the procedure repeated, less than 0.6 per cent of the activity was found in the platinum carrier sample.

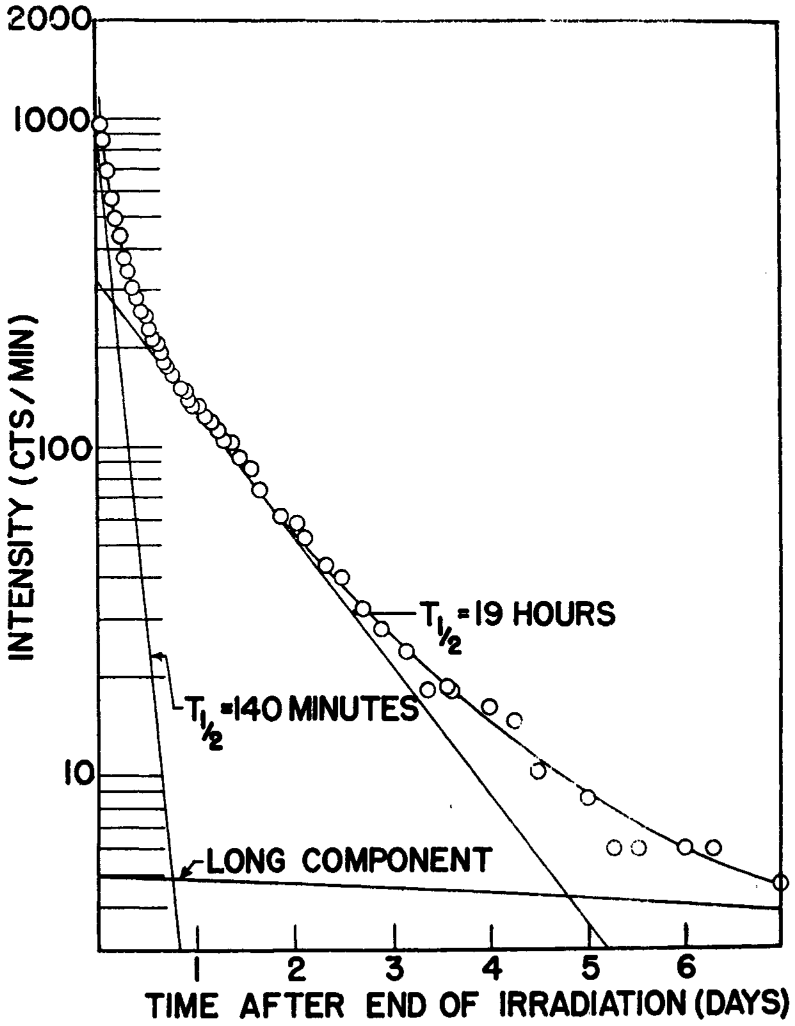

Figure 7. Iridium Fraction from 1.5 Hour Irradiation of $PtCl_4 \cdot xH_2O$

The correction factor (B)(f_S), applied to the observed counting rate, was taken from the data given by Engelkemeir and co-workers (49, p. 61) for a 2.5 Mev beta-emitter. The correction $f_W f_A$ for 4.1 mg/cm^2 absorption in air and counter window was found to be 1.11 by extrapolation of an aluminum absorption curve of the activity. From a Feather analysis of the aluminum absorption curve (Figure 8) the maximum energy of the beta-particles was found to be 2.1 Mev. This is in good agreement with previously reported values (24).

<u>70d iridium activity.</u> A low intensity of a long component (Figure 7) was found to be present in the iridium samples. It was not due to platinum contamination in the iridium sample since its half-life was much longer than 4d, which was the longest platinum activity observed. When phosphorus holdback carrier was added before the precipitation of IrO_2, the intensity of this long component was reduced to about one-sixth. Apparently, the majority of the long activity was due to P^{32} or P^{33} formed by photonuclear reactions in chlorine. The remaining very low intensity of long activity had a much longer half-life and may be due to 70d Ir^{192} formed by a (γ,pn) reaction on Pt^{194}. In five hour irradiations the half-life of this component was found to be about 65d. However, since its initial intensity was only 20-25 cts/min, an accurate half-

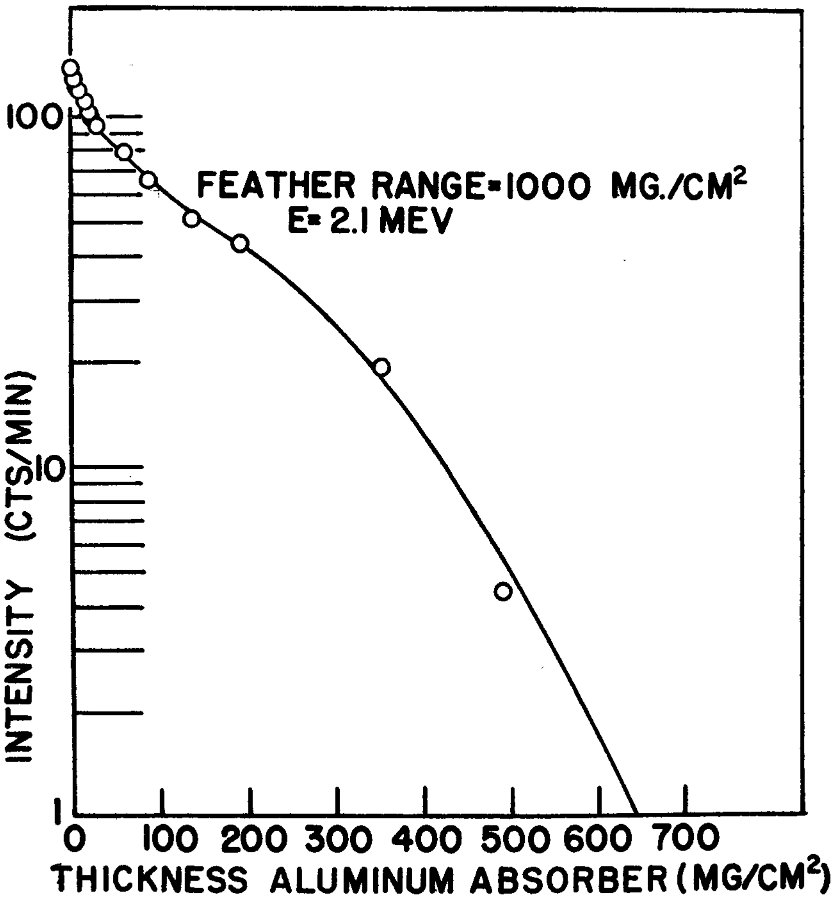

Figure 8. Aluminum Absorption Curve for 19h Ir^{194}
20 Hours after End of Irradiation

life determination was not possible. Its yield relative to 19h Ir^{194} was estimated to be 0.9. Since the 70d Ir^{192} emits a 0.67 Mev beta, its counting rate was corrected using the same factors as for the 18h Pt^{197}.

140m iridium activity. A new iridium activity having a half-life of 140m (Figure 9) was found in the iridium fraction. An aluminum absorption curve of an iridium sample was taken about three hours after the end of irradiation (Figure 10). Another was taken 20 hours later after most of the 140m activity had decayed (Figure 8). The curve shown in Figure 8 was corrected for decay during the 20 hour period and subtracted from the upper curve shown in Figure 10. The lower curve in Figure 10 shows the absorption curve for the 140m component obtained by the subtraction. From a rough Feather analysis the maximum beta energy was estimated to be 1 Mev.

The yield of the 140m iridium relative to 18h Pt^{197} was found to be 0.028 (Table 10) from the average of four determinations. The yield relative to 19h Ir^{194} was found to be 0.54. The correction for the thickness of the sample, backscatterer and cellophane covering was again obtained from data given by Engelkemeir and co-workers (49, p. 61) for a beta-emitter having a maximum energy of 1.1 Mev.

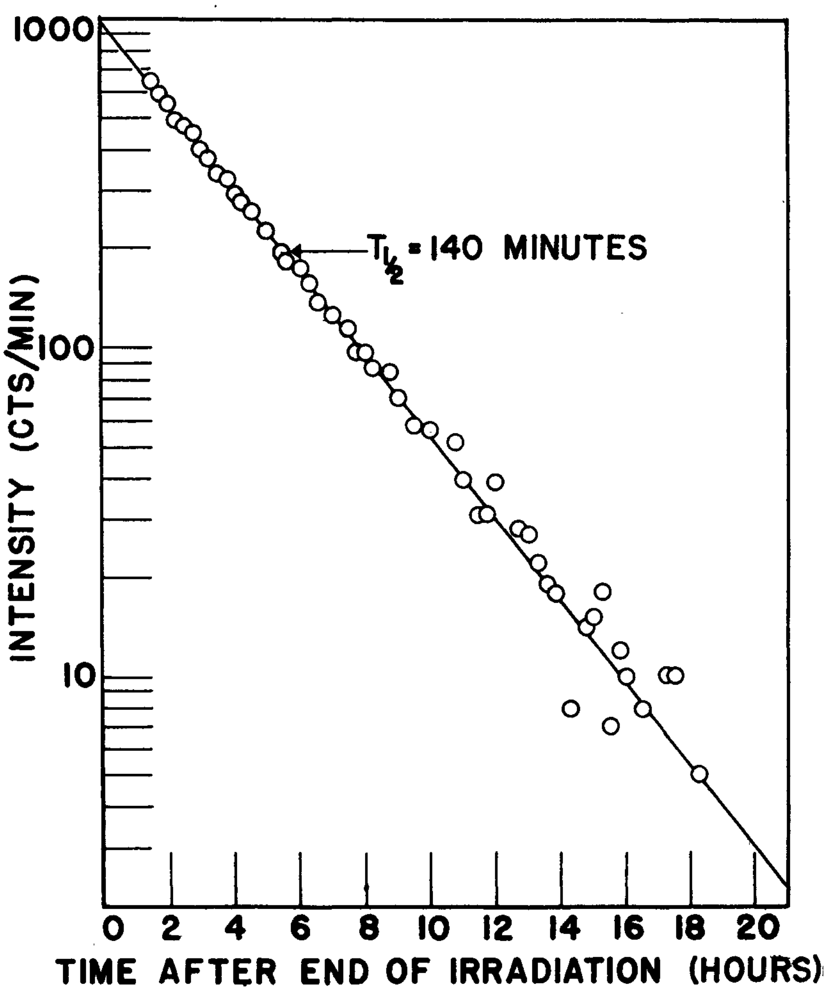

Figure 9. 140m Iridium Component from Irradiation of $PtCl_4 \cdot xH_2O$

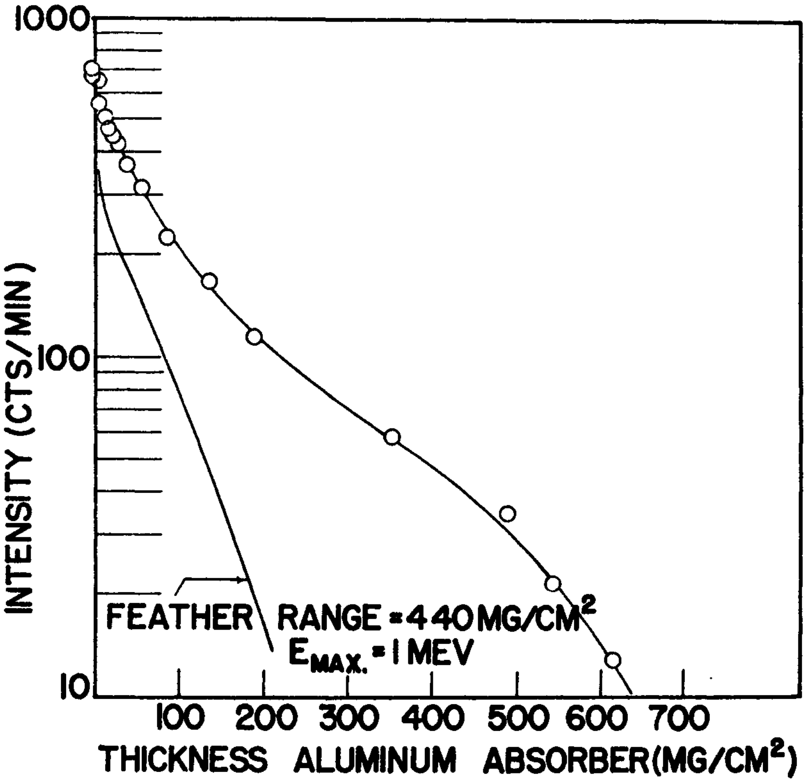

Figure 10. Aluminum Absorption Curve of Combined 140m and 19h Iridium Activities 3 Hours after End of Irradiation

(Lower curve for 140m activity obtained by subtraction of 19h component from upper curve)

$f_W f_A$ for 4.1 mg/cm^2 was found to be 1.12 by extrapolation of an aluminum absorption curve of the activity.

To determine if the 140m iridium decayed to 18h Pt^{197} the following experiment was performed. $PtCl_4 \cdot xH_2O$ was irradiated for 5.3 hours. IrO_2 was precipitated as quickly as possible, immediately dissolved and reprecipitated after the addition of platinum carrier to the solution to prevent carrying of platinum activity with the IrO_2 precipitate. The reprecipitation was completed 1.7 hours after the end of the irradiation. The IrO_2 was redissolved and after the addition of 30 mg of platinum carrier was allowed to stand for three hours. The iridium was again precipitated, filtered from the solution, redissolved and allowed to stand for 13 hours after the addition of 30 mg of platinum carrier. The platinum in the filtrate was precipitated, weighed and counted. If the 140m iridium is the parent of Pt^{197}, the 18h activity formed by decay during the three hour standing period should be found in this sample. After the second standing period IrO_2 was precipitated, filtered from the solution, weighed and counted. Another platinum sample was prepared from the filtrate and counted. It should contain any Pt^{197} formed by decay of the 140m activity during the 13 hour period of standing. The first platinum sample contained only 10 cts/min and the second only 6 cts/min. On the basis of the 2050 cts/min of 19h Ir^{194} found in the IrO_2 sample the counting rate of the 140m activity must have been about 5800 at the end of the irradiation. Therefore, the two platinum samples should have contained at least 500 cts/min of 18h platinum activity if the 140m iridium activity is the parent of the 18h Pt^{197}. These results indicate that the 140m activity should not be assigned to Ir^{197}.

The 140m activity can probably be assigned to either Ir^{195} or Ir^{196}. Its rate of formation is 0.54 times that of the 19h Ir^{194} and 3.7 times that of a 7m activity (Table 10) which was detected. The abundances of Pt^{198}, Pt^{196} and Pt^{195} are 7.2, 25.4 and 33.7 per cent, respectively. The yield of Ir^{195} formed only by a (γ,p) reaction on Pt^{196} relative to that of Ir^{194}, which is probably formed in nearly equal yields by (γ,p) and (γ,pn) reactions on Pt^{195} and Pt^{196}, would be expected to be about 0.4 on the basis of the isotopic abundances of platinum. If it were formed by a (γ,pn) reaction on Pt^{198} its yield relative to Ir^{194} would be anticipated to be only 0.1. This seems to indicate assignment of the 140m activity to Ir^{195}. Also, the observed value of 1 Mev for the maximum energy of the beta is the energy equivalent of the difference in the atomic masses of Ir^{195} and Pt^{195} as calculated by Metropolis and

Reitweisner (68). For Ir^{197} and Pt^{197} the mass difference is equivalent to an energy of 1.7 Mev and for Ir^{196} and Pt^{196} it is equivalent to 2.8 Mev.

7m iridium activity. A 7m activity (Figure 11) was found in the IrO_2 precipitated from a 1-2g sample of $PtCl_4 \cdot xH_2O$ which had been irradiated for 15 minutes. Its yield relative to the 140m iridium activity was found to be 0.27 (Table 10) if the efficiency for counting the two activities was assumed to be the same. If the 140m iridium activity is assigned to Ir^{195}, the 7m activity can probably be assigned to either Ir^{196} or Ir^{197} since it could be formed by a (γ,pn) or (γ,p) reaction on Pt^{198}.

Efficiency of the Szilard-Chalmers separations from platinum complexes. Irradiations of platinum complexes were carried out and attempts were made to separate the platinum activity ejected from the complexes in the Szilard-Chalmers process. The three general methods used were: treatment with anion exchange resins, extraction with butyl acetate and precipitation of $(NH_4)_2PtCl_6$ or $[Pt(NH_3)_4]PtCl_4$. These methods have been discussed in a previous section.

The results of the attempts to separate platinum activity away from irradiated platinum complexes by treatment with anion exchange resin are summarized in Table 11.

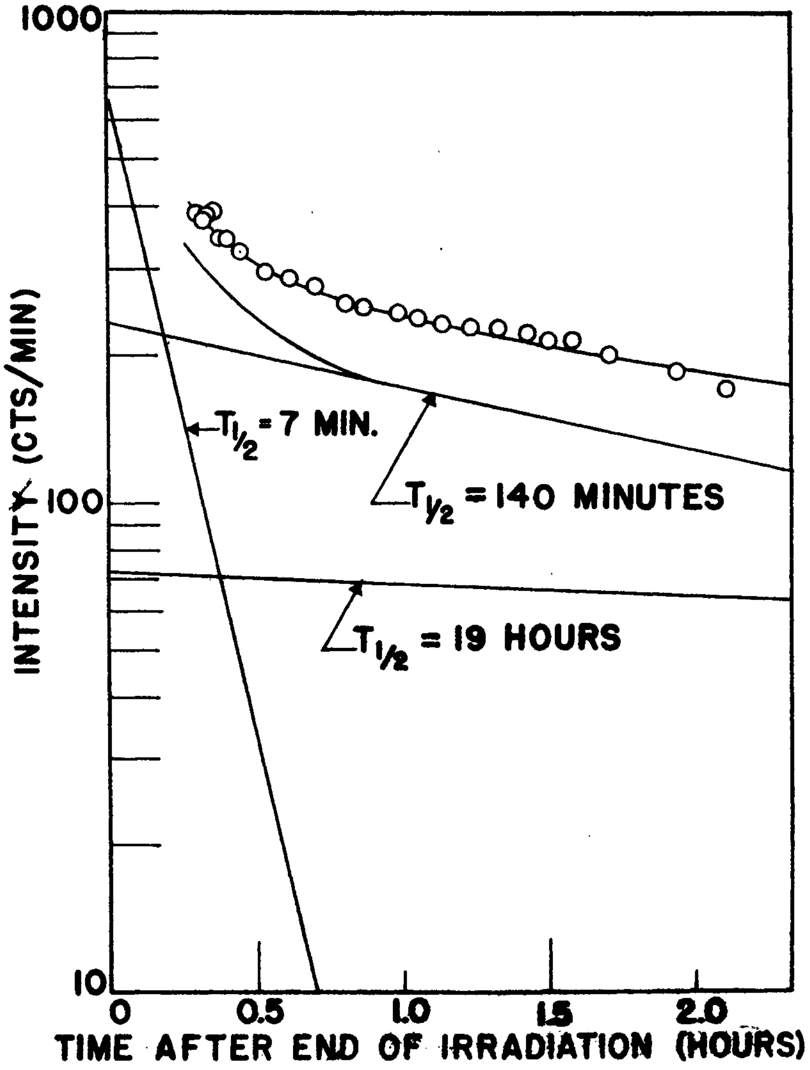

Figure 11. Iridium Activities from 0.25 Hour Irradiation of $PtCl_4 \cdot xH_2O$

Table 11. Resin Separations

Target (g)	T* (hours)	Resin used (g)	Total** activity (cts/min)	Activity separated on resin (%)	Sepn. no.
0.25 $[Pt(NH_3)_4]Cl_2$	1.5	1 IR-4B oxalate in 40 ml H_2O	2050	10 2 Total 12	(1) (2)
0.38 $[Pt(NH_3)_4]C_2O_4$	1.5	2 IR-4B oxalate in 125 ml H_2O	1340	11 4 4 Total 19	(1) (2) (3)
0.52 $[Pt(NH_3)_2Cl_4]$	1.6	1 A-2 acetate in 150 ml H_2O#	1780	17 2 Total 19	(1) (2)

* Period of irradiation

** Total 18h activity at the end of the irradiation

\# 0.3 ml of 0.06 N HCl added

The counting rates of all of the samples were corrected for differences in self-absorption. In all three experiments the resin was shaken with a solution of the complex for 15 minutes. The resin was then filtered from the solution and the solution was treated similarly with another portion of resin. In the second experiment three such separations were performed. Samples were then prepared from the activity removed by the resin in each separation. An aliquot of the complex solution was also obtained for counting, either by precipitation of platinum metal or by precipitation of the original complex by the addition of acetone to the solution. These experiments indicated that at least 12-19 per cent of the activity was present in the form of anions which could be adsorbed on the resin.

In the extraction experiments (Table 12) the irradiated sample was dissolved in 20 ml of water and the solution was made 6 N in HCl. The solution was then extracted three times with 40 ml portions of butyl acetate. The extracts were combined and the platinum in them was oxidized by heating with a 10 per cent $NaBrO_3$ solution. After the addition of platinum carrier the platinum was extracted into 6 N HCl and platinum metal was precipitated for counting. A sample of the unextracted solution from the first butyl acetate extractions was prepared by the precipitation of the original complex with acetone. In the second experiment the 6 N acid solution was filtered after the butyl acetate extractions, washed with 2-3 ml of water and the filter paper was counted to try to detect any activity that might be present as colloidal particles of $[Pt(NH_3)_4]PtCl_4$. No activity was found on the filter paper. From these experiments it appears that no more than 8-10 per cent of the activity is present as $PtCl_4^{=}$ or other platinum(II) complex anions.

Table 12. Butyl Acetate Extractions

Target (g)	T* (hours)	Total** activity (cts/min)	Fraction extracted (%)
0.400 $[Pt(NH_3)_4]Cl_2$	1.5	744	9.8
0.400 $[Pt(NH_3)_4]Cl_2$	1.5	666	8.4

* period of irradiation

** total 18h activity at the end of the irradiation

K_2PtCl_4 and K_2PtCl_6 were irradiated to determine the oxidation state of the platinum activities produced. The experiments are summarized in Table 13. In experiment 1,

Table 13. $(NH_4)_2PtCl_6$ Precipitations

Target (g)	T* (hours)	Carrier (mg)	Total** activity (cts/min)	Activity separated (per cent)	Precipitate no.
0.385		Pt^{IV} 5	2880	1.5	(1)
K_2PtCl_4	1.5	Pt^{IV} 5		1.3	(2)
		Pt^{IV} 5		4.0	(3)
		Pt^{IV} 5		2.8	(4)
				Total 9.6	
0.430		K_2PtCl_4 7	1550		
K_2PtCl_6	1.3			77.0	(1)
				23.0	(2)

* Period of irradiation

** Total 18h activity at the end of the irradiation

K_2PtCl_4 was dissolved in 17 ml of water and platinum(IV) carrier was added. Four precipitations of $(NH_4)_2PtCl_6$ were performed to determine the amount of activity present as $PtCl_6^=$. The activity found in these samples was probably just activity from the filtrate which carried with the precipitates. A known aliquot of the solution was counted to determine the amount of activity remaining in it.

In the second experiment, irradiated K_2PtCl_6 was dissolved in hot water and K_2PtCl_4 holdback carrier was added. $(NH_4)_2PtCl_6$ was precipitated. The filtrate was evaporated and platinum metal was precipitated. The platinum was redissolved and $(NH_4)_2PtCl_6$ was precipitated, filtered and weighed. As shown in Table 13, 77 per cent of the activity was found in the first $(NH_4)_2PtCl_6$ precipitate, which contained 76 mg of platinum. The $(NH_4)_2PtCl_6$ from the filtrate contained 3.7 mg of platinum, 3.3 mg of which should have been inactive platinum from the 7 mg of K_2PtCl_4 holdback carrier added to the solution. Since the specific activity of the filtrate sample is much higher than that of the first precipitate, the activity left in the filtrate appears to be due to activity actually present as $PtCl_4^=$ rather than $PtCl_6^=$ which was not completely removed by the first precipitation of $(NH_4)_2PtCl_6$.

These experiments indicate that when K_2PtCl_4 is irradiated most of the active atoms remain as $PtCl_4^{=}$ while when K_2PtCl_6 is irradiated 23 per cent of the activity seems to be present as $PtCl_4^{=}$. This result is rather unexpected since it is believed that the active atoms will usually be found in a higher oxidation state than that of the target atoms if the element has a higher stable oxidation state.

Table 14 summarizes the results obtained when $[Pt(NH_3)_4]PtCl_4$ was precipitated by the addition of $PtCl_6^{=}$ or $PtCl_4^{=}$ to solutions of irradiated complex. In the first experiment, because of the slow formation of the precipitate, three samples were filtered from the solution before the precipitation appeared to be complete. In the second experiment, the precipitate formed immediately and the added platinum carrier was recovered quantitatively. This method is much the faster although it may be less efficient.

The use of the above precipitation method in an attempt to determine the mass assignment of the 88m platinum activity was mentioned previously. A 9.4 g sample of solid $[Pt(NH_3)_4]Cl_2$ was irradiated for 1.5 hours. The complex was dissolved in 100 ml of water and $[Pt(NH_3)_4]PtCl_4$ was precipitated by the addition of a $PtCl_4^{=}$ carrier solution containing 5.3 mg/ml of platinum. The precipitation was repeated until a nearly constant specific activity was

Table 14. $[Pt(NH_3)_4]PtCl_4$ Precipitations

Target (g)	T* (hours)	Carrier (mg)	Total** activity (cts/min)	Activity separated (per cent)	Precipitate no.
0.426 $[Pt(NH_3)_4]C_2O_4$	1.6	Pt^{IV} 24	1922	25	(1)
				18	(2)
				7	(3)
			Total	40	
0.400 $[Pt(NH_3)_4]Cl_2$	1.5	solid K_2PtCl_4 20	1300	33	(1)

* Period of irradiation

** Total 18h activity at the end of the irradiation found in the precipitates. The solution was allowed to stand for about two hours and the precipitation was repeated. If all the 88m activity left after the first precipitations were in the complex, its decay to the 18h activity should result in an increase in the 18h activity of the sample precipitated after the standing period. The solution was allowed to stand for about two more hours and the precipitation was again repeated. A sample of the complex was also precipitated to determine the total activity in the irradiated complex and the specific activity of the original complex. The results of the experiment are given in Table 15. Column 1 gives the time after irradiation that each sample was precipitated. Since $[Pt(NH_3)_4]PtCl_4$ contains 64 per cent platinum, the weight of platinum given in column 3 was obtained by multiplying the actual weight of each sample by this factor. The complex contains 55 per cent platinum and its weight was similarly converted to weight of platinum. One-half of the platinum in the precipitates should be carrier platinum while the other one-half would be $[Pt(NH_3)]^{++}$ from the irradiated complex. As can be seen from Table 15, quantitative recovery of the added platinum carrier was not obtained. The specific activity of each of the precipitates was higher than that of the irradiated complex, but

Table 15. Separation of Activity from 9.4 g of $[Pt(NH_3)_4]Cl_2$

T* (hours)	Carrier (mg Pt)	Wt. sample (mg Pt)	Activity separated (per cent)	Specific activity**	Sample no.
0.25	5.3	13.4	3.2	14	1
0.38	5.3	8.5	2.6	12	2
0.50	5.3	7.9	2.0	9	3
0.75	18.3	23.2	3.7	9	4
1.00	5.3	7.0	1.4	12	5
3.00	5.3	10.9	2.6	14	6
3.08	5.3	5.7	0.6	6	7
3.58	5.3	8.3	1.2	8	8
6.00	5.3	9.0	1.4	9	9
6.08	5.3	2.6	0.2	5	10
6.50	$PtCl_6$	16.0	0.7	3	11
7.00	---	4.5	0.6	8	12
			4.0		others
		Total	24.2		
7.2		12.6		1	complex

* Time after end of irradiation

** The specific activity of the complex was arbitrarily chosen as 1.

each precipitate contained only a small fraction of the total activity. Although an increase in 18h activity was found in sample 6, none was found in sample 9 which was also precipitated after a period of standing. From these results no conclusions could be made as to the mass assignment of the 88m activity. If a clean separation procedure could be developed this might be possible. The use of butyl acetate extractions to separate any $PtCl_4^=$ formed by ejection of activity from the complex by decay of the 88m platinum might be worthy of investigation in this connection. Attempts to scavenge the activity from the solution with $Fe(OH)_3$ removed only 0.3 per cent of the activity. When the solution was allowed to stand over night in contact with the $Fe(OH)_3$ precipitate, 1.9 per cent more of the activity was removed.

From a comparison of the results in Table 14 and Table 15, it can be seen that the amounts of carrier used are quite effective in removing 30-40 per cent of the activity from small samples of the complex, but many precipitations are necessary with larger quantities of complex. This suggests that the separation was somewhat dependent on the surface. Possibly the activity is not present as the $PtCl_4^=$ or $PtCl_6^=$ species. Alternatively, it may be that precipitates which formed rapidly did not exchange with the platinum carrier. Probably all of the activity was ejected from the complexes in the (γ,n) process. The radioactive platinum undoubtedly dissolved in the aqueous solutions to form a number of complex species. To obtain optimum yields of high specific activity it would be necessary to separate all such species from the original complex. Of the separation methods investigated for obtaining high specific activities of platinum, the precipitation of $[Pt(NH_3)_4]PtCl_4$ after the irradiation of $[Pt(NH_3)_4]Cl_2$ or $[Pt(NH_3)_4]C_2O_4$ appears to be the most effective.

SUMMARY

The backscattering of four different beta-emitters ranging in maximum energy from 0.067 to 1.7 Mev was investigated in the windowless Geiger-Mueller gas flow counter. The backscattering was found to be a function of the atomic number of the backscatterer. With platinum backing, the backscattering appeared to have reached a saturation value and was nearly the same for all of the beta energies which were investigated.

Samples of $K_3[Co(C_2O_4)_3]\cdot 3H_2O$ were irradiated in the x-ray beam of the 68 Mev synchrotron. The Szilard-Chalmers process appeared to be nearly 100 per cent effective in ejecting the radioactive cobalt atoms from the complex. The 9.2h Co^{58m} and 72d Co^{58} formed during the irradiation were separated from the complex in high specific activities by adsorption on IRC-50 cation exchange resin. A solution of the complex was prepared from the active cobalt separated in this way. A method utilizing the chemical decomposition of the complex which occurred as a result of the decay of Co^{58m} to Co^{58} by emission of conversion electrons,was used to calculate the ratio of the rates of formation of the two isomers. In these experiments the ratio of the rate of formation of Co^{58} to the rate of formation of Co^{58m} was found to be 0.61 ± 0.04.

In synchrotron irradiations of $PtCl_4 \cdot xH_2O$, 88m, 18h and 4d platinum activities and 7m, 140m, 19h and 70d iridium activities were detected. Their yields relative to that of the 18h Pt^{197} and the 33m Cl^{34} were determined. The mass assignments and characteristics of the two new iridium activities were studied. The 140m activity was tentatively assigned to Ir^{195} and the 7m activity to Ir^{196} or Ir^{197}. Szilard-Chalmers process separation methods were also investigated for several complex compounds of platinum.

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ACKNOWLEDGMENTS

The author wishes to express her appreciation to Dr. D. S. Martin for the advice, encouragement and the many helpful suggestions given during the course of the research.

She also wishes to thank Dr. L. J. Laslett, Dr. D. J. Zaffarano and their assistants for performing the synchrotron irradiations.

She would further like to express her appreciation to the other members of the laboratory, especially R. F. Mitchell and W. R. Dunning, who cooperated in many of the chemical separations and helped in obtaining much of the counting data.

Appreciation is expressed to Dr. V. Fassel and his assistants for spectrographic analyses of the platinum used in the research.

Acknowledgment is made to the Ames Laboratory of the Atomic Energy Commission for providing the funds and facilities necessary for the research.