Nobelium: Tracer Chemistry of the Divalent and Trivalent Ions

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. Nobelium is the first actinide for which the +2 oxidation state is the most stable species in aqueous solution.*

Earlier studies (*1*) of the chemistry of element 102 suggest that the chemical behavior of nobelium resembles that of a + 3 actinide element. On the other hand, new results indicate an increasing tendency toward formation, with increasing *Z*, of + 2 states by the heavy actinides (*2*), which is confirmed by discovery of the Md^{2+} ion (*3*). These results suggest that nobelium may exhibit a stable divalent state in addition to the expected trivalent state.

The recent discovery of ^{255}No, with an alpha half-life of 3 minutes and alpha decay energy of 8.1 Mev (*4, 5*), has enabled application of tracer chemistry to element 102 (*6*). The short half-life and low yield of ^{255}No atoms per experiment compelled us to develop fast chemical procedures so that the total time necessary for separation, chemical study, and preparation of a source suitable for analysis of alpha energy would be less than 10 minutes. These procedures included chromatographic methods for the study of single-atom behavior and one-step coprecipitation reactions. Because only a few ^{255}No decays were observed per experiment, we had to repeat each set of experiments from 10 to 20 times in order to obtain results that were statistically significant.

The ^{255}No was produced by irradiation of a plutonium target, 0.8 mg/cm² in thickness and supported by a 25.4-μ Be foil, with ^{16}O ions from the Berkeley HILAC (Heavy-Ion Linear Accelerator). The isotopic composition of the target was (atom percentages) ^{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 to 4 μamp over an area of 0.2 cm². The nobelium atoms recoiling from the target were stopped in helium and transferred to a platinum catcher foil by gas jet (*5, 7*). The ^{255}No was identified by its alpha-decay energy. The maximum yield was obtained at an oxygen-ion energy of approximately 97 Mev as expected for the reaction $^{244}Pu(^{16}O, 5n)^{255}No$. From 36 measurements the average number of countable atoms at 50-percent geometry on the catcher foil at the beginning of the chemical operations was determined to be 6.0 ± 0.5 alpha counts per microampere of beam.

The first evidence of unexpected behavior for No was found during cathodic-electrodeposition experiments using standard procedures (*8*); the No atoms were washed from the catcher foil with a saturated NH_4Cl plating solution containing tracer quantities of the radioactive elements to be compared with the No. The *p*H during plating is very high near the cathode, and tracers are deposited in approximately inverse proportion to the solubilities of their hydroxides; Table 1 shows the percentages of tracers and nobelium that were plated (*9*), together with 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 by allowing for decay during the chemical operations. The fact that No is plated with a low yield suggests hydroxide solubility similar to that of Ra rather than the other actinides.

Our attempts to elute No from a heated (80°C) Dowex 50 × 12 column of ion-exchange resin with ammonium alpha-hydroxyisobutyrate in the predicted pre-einsteinium elution position (*10*) were unsuccessful. The elution was carried out in two fractions: five column volumes of dilute elutriant (0.3*M*, *p*H

Table 1. Summary of results of experiments with electrodeposition, cation-exchange columns, and coprecipitation.

Fraction, drops (No.)	Oxidizer	Percentages in fractions				Counts of No (obs./pred.)
		^{253}Es	^{243}Am	^{223}Ra	^{255}No	
		Electrodeposition				
Electrodeposited	None	43	48	4	4 ± 2	2/76
		Cation-exchange column				
0.3*M* Butyrate	None	43	6	< 0.1	2 ± 1	1/113
1.9*M* Butyrate		0	59	< .1	65 ± 12	52/80
		Fluoride coprecipitation				
LaF_3	None		60	15	7 ± 3	6/98
BaF_2			11	37	56 ± 10	48/87
LaF_3	Ce^{4+}		34	18	48 ± 8	63/134
BaF_2			17	33	31 ± 6	35/117
		Strontium sulfate column				
1–10	None	38	10	< 1	2 ± 1	1/122
11–22		5	36	< 1	13 ± 4	9/75
1–10	Ce^{4+}	47	3	< 1	58 ± 10	54/94
11–22		3	28	< 1	5 ± 3	3/74

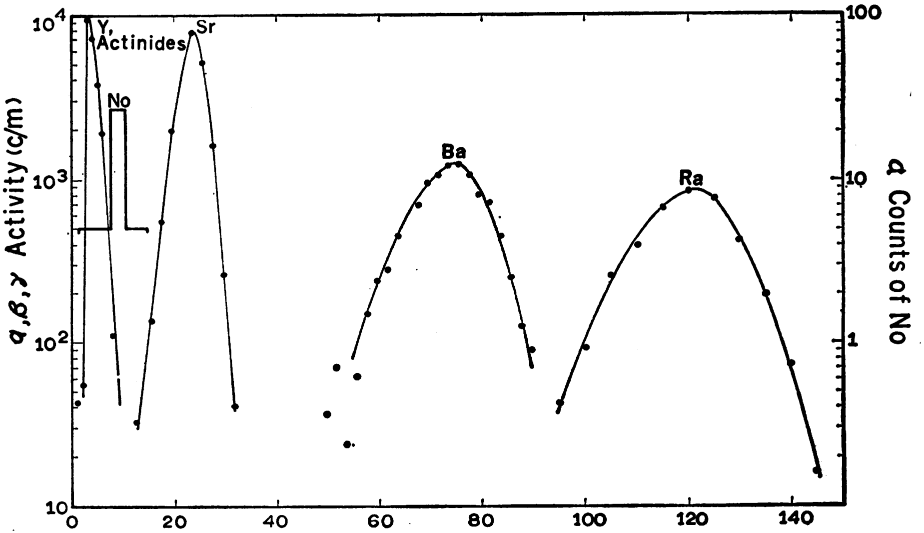

Fig. 1. Elution of nobelium from a heated (80°C) Dowex 50 × 12 cation-exchange column with 1.9*M* ammonium α-hydroxyisobutyrate (*p*H 4.8).

4.0), followed by an equal volume of concentrated elutriant (1.9*M*, *p*H 4.8). The results (Table 1) clearly show that No does not elute before Es.

An elution position for No relative to tracer quantities of Y, Sr, Ba, and Ra was obtained for a heated (80°C) column, 0.2 cm in diameter by 2 cm long, with the concentrated elution solution. The composite result for 13 experiments appears in Fig. 1. 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 in the Y position, which is promptly after the first free column volume; the same was true for Th, Pa, Pb, and Ce.

For study of the coprecipitation behavior of nobelium fluoride we used the residue-adsorption technique (*11*). A drop of 0.1*M* HCl containing the tracers to which No was to be compared, plus about 5 μg of 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-percent HF was added for conversion to the fluorides, and the solution was taken to dryness. The plate was then washed with H_2O, and both residue plate (LaF_3 fraction) and H_2O washes (BaF_2 fraction) were analyzed. The results (Table 1) suggest that the solubility of nobelium fluoride is more like that of BaF_2 than of LaF_3.

Assuming that the nobelium was exhibiting a +2 valence under the above conditions, we attempted to oxidize the No^{2+} to No^{3+} which should form a less soluble fluoride. The procedure was the same as that just described except that the oxidant ceric nitrate was substituted for the Zr. After oxidation with Ce^{4+}, the distribution was in favor of the LaF_3 phase (Table 1).

Yttrium-90 can be separated from ^{90}Sr at room temperature by elution from a $SrSO_4$ column with H_2SO_4 (*12*). Generally the more soluble sulfates are eluted before the less soluble ones. We used a similar column for study of the behavior of nobelium sulfate; in each experiment the No, tracer activities to which No was to be compared, and about 5 μg each of Zr and La were converted to the sulfate form on the platinum catcher foil and transferred to the column in the elutriant, 6*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 elution from a column 0.2 cm in diameter by 1 cm long was carried out in two fractions; the results (Table 1) show No to be more strongly adsorbed on the column than are Es and Am.

Similar experiments under oxidizing conditions used Ce^{4+} (Table 1); 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.

These tracer experiments show that the divalent ion is the most stable species for nobelium in aqueous solution; thus the element exhibits chemical behavior substantially different from those of the other actinides. This finding appears to confirm Seaborg's prediction in 1949 (*13*) of a possible stable +2 state for element 102, due to the special stability of the $5f^{14}$ electronic configuration.

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Kinetics of Protein Synthesis in Enucleate Frog Oocytes

Abstract. *Kinetics of protein synthesis were measured in oocytes of* Rana pipiens *enucleated at various times during and following pituitary-induced maturation. These enucleated oocytes were capable of the same rate of protein synthesis as nucleated controls, even when rates were measured many hours after enucleation.*

In amphibians, full-grown oocytes result from an extended period of oogenesis, during which synthetic activity is intense and the oocytes undergo extensive growth. Throughout this period, the oocytes remain in prophase of the first meiotic division. At the end of oogenesis, the full-grown oocytes remain essentially dormant in the ovary until they are stimulated to continue the developmental process. In response to hormone stimulation, synthetic activity and meiosis resume, ovulation occurs, and the eggs undergo cytoplasmic maturation; that is, they acquire the ability to be fertilized and continue development.

During oogenesis, oocytes of *Xenopus laevis* synthesize and accumulate a significant quantity of template-active RNA which persists in the full-grown ovarian oocyte (*1*). They also are reported to synthesize appreciable amounts of DNA-like RNA during the period of ovulation and maturation (*2*). Ovulated, but unfertilized, frog eggs reportedly contain RNA capable of stimulating protein synthesis in vitro (*3*). Several lines of evidence (*4*) indicate that amphibian development can continue at least to the blastula stage in the absence of a functional nucleus. And, activated, enucleated eggs of *Rana pipiens* are as capable of protein synthesis as fertilized controls (*5*). These reports suggest that the amphibian egg, prior to fertilization, synthesizes and accumulates long-lived gene products used later in development.

Protein synthesis is initiated in *R. pipiens* oocytes prior to fertilization or artificial activation. Initiation results from hormone stimulation in the adult female (*6*). We now describe the effect on protein synthesis of enucleation at various times during the hormone-induced maturation period. Our purpose was to identify possible intervals during this period in which nuclear transcription may be obligatory for subsequent protein synthesis.