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Title
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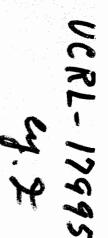# NOBELIUM: TRACER CHEMISTRY OF THE DIVALENT AND TRIVALENT IONS (1)

Jaromir Maly (2), Torbjorn Sikkeland, Robert Silva and Albert Ghiorso

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Abstract   In the absence of oxidizing or reducing agents the chromatographic and coprecipitation behavior of element 102 is similar to that of the alkaline earth elements. After oxidation with ceric ions, the behavior is that expected of a trivalent actinide. Our conclusion is that nobelium is the first actinide for which the +2 oxidation state is the most stable species in aqueous solution.

Introduction

Results of the first attempts (3) and other more recent efforts (4) to study the chemistry of element 102 suggested the chemical behavior of nobelium to be that of a +3 actinide element. On the other hand, new results indicated an increasing tendency toward formation of +2 states with increasing Z by the heavy actinides (5) and this was confirmed by the discovery of the Md^{+2} ion (6,7). These results suggested that nobelium might exhibit a fairly stable divalent state in addition to the expected trivalent state.

The recent discovery of ^{255}No, with an alpha half-life and decay energy of approximately 3 minutes and 8.1 MeV (8,9,10), has made it possible to carry out tracer chemistry on element 102 (11). The short half-life and low yield of ^{255}No atoms per experiment compelled us to modify and develop 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 than 10 minutes. These procedures included chromatographic methods for the study of single-atom behavior and one-step coprecipitation reactions. As only a few ^{255}No decays were observed per experiment, it was necessary to repeat each set of experiments 10-20 times in order to obtain statistically significant results.

Experimental Procedures and Results

a. Production and Identification

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 (9,12). 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 measurements, to be 6.0 ± 0.5 α cts/μamp of beam.

The ^{255}No was identified by its alpha decay energy. The alpha spectrum

is known to be complex and there is good indication of more than one alpha

group spread over energies of 7.7 to 8.25 MeV. A composite decay curve of

this energy range was constructed from 36 measurements and gave a half-life of

3.6 ± 0.5 minutes. 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.

b. Electrodeposition

The first evidence of unexpected behavior for No was found during

cathodic electrodeposition experiments using standard procedures (13). In

these experiments the No atoms were washed from the catcher foil with a

saturated NH_4Cl plating solution containing tracer quantities of the radio-

active elements to be compared with the No. 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. In Table 1 is

shown the percent of tracers and nobelium that were plated (14). 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, Th and Pa suggesting a hydroxide solubility

akin to the former rather than the latter elements.

c. Chloride Volatility

In these experiments the volatility of nobelium chloride was compared

to the volatility of tracer quantities of Pa, Am, Th, Pb and Ra by heating

the platinum catcher foil to ~ 1000°C with a Bunsen flame after conversion to

the chlorides by evaporation to dryness with HCl. The results in Table 1

indicate that nobelium does not exhibit an unusually volatile chloride as does

Pb.

d. Cation Exchange Column

Our attempts to elute No from a heated (80°C), Dowex 50x12 ion exchange

resin column with ammonium alpha-hydroxyisobutyrate in the predicted

preeinsteinium elution position (15) were unsuccessful. The procedure was to

first elute the tracer +3 actinide ions with Z higher than Am with 8 drops of

dilute eluting solution ($0.3\underline{M}$, pH 4.0) and then to elute Am and several lower

Z elements (Pb, Sr, Ra, Ac and Ce) with 8 drops of concentrated eluting solution

($1.9\underline{M}$, pH 4.8). The results given in Table 2 clearly show that No was not

eluted before Am.

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. 1. The results show that under these conditions nobelium

does not exhibit the slightest resemblance to the +3 actinides, for in similar

tracer experiments, Es, Cm, Am and Ac were eluted in the Y position which is

promptly after the first free column volume. 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 predicted +3 position, but when rapid oxidizing agents such as Ce^{+4} were present in sufficiently dilute concentrations/ so as not to effect the column operation, they were immediately reduced by the hot butyrate solution.

e. Fluoride Behavior

For the study of the coprecipitation behavior of No fluoride, we used the residue adsorption technique (16,17). A drop of $0.1\underline{M}$ HCl containing the tracers to which No was to be compared plus $\sim 5\mu g$ 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 to convert to the fluorides and taken to dryness. The plate was then washed with H_2O several times and both residue plate and H_2O washes were alpha energy analyzed. The results are given in Table 2 and suggest that the solubility of No fluoride is more like BaF_2 than LaF_3.

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 2, after oxidation with Ce^{+4} the distribution was in favor of the LaF_3 phase.

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.

f. Sulfate Behavior

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. In each experiment the No, tracer activities to which No was to be compared, and $\sim$ 5μg each of Zr and La were converted to the sulfate form on the platinum catcher foil by evaporation to dryness with $1\underline{N}$ 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 washed from the foil with $6\underline{N}$ H_2SO_4 and transferred to the 0.2 cm dia. x 1 cm long $SrSO_4$ column and the elution carried out with $6\underline{N}$ H_2SO_4. Time and counter limitations made the elution in fractions rather than dropwise necessary. The results are given in Table 2 and show No to be more strongly adsorbed on the column than Es and Am.

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

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 their +3 state:

1) Its hydroxide or hydrous 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 50x12 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 (3).

5) Though No chloride exhibits a low volatility, probably in the
   range of the +3 actinides, we do not agree with the generalization
   made in Ref. 19 that the chemical behavior of nobelium is similar
   to +3 actinides.

6) In two types of experiments, fluoride coprecipitation and sulfate
   column, there were strong indications that nobelium was oxidized
   by Ce^{+4} to a form where it behaved like a trivalent heavy actinide
   (Ce^{+3} - Ce^{+4} couple ~ -1.5 volts).

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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1. The work discussed in this article was done under the auspices of the U. S. Atomic Energy Commission.

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Table 1. Results of Electrodeposition (A) and Chloride Volatility (B) Experiments.

Experiment	^{253}Es	^{243}Am	^{231}Pa	^{227}Th	^{211}Pb	^{223}Ra	^{255}No	Observed/Expected Counts of No
			Percent in Fraction					
A	43	48	86	77	--	4	4±2	2/76
B	--	76	100	.82	23	87	88±31	14/17

Table 2. Results of Elution from Cation Exchange Column with ammonium α-hydroxisobutyrate(A), Fluoride Coprecipitation with La and Ba Carrier (B), and Elution from $SrSO_4$ column with $6\underline{N}\ H_2SO_4$ (C).

Experiment-Fraction	Oxidizing Conditions	Percent in Fraction					Observed/Expected Counts of No
		^{253}Es	^{243}Am	^{223}Ra	^{133}Ba	^{255}No	
A $\{$ 0.3$\underline{M}$	no oxidation	43	6	<0.1	--	2±1	1/113
1.9$\underline{M}$		0	59	<0.1	--	65±12	52/80
B $\{$ LaF$_3$	no oxidation	--	60	15	13	7±3	6/98
BaF$_2$		--	11	37	44	56±10	48/87
LaF$_3$	Ce^{+4} oxidation	--	34	18	23	48±8	63/134
BaF$_2$		--	17	33	31	31±6	35/117
C $\{$ Drop No. 1-10	no oxidation	38	10	< 1	--	2±1	1/122
11-22		5	36			13±4	9/75
1-10	Ce^{+4} oxidation	47	3	< 1	--	61±15	27/44
11-22		3	28			3±3	0/34
1-7	Ce^{+4} oxidation	33	16		--	41±10	23/57
8-17		7	29	< 1		13±6	5/45
18-27		2	2			3±3	1/35

Figure Caption

Fig. 1   Elution of nobelium from a heated (80°C), Dowex 50x12 cation

exchange column with 1.9$\underline{M}$, pH 4.8 ammonium α-hydroxyisobutyrate.

Fig. 1