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ABSTRACT

In these experiments the isotope ^{255}No, with alpha half-life of 3-1/2 minutes, was used to study the tracer chemistry of element 102. In ion exchange and coprecipitation studies, nobelium did not exhibit the behavior expected for a member of the actinide series in the +3 valence state. Work on elution positions and solubilities of hydroxides, sulfates and fluorides suggests that the +2 oxidation state, predicted to exist in addition to the +3 state for nobelium, was the stable species in aqueous solution. Results of oxidation experiments are presented and preliminary results suggest a potential for the No^{+2} - No^{+3} couple of approximately -1 volt.

I. Introduction

Results of the first[1] and other more recent efforts[2] to study the chemistry of this element suggested the chemical behavior of No to be that of a heavy actinide element in its +3 oxidation state. On the other hand, new results indicated an increasing tendency toward formation of +2 oxidation states with increasing Z by the heavy actinides[3] and this was confirmed by the discovery of the Md^{+2} ion.[4,5] These results suggested that nobelium might exhibit a fairly stable +2 state in addition to the expected +3 state.

The recent discovery of ^{255}No, with an alpha half-life of approximately

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* On leave of absence from the Institute of Nuclear Research, Prague, Czechoslovakia.

3 minutes,[6,7,8] has made it possible to carry out tracer chemistry on element 102.[9] The short half-life and low yield of ^{255}No atoms/experiment compelled us to modify and develop new fast chemical procedures so that the total time necessary for separation, chemical study and preparation of a source suitable for alpha energy analysis would be less that 10 minutes. These procedures involved comparing the chemical behavior of nobelium with tracer quantities of elements of known chemical behavior using both chromatographic methods for the study of single-atom behavior and one-step coprecipitation reactions. As only a few ^{255}No were observed per experiment, it was necessary to repeat each set of experiments 10-20 times in order to obtain statistically significant results. In all, some 490 irradiations were performed.

II. Production and Identification of ^{255}No

The ^{255}No was produced by irradiating a 0.8 mg/cm^2-thick plutonium target supported by a 1-mil thick Be foil with ^{16}O ions from the Berkeley Hilac. The isotopic composition of the target in atom percent was ^{244}Pu - 74.21, ^{242}Pu - 25.32, ^{241}Pu - 0.094, ^{240}Pu - 0.312, ^{239}Pu - 0.064 and ^{238}Pu - 0.002. The beam current was 2 - 4 μamps over an area of 0.2 cm^2. The nobelium atoms recoiling from the target were stopped in He gas and transferred to a platinum catcher foil by gas jet as described elsewhere.[10] The Pt foil was then either alpha-energy analyzed immediately for yield measurements or used for chemical study prior to alpha energy analysis.

The maximum yield was obtained at an oxygen-ion energy of approximately 97 MeV as expected for the ^{244}Pu(^{16}O,5n)^{255}No reaction. The average number of countable atoms at 50% geometry on the catcher foil at the beginning of the chemical operations was determined from 36 yield measurements to be

6.0±0.5 α counts/μampere of beam. Yield checks were made approximately every sixth irradiation.

The ^{255}No was identified by its alpha decay energy using a Frisch-gridded ion-chamber. The alpha spectrum should be complex as alpha decay involves the same odd neutron (N=153) as in ^{251}Cf and ^{253}Fm where several alpha decay groups are spread over 1/2 MeV or more in energy.[11,12] Figure 1 shows a composite alpha spectrum constructed from the yield measurements. Unfortunately, the energy resolution was rather poor due to the intense β-activity produced by the target foil; however, there is good indication of more than one alpha group spread over energies of 7.7 to 8.25 MeV. A decay curve was constructed from the composite data and is shown in Fig. 2. Subportions of the main alpha spectrum gave half-lives in general agreement with the composite value so all alphas from 7.7 to 8.25 MeV in energy were assumed to come from ^{255}No.

In order to determine if other isotopes with similar α-decay energies and half-lives were produced by transfer reactions from our target, e.g., the 8.01-MeV α-particles of ^{215}At associated with the 2.2 minute decay of ^{223}Ac, a ^{240}Pu target was irradiated under similar conditions with ^{16}O. We found the contribution of α-particles to the 7.7 to 8.25-MeV energy range to be < 5% of the ^{255}No alpha decay yield.

III. Chemical Experiments and Results

A. Hydroxide and Oxide Behavior

1. Electrodeposition.

The first evidence of unexpected behavior for No was found during cathodic electrodeposition experiments. In these experiments, the No atoms were washed from the catcher foil with 3 - 200λ portions of saturated NH_4Cl plating solution containing tracer quantities of the radioactive elements to be compared with the No. The electrodeposition was carried out in a quartz cell with a Pt wire anode and Pt plate cathode for 2 minutes at a potential of ~ 5 volts dc and a current density of ~ 1 amp/cm^2. During plating the pH is very high near the cathode and tracers are known to be deposited in approximately inverse proportion to the solubility of their hydroxides.[13] In Table 1 is shown the percent of tracers and nobelium that were plated.* Also shown is the number of ^{255}No alpha decays observed per number of decays expected. The latter was computed for each experiment from the average number of countable atoms given above by allowing for decay during the chemical operations. As shown in Table 1, No is plated with a low yield similar to Ra rather than a high yield as are the +3 actinides, Pu, Th and Pa suggesting a hydroxide solubility akin to the former rather than the latter elements.

TABLE 1

			Percent Plated					Observed/Expected
^{243}Am	^{244}Cm	^{253}Es	^{227}Th	^{239}Pu	^{231}Pa	^{223}Ra	^{255}No	Counts of No
48	48	43	77	51	86	4	4±2	2/76

2. Oxide Behavior.

To further check the solubility of No hydroxide, we studied the coprecipitation behavior of No using the residue adsorption technique.[14,15] The catcher foil was washed with 15λ of a 0.1M HCl solution containing the tracers to be compared with the No plus ~ 1μg each of Ba and La chlorides. Conversion to the oxide was achieved by evaporation to dryness with 25λ of concentrated NH$_4$OH and heating the residue in a Bunsen flame for a few seconds. The

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*In this, and subsequent experiments, the probable error in the tracer percentages is < 10%.

residue was washed 4 times with 50λ of H_2O and both the residue plate and H_2O washings alpha energy analyzed. A summary of some preliminary results obtained by this method is given in Table 2. The data is far from conclusive but No oxide appears to behave more like Ba and Ra oxides than Am or Pb oxides.

TABLE 2

	Percent in Fraction					Observed/Expected Counts of No
Fraction	^{243}Am	^{211}Pb	^{223}Ra	^{133}Ba	^{255}No	
La_2O_3	79	83	61	67	58±15	20/35
BaO	6	11	20	23	29± 10	7/27

Assuming the nobelium was exhibiting a stable +2 valence, attempts were made to oxidize No^{+2} to No^{+3} with HNO_3 and form a less soluble oxide, such as La_2O_3, by evaporation to dryness and conversion of the nitrates to oxides by flaming. The distribution of the various tracers were very similar to those obtained without HNO_3 suggesting no oxidation had taken place and thus a fairly stable +2 state for No.

B. Cation Exchange Columns.

Our attempts to elute No from a heated (80°C), 0.1 cm dia. x 2 cm long, Dowex 50x12 ion-exchange resin column with ammonium alpha-hydroxisobutyrate in the predicted pre-einsteinium elution position[16] were unsuccessful. The procedure was to first wash the No from the catcher foil with 2 drops of eluting solution containing the comparison tracers. After transfer to the column, the method was to elute the tracer +3 transamericium actinides with

8 drops of dilute eluting solution (0.3M, pH 4.0) and then to elute Am and several lower Z elements (Ac, Sr, Pb, Ra and Ce) with 8 drops of concentrated eluting solution (1.9M, pH 4.8). The results given in Table 3 clearly show that No was not eluted before Am.

TABLE 3

Butyrate Fraction	Percent in Fraction ^{243}Am	^{253}Es	^{144}Ce	^{223}Ra	^{255}No	Observed/Expected Counts of No
0.3M	6	43	4	< 0.1	2±1	1/113
1.9M	59	0	60	< 0.1	65±12	52/80

An elution position for No relative to tracer quantities of Y, Sr, Ba and Ra was obtained for a heated (80°C) 0.2 cm diameter by 2 cm long column using the concentrated eluting solution. The composite result for 13 experiments is presented in Fig. 3.

The strontium number, defined as the elution peak position of an element relative to that of Sr, for the elements used in this experiment is shown in Table 4. Strontium numbers reported elsewhere[17] for a similar column using 1.5M,pH 7.0, ammonium lactate are also given in Table 4 for comparison.

TABLE 4

	Element No	Ca	Sr	Ba	Ra
Sr # (This work)	0.35		1.0	3.5	5.7
Sr # (Ref. 17)		0.32	1.0	3.2	6.7

The results show that under these conditions nobelium does not exhibit the slightest resemblance to the +3 actinides; in similar tracer experiments

Es, Cm, Am and Ac were eluted promptly after the first free column volume, e.i., the Y position. This was also the case for Th, Pa, Pb and Ce. The elution of No near the Sr position strengthened our growing suspicion that No was exhibiting a +2 valence.

Unsuccessful attempts were made to oxidize the suspected No^{+2} to No^{+3} and elute it from the ion exchange column in the position predicted for the +3 oxidation state. However, when rapid, oxidizing agents were present in sufficiently dilute concentrations as not to effect the column operation, they were immediately reduced by the hot butyrate solution.

C. Chloride Volatility

In these experiments the volatility of nobelium was compared to the volatility of tracer quantities of Pa, Am, Th, Pb, Ra and Ce by heating the platinum catcher foil to ~ $1000^{\circ}C$ with a Bunsen flame after conversion to the chloride or oxychloride by evaporation to dryness with 25λ of HCl containing the tracers. The results in Table 5 indicate that nobelium does not exhibit an unusually volatile chloride as does Pb.

TABLE 5

Percent Left on Plate						
^{231}Pa	^{243}Am	^{227}Th	^{223}Ra	^{211}Pb	^{255}No	Observed/Expected Counts of No
100	76	82	87	23	88±31	14/17

D. Fluoride Behavior

For the study of the coprecipitation behavior of No fluoride, we used the residue adsorption technique described above. A drop of 0.1M HCl containing the tracers to which No was to be compared plus ~ 5μg each of the various charge-state carriers, Ba, La and Zr, was used to dissolve the No atoms from the catcher foil. Two drops of 40% HF were added and taken to dryness to convert to the fluorides. The plate was washed 4 times with 50λ of H_2O and both residue plate and H_2O washes were alpha energy analyzed. The results are given in Table 6 and suggest that the solubility of No fluoride is more like BaF_2 than LaF_3.

TABLE 6

Fraction	Conditions	Percent in Fraction					Observed/ Expected Counts of No
		^{243}Am	^{211}Pb	^{223}Ra	^{133}Ba	^{255}No	
LaF_3	no oxidation	60	54	15	13	7±3	6/98
BaF_2		11	24	37	44	56±10	48/87
LaF_3	Ce^{+4} oxidation	34	51	18	23	48±8	63/134
BaF_2		17	28	33	31	31±6	35/117

Assuming that the nobelium was exhibiting a +2 valence under the above conditions, attempts were made to oxidize the No^{+2} to No^{+3} which should form a less soluble fluoride. The procedure was the same as described above except the oxidant, ceric nitrate, was substituted for the Zr. As seen in Table 6, after oxidation with Ce^{+4} the distribution was in favor of the LaF_3 phase. However, the results suggest that either the nobelium fluoride is slightly more soluble than Am fluoride or not all the No was oxidized to the +3 state.

The behavior of No fluoride after oxidation appears to be better explained by the formation of NoF_3 rather than NoF_4. Under these dilute conditions, CeF_4 was found to have a high solubility. If it were formed, NoF_4

might be expected to be as soluble as CeF_4 and ZrF_4.

E. Sulfate Behavior

1. $SrSO_4$ Column

Recent work has shown that ^{90}Y can be separated from ^{90}Sr at room temperature by elution from a $SrSO_4$ column using 0.5$\underline{N}$ H_2SO_4.[18] In general it appears that the more soluble sulfates are eluted before the less soluble ones. We used a similar column for the study of the behavior of nobelium sulfate.

We found that the sulfate column behavior was similar to the organic cation exchange column in that individual actinides were separated from each other with the higher Z actinides eluting first. Figure 4 shows elution curves obtained at room temperature for Am, Cm, Es, Sr, Y using 0.2 cm dia. x 1.2 cm-long $SrSO_4$ column and 6$\underline{N}$ H_2SO_4 as eluant. Ba and Ra were run at the same time but were not eluted in 100 drops.

In each experiment the No, tracer activities to which No was to be compared, and ~ 5μg each of Zr and La were converted to the sulfate form on the platinum catcher foil by evaporation to dryness with 1$\underline{M}$ H_2SO_4. The mass of Zr and La added was the same as the mass of Ce^{+4} and Ce^{+3} used in later oxidation experiments in order to duplicate the mass effects on the column. The No and other elements were dissolved from the foil with 6$\underline{N}$ H_2SO_4 and transferred to the 0.2 cm x 1 cm-long $SrSO_4$ column and the elution carried out with 6$\underline{N}$ H_2SO_4. In all runs we found that < 5% of the No was left on the catcher foil after transfer. Time and counter limitations made the elution in fractions rather than dropwise necessary. The results are given in Table 7 under conditions of no oxidation and show that nobelium was strongly adsorbed on the column and eluted after Am and Es.

TABLE 7

Fraction (Number of Drops)	Conditions	Percent in Fraction ^{253}Es	 ^{243}Am	 ^{255}No	Observed/Expected Counts of No
1-10	no oxidation	38	10	2±1	1/122
11-22		5	36	13±4	9/75
1-10	Ce^{+4} oxidation	47	3	61±15	27/44
11-22		3	28	3±3	0/34
1-7	Ce^{+4} oxidation (in 1$\underline{M}$ HNO_3) cold	33	16	41±10	23/57
8-17		7	29	13±6	5/45
18-27		2	2	3±3	0/35

Similar experiments were carried out under oxidizing conditions using Ce^{+4} and the results given in Table 7. In the experiments with oxidation, the No was eluted with Es and probably before Am. This apparent change in solubility of nobelium sulfate is consistent with a change in valence state from +2 to +3.

2. $BaSO_4$ Column

Experiments using a 0.3 cm x 1 cm $BaSO_4$ column were also carried out in a manner similar to the $SrSO_4$ column. The No was washed from the catcher foil with 1 drop each of 1$\underline{M}$ HCl and 1$\underline{N}$ H_2SO_4 containing the tracers and ~ 15μg each of Ba and La chlorides as carriers and the drop transferred to the column. Elution was carried out with 6$\underline{M}$ HCl and the first 10 drops were dried and alpha energy analyzed. The results are given in Table 8.

TABLE 8

Fraction (Number of Drops)	Conditions	Percent in Fraction ^{243}Am	^{253}Es	^{223}Ra	^{255}No	Observed/Expected Counts of No
1-10	no oxidation	61	51	< 1	26±8	11/45
1-10	Ce^{+4} oxidation	63	59	< 1	55±12	31/58

Similar experiments were carried out with 15μg of the oxidant Ce^{+4} added to the transfer solution. The results run under these oxidizing conditions are also shown in Table 8. The results are in general agreement with those of the $SrSO_4$ column. However, it appears from the non-oxidation experiments that the solubility of $NoSO_4$ may be between that of Am and Es, and Ra.

IV. Discussion

The results presented in this work indicate a very interesting behavior by nobelium when compared to other elements of the actinide family. Under the conditions of our experiments, nobelium exhibited the following properties relative to the other heavy actinides in +3 state:

1) Its hydroxide or oxide has a high solubility.
2) Its fluoride has a high solubility.
3) Its sulfate has a low solubility.
4) Nobelium did not elute from a Dowex 50 x 12 ion exchange column with ammonium α-hydroxisobutyrate in the position predicted for the +3 ion. In fact, No was eluted near Sr^{+2} and about the same position as Ca^{+2} under conditions where all other actinides were

eluted immediately. This behavior shows that previous claims that No is eluted in the pre-Es position must be in error.[1]

5) Though nobelium chloride exhibits a low volatility, probably in the range of the +3 actinides, we do not agree with the generalizations made in Ref. 9 that the chemical behavior of nobelium is similar to those of the normal +3 actinides.

6) In two experiments, fluoride coprecipitation and sulfate column, there were strong indications that nobelium was oxidized by Ce^{+4} in both $1\underline{N}$ H_2SO_4 and $1\underline{M}$ HNO_3. Preliminary results, though as yet not conclusive, indicate that No is not oxidized by Ag^+ or HNO_3 which suggests that the potential of the No^{+2} - No^3 couple is around -1 volt.

We feel that the best interpretation of our results is that the divalent ion is the most stable species for nobelium in aqueous solution and thus it exhibits a substantially different chemical behavior from the other actinides. This would appear to confirm the prediction made by Seaborg in 1949[20] of a possible stable +2 state for element 102 due to the special stability of the $5f^{14}$ electronic configuration.

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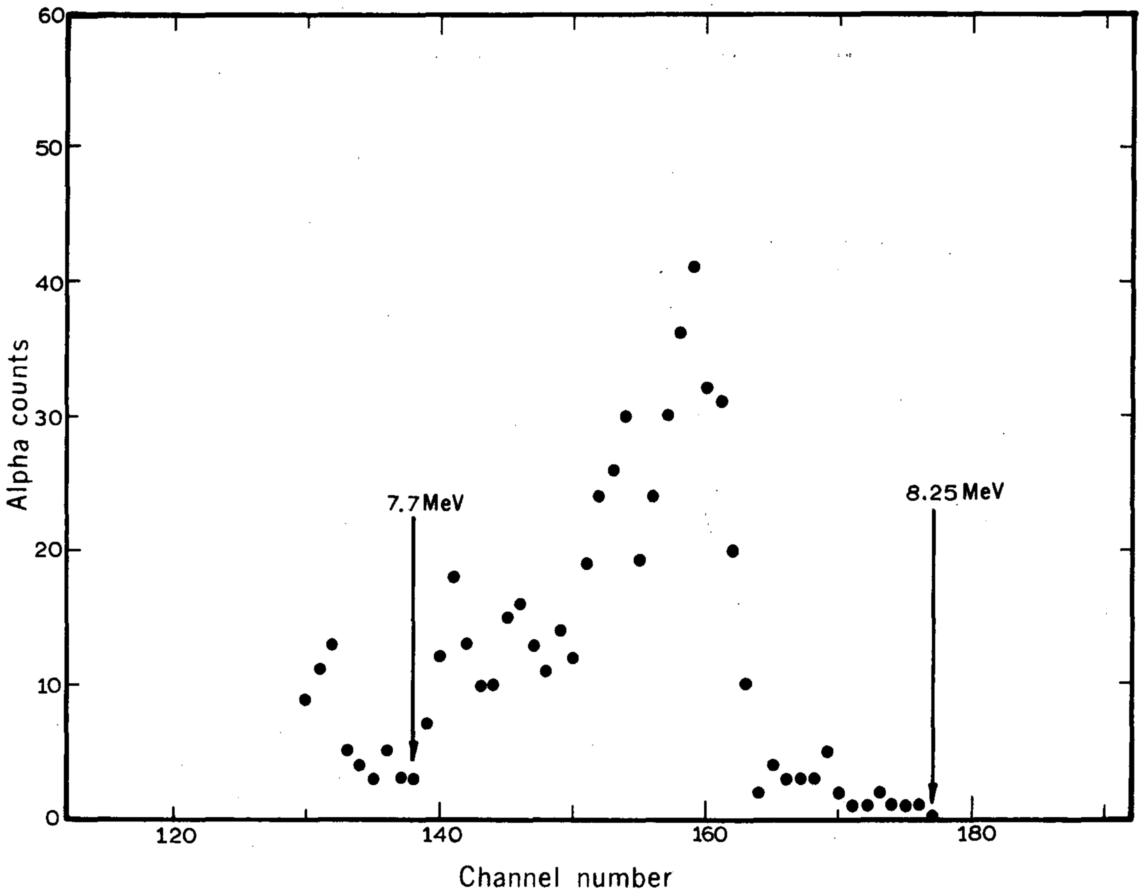
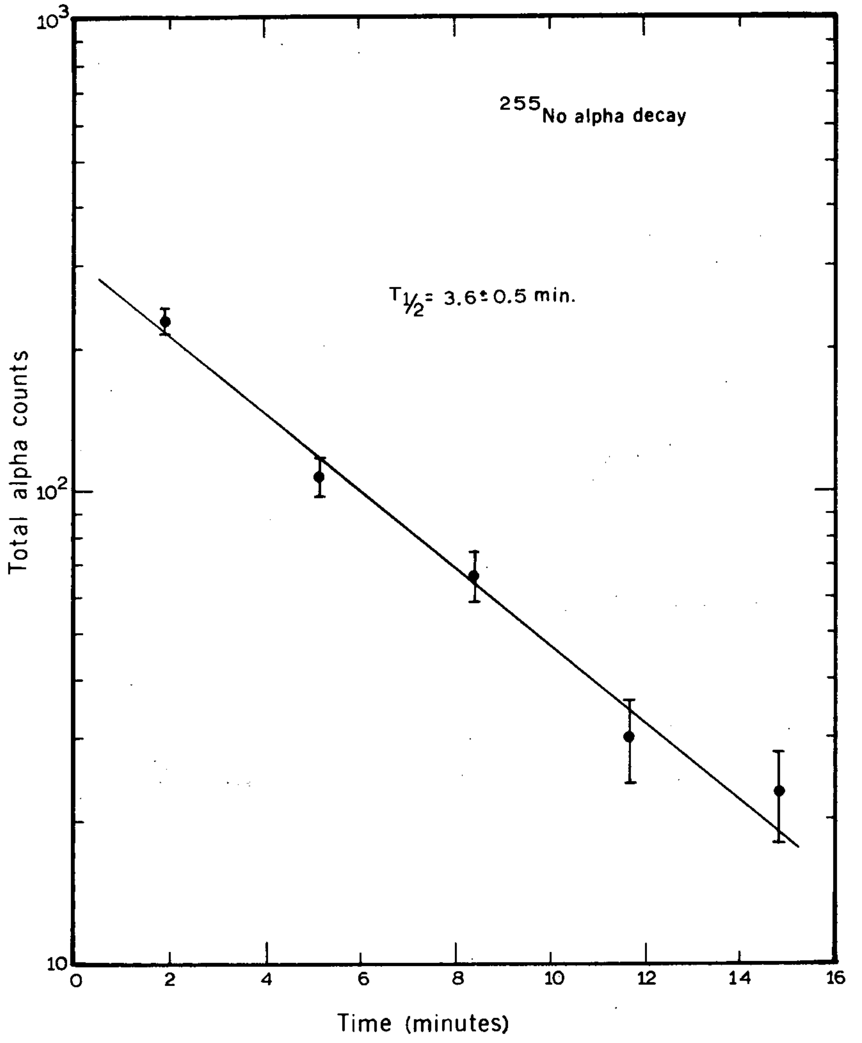


XBL 681 4437

Fig. 1. Alpha particle spectrum of Nobelium constructed from 36 yield measurements taken with a Frisch gridded ion-chamber.



XBL 681 4438

Fig. 2. Decay curve for ^{255}No constructed from 36 yield measurements.

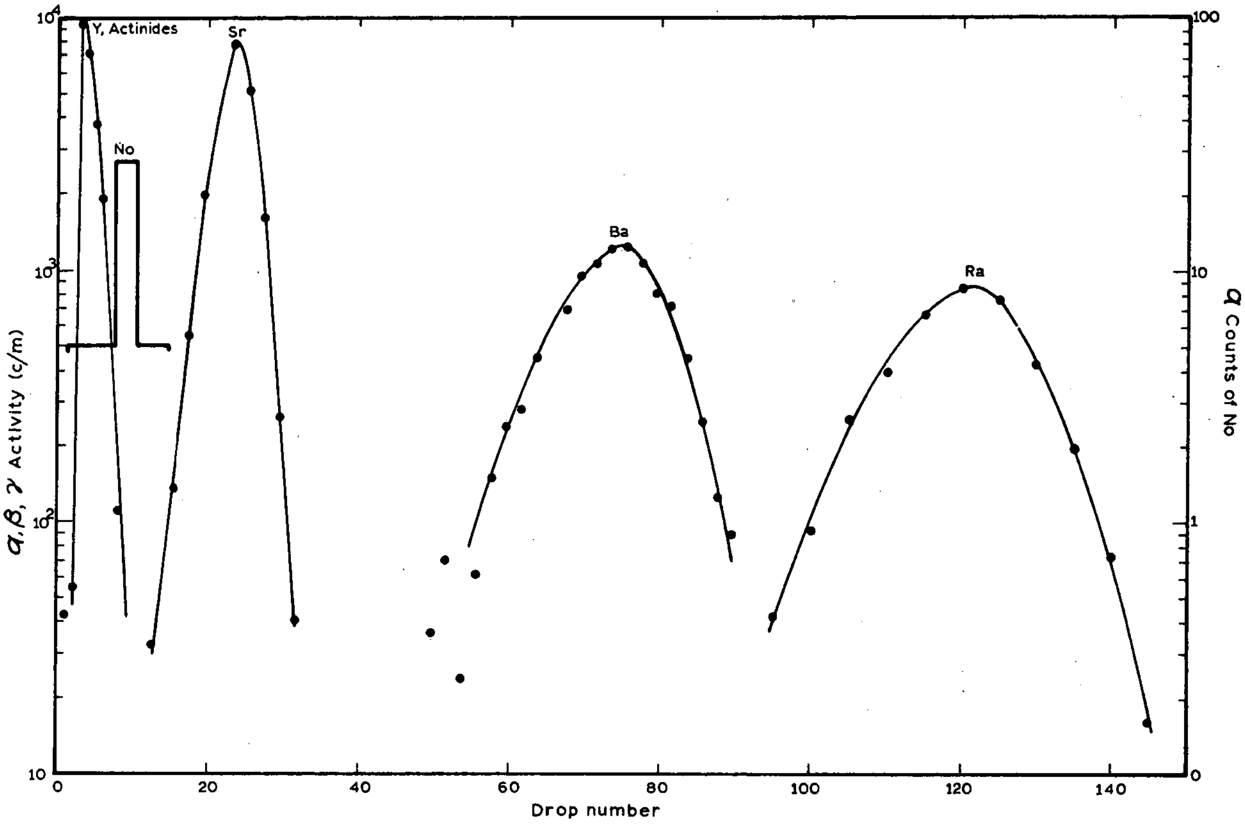


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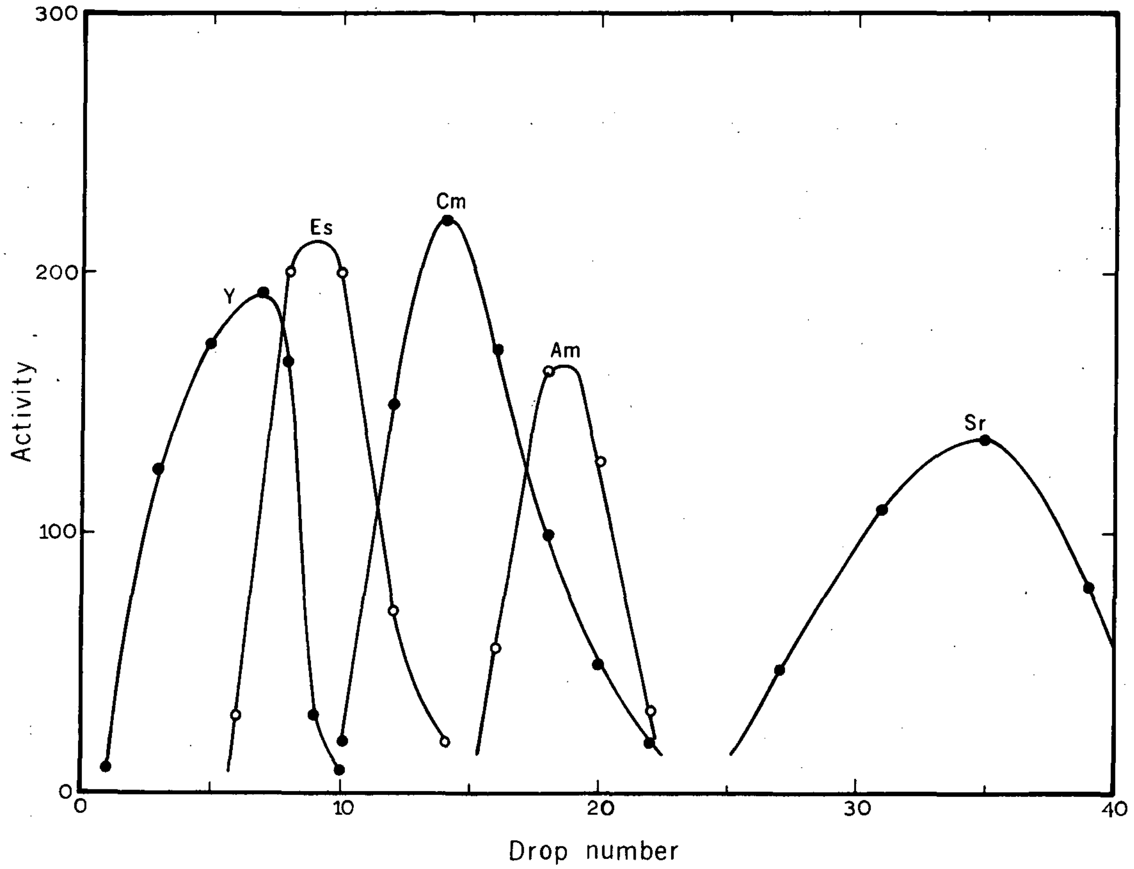
Fig. 3. Elution of No from a Dowex 50 × 12 cation exchange column with 1.9M, pH 4.8, ammonium α-hydroxyisobutyrate.



XBL 681 4439

Fig. 4. Elution of Am, Cm, Es, Sr and Y from a $SrSO_4$ column with 6N H_2SO_4.