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Mass Spectrographic Mass Assignment of Radioactive Isotopes

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Characteristics of positive ion emission for various compounds on a tungsten filament are noted. Methods of analysis of mixtures of radioactive isotopes by mass spectrograph are described. The following mass assignments are made: 108-day yttrium, 88; 57-day yttrium, 91; 1-year ruthenium, 106; 300-day cerium, 144; 3.7-year element 61, 147; 55-day strontium, 89; 25-year strontium, 90; 60-hour yttrium, 90; 12.6-day barium, 140; 40-hour lanthanum, 140.

1. INTRODUCTION

THE phenomenon of fission gave rise to a great number of new radioactive isotopes that had not been previously observed. Many could be identified from the fact that most occurred in "chains," a sequence of beta-emitting isotopes of the same mass leading to a stable isotope. However, among the one hundred and fifty new radioactive isotopes many could not be so identified, and the question arose whether the masses of these new isotopes could be determined by the mass spectrograph.

In early experiments, a 4-mg sample of uranium with a quarter of a millicurie activity due to the fission products formed in it by the Clinton pile was analyzed with a spark source and a double focusing mass spectrograph, and gave a radioactive deposit on a photographic plate in the fission mass range whose beta-rays could be observed with a counter.[1] However, only one in 10 or 100 million of the active isotopes was collected, and attempts were made to find more efficient ion sources. Blewett and Jones[2] in 1936 had observed ion emission from the heated oxides of Sr, Ba, Y, and Cs, elements in the fission product range, and experiments by Lewis, Hayden, King, and Garrison[3] confirmed these results and extended the list to include the oxides of columbium, lanthanum, praseodymium, and neodymium. In the case of lanthanum it was found that 16 percent of the molecules that are evaporated from a tungsten filament appear as positively charged oxide ions, and since about one in fifty of the ions formed appear in the analyzed deposit, we obtained in the analyzed deposit one out of 300 of the original radioactive isotopes. That many rare earth oxides are good ion emitters was a welcome discovery, as the opposite was suggested by Dr. Aston's experience with hot anodes made from the bromides of these elements. He obtained very weak rays and was able to photograph only the stronger stable isotopes. If the yield is as much as one atom deposited for 1000 atoms evaporated from the source, a source with only one microcurie of radioactivity will give a deposit with 2000 counts/minute, which is ample for detecting the active isotopes, and even identifying their half-lives. However, if the yield is only 1 in 10^8, as with the spark source, 20 counts/minute from the deposit would require a millicurie of activity in the source and this amount requires special shielding and precautions in handling.

The instrument used for the analyses reported in the paper will be described in detail elsewhere.[4] The ions were produced by heating the oxides of the active fission products on a tungsten filament and analyzing by a magnetic field. The ions were collected on photographic plates, and after identifying the active isotopes as explained below, the plates were developed to provide the mass scale. Thus the position of the active lines could be obtained by comparison with the normal spectrum. Measurements for fission activities were simpler than for isotopes made by (n,γ) reactions because the former could be obtained carrier-free and in high concentration, whereas the (n,γ) active atoms were usually

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[1] A. J. Dempster, CP-1507, p. 25, March, 1944.
[2] J. P. Blewett and E. J. Jones, Phys. Rev. **50**, 464 (1936).
[3] Lewis, Garrison, King, and Hayden, CP-2122, August 5, 1944.
[4] Lloyd G. Lewis and Richard J. Hayden, Rev. Sci. Inst. (to be published).

only a very small fraction of the total sample. Measurements for various fission products are described below.

2. ION SOURCE CHARACTERISTICS

The ion source in the spectrograph was a 0.001-in. by 0.030-in. tungsten ribbon, about $\frac{1}{2}$-in. long. This filament could be removed for loading through a ground glass joint. Samples contained in solutions were placed on the filament from calibrated micropipettes and then were evaporated to dryness in air. To produce the ions the filament was heated by a 6.3-volt transformer. Many of the materials tested emitted ions other than those of the metallic element. In general, the emission from nitrates or oxides of elements of normal valence one or two was, when emission occurred, of the form R^+. Emission from nitrates or oxides of elements of normal valence three or four was of the form RO^+. No multiply charged ions were observed. Table I gives the types of ions emitted by various compounds. Care must be taken to avoid confusing compound ions with atomic ions. For example, the compound ion $NaKCl^+$ gives masses at 97 and 99 which may easily be misinterpreted.

A tungsten filament was chosen as the ion source for this radioactive work because, although it does not give ions of all elements, it is usually more efficient (i.e., gave a larger ratio of ions given off to molecules given off) for the elements with which it could be used than were other ion sources. Thus smaller samples could be used. A list of ionization efficiencies for various compounds is given in Table II. Of every 50 ions formed by the filament one reached the photographic plate. Thus the percentages given in Table I must be multiplied by 0.02 to give the over-all efficiency of the spectrograph for the compound in question.

The data which gave these ionization efficiencies were observed by placing a metallic ion collector, connected to a Dershem electrometer, in place of the photographic plate. Then, when ions of a single mass were being emitted from the filament, the ratio of the current to a grounded diaphragm which defined the ion beam to the current to the electrometer was the factor of fifty previously mentioned. Thus,

TABLE I. Types of ionic emission.

Compound	Types of Ions
NaCl	Na^+, Na_2Cl^+
KCl	K^+, K_2Cl^+
NaCl+KCl	Na^+, K^+, Na_2Cl^+, K_2Cl^+, $NaKCl^+$
$Ba(NO_3)_2$	Ba^+
$Sr(NO_3)_2$	Sr^+
$Ca(NO_3)_2$	Ca^+
$Y(NO_3)_3$	YO^+
ZrO_2	ZrO^+
$RuCl_3$, $Ru(NO_3)_3$	Ru^+
$RhCl_3$	Rh^+
$La(NO_3)_3$	LaO^+
$Ce(NO_3)_3$	CeO^+
$Pr(NO_3)_3$	PrO^+
$Nd(NO_3)_3$	$Nd^+(\sim 1\%)$; $NdO^+(\sim 99\%)$
$61(NO_3)_3$	$61^+(\sim 5\%)$; $61O^+(\sim 95\%)$
$Sm(NO_3)_3$	$Sm^+(\sim 60\%)$; $SmO^+(\sim 40\%)$
$Eu(NO_3)_3$	Eu^+
$Gd(NO_3)_3$	$Gd^+(\sim 40\%)$; $GdO^+(\sim 60\%)$
U_3O_8	U^+, UO^+, UO_2^+

when a known number of molecules was placed on the filament, and when, after heating the filament, the voltage across the capacity in parallel with the electrometer was observed, the over-all efficiency of the spectrograph was calculated. Two successive runs with the same filament and the same size samples which were heated in the same manner always gave over-all efficiencies which were within 20 percent of each other. Measurements of memory in the filament indicated that in every case less than 5 percent of the sample remained on the filament after heating. With use a given filament became more efficient in the formation of ions. For example, one filament, which was used for more than fifty samples began by giving 0.5 percent ionization efficiency for $Nd(NO_3)_3$ and ended by giving 1 percent ionization efficiency. The ionization efficiencies in Table I were measured with frequent checking of the $Nd(NO_3)_3$ efficiency. Only values obtained when the $Nd(NO_3)_3$ efficiency was 1 percent were used. The ionization efficiency seemed independent of the size of the sample so long as the amount of material on the filament was small (roughly, less than 100 micrograms). This was checked with the electrometer method for $Nd(NO_3)_3$ by using different size samples, and was verified for many other compounds by counting plates after a known activity was placed on the filament. The efficiency of $61(NO_3)_3$ was obtained only in this manner. It was found that heating the filament

TABLE II. Ionization efficiencies.

Compound	Ionization Efficiency (%)
$Ba(NO_3)_2$	0.02
$Sr(NO_3)_2$	0.08
$Y(NO_3)_3$	0.025
$La(NO_3)_3$	16.
$Ce(NO_3)_3$	0.12
$Pr(NO_3)_3$	12.
$Nd(NO_3)_3$	1.
$61(NO_3)_3$	0.5
$Sm(NO_3)_3$	0.16
$Eu(NO_3)_3$	0.16
$Gd(NO_3)_3$	0.05
U_3O_8	0.008
$RuCl_3$, $Ru(NO_3)_3$	0.01
$RhCl_3$	0.005

rapidly so as to obtain a short, intense burst of ions was, by as much as a factor of four, less efficient than slowly raising the filament temperature. The above measurements were made by adjusting the filament current so as to keep the positive ion current constant at 0.05 microampere.

3. METHODS OF ANALYSIS

Two general methods were used to determine the mass of an active isotope after its ions had been deposited on the photographic plate. In the first method the radioactive material and also an inactive compound which would give a mass spectrum in the mass range of the active isotope were placed on the filament. After the spectrograph was run, the plate was removed and, before being developed, was placed under a Geiger counter tube which, except for an adjustable slit, was shielded from the plate by $\frac{1}{8}$ in. of lead. By observing the counting rate with different portions of the plate next to the slit, the activity was plotted as a function of the distance from the end of the plate. Thus the position of the radioactive line was determined. After this was done the plate was developed to give the standard mass spectrum. Knowing the position of the active isotope, the position of known masses, and the dispersion, the mass of the active isotope was calculated. The standard mass spectrum was necessary because, due to the hysteresis in the magnetic circuit, the same current through the magnet coils did not always give the same magnetic induction in the gap. Thus a knowledge of the position of a line on the plate, the accelerating voltage, and the current through the magnet coils was not sufficient to determine the mass number corresponding to that line.

In the second method the loading of the sample and exposure of the plate were made as in the first. When the plate was removed from the spectrograph, it was placed face to face with an unexposed plate and left in this position for a time calculated to be long enough for the beta- or gamma-rays from the deposit to give developable lines on both plates. The plates were then developed. The lines on the transfer plate showed that corresponding lines on the original plate were due, at least in part, to a radioactive deposit. This, together with the known mass spectrum, determined the mass numbers at which the active isotopes were located. The photographic plates used were Eastman III-O spectroscopic plates. To produce a developable line (about 0.2 mm by 1 cm) on one of these plates roughly 10^{10} mass 100 to 150, 8000 volt positive ions or 10^6 1-Mev gamma-rays or 10^5 beta-rays were needed. Dependence of blackening on energy and mass of particles was not studied. The counter method was more sensitive if the half-life of the isotope was less than twelve hours; the plate method was more sensitive if the half-life was greater than twelve hours.

In cases where two or more activities which could not be separated were present in the original sample, a half-life determination of the activity on each line of the plate was desirable. In cases where high activity was deposited on the plate, this was accomplished by watching the decay of a given line. In addition, relative half-lives (i.e., which of two activities had the longer half-life) were obtained by taking successive transfer plates from a given plate and observing the change in the relative darkening of the lines in question.

4. MASS DETERMINATIONS

108-Day Yttrium

A 108-day isotope of yttrium was first produced by Dubridge and Marshall[5] by a (p,n)

[5] L. A. Dubridge and J. Marshall, Phys. Rev. **57**, 348 (1940).

reaction on strontium. Later[6] it was produced by $(n,2n)$ on yttrium. This isotope decays by K capture and accompanying emission to stable Sr. Gamma-rays of 0.908 Mev and 1.89 Mev have been observed.[7] Formation of this isotope by (p,n)(or $d,2n$ as was later done) reaction on strontium states only that its mass must be 84, 86, 87, or 88. Formation by fast neutron bombardment establishes the mass at 88 only if the production of two neutrons is assumed. Thus, though the previous assignment of the isotope to mass 88 seemed well founded a direct measurement was made.

About 10 mC of 108-day yttrium, obtained from Paul Tompkins at Clinton Laboratory, and 3 micrograms of normal Y_2O_3, both in nitric acid solution, were placed on the filament. After the run the plate transfer technique was used and a twelve-hour transfer was made. Upon development the original plate showed two lines one mass number apart, and the transfer plate showed one line which corresponded to the lower mass line on the original plate. Therefore the higher mass line was the normal $Y^{89}O^+$, and the active line one mass unit lighter was $Y^{88}O^+$. Thus the mass of the 108-day yttrium isotope is 88.

57-Day Yttrium

A 57-day yttrium activity was first observed by Hahn and Strassman[8] who observed this activity among uranium fission products and made chemical identification of the element. Later work on the Manhattan Project[9] showed the emitted beta-particles to have a maximum energy of 1.53 Mev. No accompanying gamma-radiation was observed.[10] Since this activity had been observed only in fission, determination of the mass by formation by known reactions was never accomplished. The fact that the fission yield of this isotope was near the top of the lower fission yield maximum made this type of mass assignment unreliable.

About 8 microcuries of 57-day yttrium, separated from other fission products by Waldo Cohn at the Clinton Laboratories, 3 micrograms of normal Y_2O_3, and 1 microgram of normal SrO, all in nitric acid solution, were placed on the filament. After the run an activity of 33 counts/minute above background at about 50 percent geometry was found on the plate. The position of this activity was located with the counter-slit technique and a scratch was made on the edge of the plate to indicate the position of the activity. After fifty-six hours the plate was developed. It showed lines of masses 86, 87, and 88 (the Sr^+ lines), a line at 105 (the $Y^{89}O^+$ line), and a line at 107. The line at 107 corresponded in position to the scratch on the edge of the plate. It, therefore, was the radioactive line $Y^{91}O^+$. Thus the mass of the 57-day yttrium isotope is 91.

1-Year Ruthenium

One-year ruthenium from fission was first observed by Glendenin.[11] It emits only a very weak beta, decaying to 30-sec. rhodium. This rhodium daughter emits 2.8-Mev and 3.9-Mev betas and 0.3-Mev and 0.8-Mev gamma-rays. It is by this daughter that the ruthenium is usually detected. Steinberg[12] found the fission yield for this isotope to be 0.48 percent and on this basis placed one-year ruthenium at mass 106. Direct measurement by the mass spectrograph has led to the same result.

About 5 microcuries of 1-year ruthenium, separated from a two-year-old fission product mixture by Mr. Robert Schumann of the Metallurgical Laboratory, and 50 micrograms of normal ruthenium, both in hydrochloric acid solution, were placed on the filament. After the run, the plate transfer technique was used and a six-day transfer made. Upon development the original plate showed the normal ruthenium spectrum and also a line at mass 106, two mass numbers above the heaviest normal isotope. The transfer plate showed one line, corresponding to the line at 106. Thus the mass of the 1-year ruthenium isotope is 106.

300-Day Cerium

In a separation of cerium from a fission product mixture which is made a few days after

[6] A. C. Helmholz, Phys. Rev. **62**, 301 (1942).
[7] Downing, Deutsch, and Roberts, Phys. Rev. **60**, 470 (1941).
[8] O. Hahn and F. Strassman, Naturwiss. **28**, 543 (1940).
[9] P. W. Levy, MonP-104, p. 13, April, 1946.
[10] N. E. Ballou, CC-298-D, p. 3, October, 1942.
[11] L. E. Glendenin, Plutonium Project Report, Vol. 9B, 7.18.3.
[12] E. P. Steinberg, CC-2310, p. 106, January, 1945.

irradiation, only two active cerium isotopes should be present in appreciable quantity. These are the 28-day cerium discovered by Pool and Kurbatov,[13] and investigated in fission by Burgus;[14] and the 300-day cerium activity.[15] The 28-day isotope emits a 0.65-Mev beta and a 0.2-Mev gamma,[13] and was known to decay to stable praseodymium. Since praseodymium has only one known stable isotope at mass 141, this was very strong evidence for the assignment of 48-day cerium to mass 141. The 300-day cerium isotope emits a 3.07-Mev beta and a 0.135-Mev gamma.[16] It has been formed only in fission. On the basis of a fission yield of 5.3 percent measured by Rubinson[17] it was assigned to mass 144. Direct measurement gave masses 141 and 144 for these isotopes.

Two hundred and fifty microcuries of fission product cerium, separated from a fission product mixture by Waldo Cohn at Clinton Laboratories, together with 0.3 microgram of normal Nd_2O_3, both in nitric acid solution, were placed on the filament. After the run a transfer plate was made and both transfer and original plate were developed. This showed that there were activities on the plate at masses 157, 159, 160, and 163. Another run was then made, this time using an exposed x-ray film as an ion collector. Five minutes after the run the film was counted and a counting rate of 15,000 counts/minute was observed. The film was then placed against an unexposed photographic plate for twenty minutes. This plate was then developed and showed one line; this served to locate the major activity on the film. Two cuts were then made across the film, each 0.5 mm from the position corresponding to the line. The 1-mm wide center section was counted and the decay observed. The half-life for the short-lived activity was 17.5 ± 0.5 min. Thus the short-lived activity on the plate, the activity which produced the blackening on the twenty-minute transfer plate, was seen to be due to the previously observed 17-minute praseodymium[7] which was known to be a beta-decay daughter of the 300-day cerium. After the praseodymium and the cerium came to equilibrium on the film, the three sections of the film were placed together in their original position and a two-day transfer made. Again the four lines appeared, and the 1-mm strip, with the 300-day cerium, corresponded to the second heaviest of the masses, the one which was identified in the first exposure as 160. Since both praseodymium and cerium ionize with oxygen atoms attached, the mass of 300-day cerium and of 17-minute praseodymium is 144. After the last transfer was taken, the film was cut so that one active line was on each piece of the film. An attempt was made to determine the half-life of each of the activities; but, due to the instability with time of the counter used and due to the scattering of $Ce^{144}O^+$ over the plate, only rough limits could be set. These results were: 157 (40d); 159 (30d); 160 (300 ± 50d); 163 (−). These half-life limits are consistent with an assignment of the mass 157 line to 28-day Ce^{141} with oxygen attached and the mass 159 line to 14-day Pr^{143} with oxygen attached.[18] This sample told nothing of the mass 163 activity except that there was a relatively long-lived fission activity of mass 147. The nature of this activity is described below.

3.7-Year Element 61

A long-lived isotope of element 61 was discovered in fission by Ballou.[19] Seiler and Winsberg[20] give its half-life as 3.7 yr. Marinsky and Glendenin[21] observed its radiation and by aluminum absorption curves gave the maximum energy as 0.20 Mev. They observed no accompanying gamma-radiation. Because this isotope was so long-lived and because of the known masses of the shielding neodymium isotopes, the mass of this isotope was very certainly either 147 or 149. Direct measurement decided in favor of 147.

About 2 microcuries of 3.7-year element 61, separated by resinous column from other fission activities by Glendenin and Marinsky at Clinton

[13] M. L. Pool and J. D. Kurbatov, Phys. Rev. **63**, 463 (1943).
[14] W. H. Burgus, CC-465B, p. 13, February, 1943.
[15] W. H. Burgus, CC-2310, p. 210, January, 1945.
[16] V. A. Nedzel, CC-2283, October, 1944.
[17] W. Rubinson, Plutonium Project Report, Vol. 9B, 7.52.1.
[18] N. E. Ballou, CC-298-D, p. 3, October, 1942.
[19] N. E. Ballou, CC-680, p. 22, May, 1943.
[20] J. A. Seiler and L. Winsberg, Plutonium Project Report, Vol. 9B, 7.54.2.
[21] J. A. Marinsky and L. E. Glendenin, Plutonium Project Report, Vol. 9B, 7.54.1.

Laboratories, together with a 0.3 microgram sample of normal Nd_2O_3, both in nitric acid solution, were placed on the filament. After the run a transfer was made; and, after eighteen hours, both plates were developed. The original plate showed the NdO^+ spectrum (158, 159, 160, 161, 162, 164, and 166), and also a line at 163. This last line corresponded to the single line on the transfer plate. Thus this blackening was due to the $61^{147}O^+$, and the mass of 3.7-year element 61 is 147. Evidently this was the 147 activity observed in the cerium sample.

55-Day Strontium[22]

Four microcuries of 55-day strontium separated from fission products by Mr. Waldo Cohn of the Clinton Laboratories in the form $SrCl_2$, together with 5×10^{-4} ml of $16N$ HNO_3 and 5×10^{-4} ml of $0.1N$ inactive $Sr(NO_3)_2$ solution, were placed on the filament. After running the spectrograph, the plate was placed in a slit counter and moved until a maximum count was obtained. A scratch was made on the plate at the position of maximum activity. Development of the plate showed this scratch to be located one mass unit above the Sr^{88} line, heaviest of the normal strontium isotopes. Thus the mass of 55-day strontium is 89.

25-Year Strontium[23]

A strontium sample was allowed to stand for approximately a year after separation from a fission product mixture. After this length of time the activity in the sample was primarily that of the 25-year strontium and its 60-hr yttrium daughter. Twenty microcuries of this activity in nitrate solution were placed on the filament. After running the spectrograph approximately 250 counts/minute were observed on the plate. After a two-day transfer, lines were observed at masses 89, 90, and 106. The first of these was attributed to the previously discussed Sr^{89} which had not completely decayed from the sample. The other two lines can be attributed to Sr^{90+} and $Y^{90}O^+$, respectively. Three other successive transfers were made and showed the activity at mass 106 to decay at a rate consistent with the known 60-hr. half-life of yttrium. This shows that the 25-year strontium and the 60-hr. yttrium both have mass 90.

40-Hr. Lanthanum and 12.8-Day Barium[24]

Normal barium and about 20 microcuries of barium-lanthanum activity were placed on the filament of the spectrograph. After the run 1500 counts/minute were observed on the photographic plate. This activity was shown by the slit counter to be all at one position on the plate. The decay of this activity with time was observed through the slit counter. The activity observed was the 40-hr. lanthanum and not the 12.5-day barium. This is an expected result because La_2O_3 is ionized much more efficiently by the filament than is BaO. After the decay of the 40-hr. activity had been observed for a period long enough to establish the half-life, the plate was placed against a transfer plate to check the position of the activity. Development of the original plate showed the normal Ba^+ spectrum at masses 134, 135, 136, 137, and 138, and also another line at 156. This 156 line corresponded to the activity as located both by the slit counter and the photographic plate. Since lanthanum oxide is known to emit only ions of the form LaO^+, this line at mass 156 must be due to $La^{140}O^+$ and thus the mass of 40-hr. lanthanum and hence, also, of the daughter 12.8-day barium is 140.

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[22] Stewart, Lawson, and Cork, Phys. Rev. **52**, 901 (1937).
[23] Hahn, Strassman, and Gotte, Abhandl. Preuss. Akad. Wiss., Math.-Naturw. Klasse No. 3 (1942).
[24] O. Hahn and F. Strassman, Naturwiss. **28**, 543 (1940).