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DISCLAIMER

Dedicated to Earl K. Hyde on the Occasion of his Retirement from the Lawrence Berkeley Laboratory.

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Abstract

Studies of the aqueous phase chemistry of hahnium (element 105) were performed on 34-s ^{262}Ha produced by the ^{249}Bk(^{18}O,5n) reaction. The reaction products were subjected to various rapid aqueous phase chemical separation procedures. ^{262}Ha was identified by measuring the energy and time distribution of the alpha particles and fission fragments emitted in its decay. Time-correlated pairs of alpha particles from the decay of ^{262}Ha and its 4.3-s daughter, ^{258}Lr, were also measured. Hahnium was found to adhere to glass surfaces upon fuming with concentrated nitric acid, a property very characteristic of the group 5 elements, niobium and tantalum. In other experiments, the

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*Visiting Miller Research Professor, Berkeley, spring 1987 extraction behavior of hahnium from mixed nitric acid / hydrofluoric acid solutions into methyl isobutyl ketone was found to be different from that of tantalum.

1. Introduction

Expected Electronic Structure of Aqueous Hahnium Ions

The expected ground state electronic configuration of hahnium (element 105) is $[Rn]5f^{14}6d^{3}7s^{2}$. The ionization of hahnium in aqueous solution is expected to stop with the $[Rn]5f^{14}$ core intact, leading to Ha^{5+}, analogous to Ta^{5+} (with the $[Xe]4f^{14}$ configuration). The 5+ oxidation state probably exists in aqueous solution as a hydrolyzed or complexed species, such as MO^{2}. The aqueous phase chemical properties of hahnium would therefore be expected to be analogous to those for the group 5 elements. Trends in chemical properties between niobium and tantalum are expected to continue, allowing extrapolation to the chemical properties of hahnium as the heaviest group 5 element. However, relativistic effects have been predicted to play an increasingly important role in determining the chemical properties of the heaviest elements [1-3]. These relativistic effects cause significant contraction of radii and strong stabilization of the low spin electronic orbitals. In the case of element 105, the relativistic stabilization of the 7s electrons may be strong enough to allow them to remain, leading to Ha^{3+} with a $[Rn]5f^{14}7s^{2}$ configuration.

The calculations of Desclaux [4] indicate that the existence of Ha^{3+} seems unlikely under all but very strongly reducing conditions. In these calculations, 7s electrons are found to be only slightly more bound than are the 6d electrons. The removal of the 6d electrons from the neutral hahnium atom should have little effect on the binding energies of the 7s electrons because the shielding of the nuclear charge from the 7s by the 6d electrons is expected to be small. For this reason, under conditions in which the 6d electrons are removed, the 7s electrons would also be expected to be removed.

Previous Chemical Studies (Gas Phase Thermochromatography)

The only studies of the chemistry of element 105 published so far were performed by Zvara et al. [5,6] using gas phase thermochromatography on the relatively volatile bromide and chloride complexes. They used the $^{243}Am(^{22}Ne,4\text{-}5n)$ reaction to produce 2-s $^{261-260}Ha$ which they detected by spontaneous fission (SF) decay. Because the activity in these experiments was measured by checking the position of fission tracks in track detectors along the thermochomatographic column after the completion of the bombardments, it is not clear that the activity observed was exclusively due to the decay of isotopes of element 105. Furthermore, the adsorption range of the activity, which was similar to that for isotopes of hafnium, was interpreted by Zvara et al. as being the expected position of eka-tantalum. However, a quite different interpretation is put forth by Keller and Seaborg [7] and also by Hyde, Hoffman, and Keller [8] who suggest that the gas thermochromatography results indicate that hahnium is behaving more like the group 4 element, hafnium, or the lightest member of group 5, vanadium, than like niobium or tantalum.

Expected Aqueous Phase Chemical Properties of Hahnium

A different approach for characterizing the chemistry and establishing the position of of a new element in the periodic table is the study of its behavior in aqueous solutions relative to the established behavior of known elements. Due to the lack of any pertinent information for hahnium, we decided to attempt a first investigation of its aqueous chemistry. A large variety of techniques could be used to prove the classification of hahnium as a group 5 element and to search for deviations from the systematics of the periodic table due to relativistic effects. The choice of experimental techniques is limited, however, by the short half-lives and low production rates of hahnium isotopes. For our studies, we selected two approaches which are based on properties which are very characteristic of group 5 elements. These approaches led to procedures which could be performed on a short time scale and could be repeated frequently in order to obtain sufficient counting statistics.

The first approach used the strong adsorption of the group 5 elements on glass surfaces from strong nitric acid solutions. Efficient adsorption of carrier-free niobium dissolved in 12 M nitric acid has been observed in rapid filtration through glass fiber filters [9]. This behavior has been interpreted as a rapid ion exchange reaction between the Si-OH groups at the glass surface and the simple cationic species of niobium formed in strong acids. (At lower acid concentrations, polymeric species dominate.) The rapid sorption reaction has been used for the selective separation of short-lived niobium isotopes from fission product mixtures [10,11]. Although pertinent information was not available for tantalum, the adsorption of the pseudo-group 5 element, protactinium, from strong acid solution on different materials [12] gave evidence that the heavier members of the fifth group may also follow this trend. Therefore, it was expected that the adsorption of hahnium on glass surfaces could be used as a rapid and characteristic separation procedure.

In the second approach, the extraction of hahnium from fluoride solutions into an organic solvent was attempted. The extraction of niobium and tantalum from acidic fluoride solutions into methyl isobutyl ketone (MIBK) is well known, and has been used as a separation and purification process for these elements [13-15]. Tantalum extracts under a broader range of conditions than does niobium. If this group 5 trend continues, hahnium should also form extractable species and be quantitatively extracted under the same conditions as tantalum is extracted.

Nuclear Decay Properties of ^{262}Ha

There have been a number of studies of the decay of ^{262}Ha [16-21]. The ^{262}Ha half life is about 34 s, and its alpha-decay energies are fairly well known. A unique identification can be made on the basis of the detection of an alpha particle from the decay of ^{262}Ha followed closely in time by an alpha particle from its 4.3-s daughter activity, ^{258}Lr. A summary of the alpha-decay energies and relative abundances [22] is given in table 1.

A spontaneous fission activity with a half-life similar to that for the alpha activity assigned to ^{262}Ha has been observed by several groups [16-21] in the same reactions used to produce the alpha activity. It is possible that this is due to a SF branch in ^{262}Ha or to the fission decay of its electron-capture daughter, 60-ms ^{262}Rf. However, because of the unspecific nature of the SF decay mode, it is not clear that this SF activity is actually due to the decay of ^{262}Ha; it may, in fact, be due to the decay of another actinide or transactinide isotope.

Table 1. Alpha decay energies of ^{262}Ha and ^{258}Lr [22]

^{262}Ha ($t_{1/2}$ = 34±4 s)		^{258}Lr ($t_{1/2}$ = 4.3±0.5 s)	
Energy (keV)	Abundance	Energy (keV)	Abundance
8450	75%	8565	20%
8530	16%	8595	46%
8670	9%	8621	25%
		8654	9%

In this work, it was decided to base the identification on the most specific method for detecting ^{262}Ha: the detection of alpha particles from the decay of ^{262}Ha, or its daughter, ^{258}Lr. Both the alpha particle energies and the half life of ^{262}Ha were used as identification criteria. With sufficient chemical separation from competing activities in the heavy actinides and in the Bi-Po region, these criteria provide an unambiguous identification. The detection of time correlated parent-daughter pairs of alpha particles provides an even more unique identification. The production cross section of ~1 nb given or inferred from refs. 16-21 is sufficient for the detection of several alpha particles and perhaps a few alpha-alpha correlations due to the decay of ^{262}Ha and its ^{258}Lr daughter per day of continuously repeated 1-minute irradiation and chemical separation cycles.

2. Production, transport, and detection of ^{262}Ha

Production of ^{262}Ha

^{262}Ha was produced at the LBL 88-inch Cyclotron by the ^{249}Bk(^{18}O, 5n) reaction. The 117-MeV $^{18}O^{5+}$ beam from the cyclotron was degraded to 101 MeV by passing through a 1.8-mg/cm^2 HAVAR vacuum window, 0.2 mg/cm^2 of rapidly flowing N_2 cooling gas and the 3.06-mg/cm^2 Be target backing foil before passing through the ^{249}Bk target material. The target originally consisted of 0.880 mg/cm^2 of ^{249}Bk deposited on the Be backing by the molecular plating method and converted to the oxide [23,24]. Due to decay of the 330-d ^{249}Bk, during the experiments, the target composition varied between 0.65 and 0.55 mg/cm^2 of ^{249}Bk with the remainder of the total thickness of 0.880 mg/cm^2 being its ^{249}Cf daughter.

This target system was capable of accepting 0.5-particle microamperes of the $^{18}O^{5+}$ beam (3.1×10^{12} ions/s) without damage to the target. Actual beam currents in these experiments varied between 0.4 and 0.5 particle microamperes. With these irradiation parameters, the production rate for the alpha decay of ^{262}Ha is about 0.5 /m which gives about 0.3 of an alpha decaying atom at the end of a one minute irradiation.

Transport and Collection of Activity

The reaction products which recoiled out of the target were stopped in He gas at 1.3 bar which had been seeded with potassium chloride aerosols. The activity, after attaching to the aerosols was swept out of the recoil chamber into a polyvinyl chloride capillary (1.2-mm i. d.) and transported a distance of 5 m to the collection site outside the concrete shielding. The pressure at the end of the capillary was kept under 0.01 bar by means of a mechanical pump, and the activity-bearing potassium chloride aerosol was collected on a Pt foil or a thin glass plate (microscope cover slip). At the end of the collection time, the collector was removed for chemical processing of the activity.

The He-jet transport efficiency was measured at regular intervals during the experiments. This was accomplished by collecting the transported activity on Pt foils, carefully flaming away the potassium chloride, and determining the apparent production rate of $^{252-255}$Fm isotopes by alpha pulse-height analysis. At the same time as the hahnium chemistry experiments, a separate bombardment of the Bk target was performed in which all of the products recoiling out of the target were caught in a gold catcher foil located directly behind the target. At the end of a one hour bombardment, the foil was chemically processed by dissolving in concentrated hydrochloric acid / nitric acid to which an aliquot of ^{241}Am tracer had been added to trace the chemical yield. The gold was removed by adsorption on an anion exchange column pretreated with hydrochloric acid. The actinide fraction, which passed through the column, was collected and dried. This actinide fraction was then electroplated [25] for alpha pulse height analysis.

By comparing the apparent production rates measured after transport through the He-jet system with the actual production rates measured from these direct catcher foil experiments, the He-jet efficiency for the hahnium experiments was determined. The He-jet efficiency measured several times during the hahnium experiments was found to be consistently near 85%.

Production and Transport of Zirconium, Hafnium, Niobium, and Tantalum Tracers for On-Line Chemical Studies

Because of the problems associated with keeping the group 4 and 5 elements in solution, it was necessary to study the chemical properties of these elements using isotopes which were freshly produced on-line, and subject them to the same chemical procedures used for the hahnium separations. 78.4-h ^{89g}Zr, 23.6-h ^{173}Hf, 14.6-h ^{90}Nb, and 1.1-h ^{174}Ta were produced by (^{4}He, xn) reactions with a 50-MeV ^{4}He beam on strontium chloride and ytterbium, yttrium, and lutetium metal targets, respectively. These bombardments were performed in the same target system that was used for the hahnium experiments. Because of the much smaller recoil range of compound nucleus products from reactions with alpha particle beams, the gas-jet transport system parameters were changed for some of these tracer experiments.

In other experiments, 34-m ^{172}Ta was produced in the ^{159}Tb(^{18}O, 5n) reaction with a 101 MeV ^{18}O beam. This activity was transported to the collection site under exactly the same conditions used for the hahnium separations.

Detection of Alpha and SF Activities

After chemical separation, alpha particle and fission fragment pulse height analysis was performed using a series of ten 300-mm^2 Si(Au) surface barrier detectors. Pulse heights of all alpha events between 5 MeV and 10 MeV and all fission events up to 200 MeV were digitized to 11-bit accuracy by ORTEC AD-811 Octal ADC's and stored in list-mode on magnetic tape by a Digital Equipment LSI 11-73 computer. Each event was stored along with the time at which the event occurred and the identification of the detector in which the event occurred. The start and stop times of the measurements of each of the samples in each detector were also recorded on magnetic tape. This list-mode data storage allowed versatile off-line processing of the data, including histogramming and searches for time-correlated alpha events from the decay of 34-s ^{262}Ha followed by the decay of its 4.3-s ^{258}Lr daughter.

The Si(Au) surface barrier detector efficiency was measured to be 30% for sources counted at the same geometry as in these experiments. This 30% geometry implies a 60% efficiency for the detection of a fragment from SF decay. Since the alpha decay of ^{262}Ha is followed closely in time by the alpha decay of the daughter ^{258}Lr, we can calculate the efficiency for detection of these alpha particles as follows: The efficiency for detecting the parent decay and missing the daughter is 0.30 x 0.70 = 0.21: similarly, for missing the parent and detecting the daughter it is 0.21. The efficiency for detecting both alpha particles is 0.30 x 0.30 = 0.09. Since, in this last case, two alpha particles are detected, the overall alpha particle detection rate is calculated to be 2 x 0.21 + 2 x 0.09 = 0.60.

The energy resolution of the surface barrier detectors was 35 keV full-width at half-maximum for alpha energies between 5 and 10 MeV.

3. Surface adsorption behavior of zirconium, hafnium, niobium, tantalum, and ^{262}Ha

Zirconium, Hafnium, Niobium, and Tantalum Adsorption Experiments

The chemical separation of the group 4 and 5 elements by adsorption on surfaces from strong acid solutions was developed and tested by making use of gamma-ray emitting isotopes of zirconium, hafnium, niobium, and tantalum produced, as described earlier, in alpha particle bombardments. The activity bearing aerosol was collected at the end of the gas-jet capillary on a collector made of the adsorption substrate being tested. The amount of activity on the substrate was determined by measuring the prominent gamma-rays from the potassium chloride spots on the substrates before the separations. The chemical separations were made by fuming the potassium chloride spot on the substrate one or two times with 3 to 7 µl of concentrated acid and then thoroughly rinsing the substrate with 1.5 M nitric acid from a squirt bottle. Residual aqueous solution was removed from the substrate by rinsing with acetone from a second squirt bottle, and the substrate was dried by heating in a stream of hot air from an electric 'heat gun'. After the chemical separation, the gamma-ray activity remaining on the substrate was measured and the chemical yields for the isotopes of interest were determined by comparing the activities before and after the separation. The results of these on-line tracer experiments are presented in Table 2.

Table 2. Adsorption chemical yields for some Group 4 and 5 elements

Surface	Glass	Glass	Glass	Pt	Pt	Teflon	Teflon
Treatment	HNO_3 1x	HNO_3 2x	HCl 1x	HNO_3 1x	HCl 1x	HNO_3 1x	HCl 1x
Group 4							
Zr	4%	0%	30%	---[a]	---	---	---
Hf	28%	11%	59%	27%	---	5%	---
Group 5							
Nb	35%	42%	28%	22%	---	4%	5%
Ta	74%	80%	76%	60%	58%	35%	10%

a. --- indicates that no experiment was performed

From Table 2 it can be seen that the group 5 elements adsorb on the glass much better from strong nitric acid than do the group 4 elements. Also, the heavier members of the groups adsorb better than do the lighter members. If these trends were to continue to rutherfordium and hahnium, one would expect that hahnium would adhere under these conditions with a high chemical yield, and that rutherfordium may also have a significant yield.

A second fuming with nitric acid caused the adsorption yields on glass of the group 5 elements to increase (this may be due to kinetic effects) while it caused the adsorption yields on glass of the group 4 elements to decrease. In light of the high yields of the group 4 elements when fuming with hydrochloric acid, it seems that the first fuming with nitric acid removes the chloride (from the potassium chloride aerosols) in the form of more volatile hydrochloric acid and that the adsorption yield of group 4 elements in the absence of chloride during the second fuming is small. The adsorption yields of tantalum on Pt and teflon are also rather high, so it appears that the adsorption of the heaviest group 5 elements on almost any surface they come into contact with may be a general phenomenon. Apparently, the SiOH groups from the glass surface are not required for the sorption of th heavier group 5 elements.

Adsorption Separation Procedure for Hahnium

The activity bearing aerosol was collected on a glass plate. At the end of the 60-s collection time, the glass plate was removed from the collection site and placed on a hot plate. The potassium chloride spot on the glass plate was fumed with 3 µl of 15 M nitric acid. After this nitric acid dried, a second fuming was performed with 7 µl of 15 M nitric acid. When the second drop of nitric acid had dried, the potassium nitrate and the actinide activities on the glass plate were removed by washing the plate with 1.5 M nitric acid from a squirt bottle. Any remaining dilute nitric acid was removed by washing the glass plate with acetone from a second squirt bottle. The glass plate was immediately dried in a stream of hot air from an electric 'heat gun' and placed onto one of the Si(Au) surface barrier detectors. The average time from the end of accumulation of the aerosol on the glass plate to the beginning of counting for alpha and SF decays was 51 s.

Results of the Hahnium Adsorption Experiments

In the ^{18}O + ^{249}Bk bombardments, 801 adsorption experiments were performed. The decontamination from actinide elements was very good. The decay rates of $^{252-255}Fm$ indicated that only 0.25% of the fermium activities remained on the glass. A total of 26 alpha events in the energy range from 8.42 MeV to 8.70 Mev was observed during the first 140 s of counting (~4 half-lives of ^{262}Ha). By looking at the time distribution of alpha events in this energy range out to 500 s, we estimate that the time interval from 0 s to 140 s contains ~2 background events from longer-lived activities, leaving ~24 alpha events due to the decay of ^{262}Ha or its ^{258}Lr daughter.

A spectrum containing the alpha data from the first 30 s of counting for all 801 samples is presented in figure 1. For comparison, a summed spectrum of unseparated products from this reaction, taken using our rotating wheel system, [26,27] for a 20-s interval starting 60 s after the end of collection of aerosols, is presented in fig.2. It appears that in fig.1 there has been little fractionation between the francium-polonium activities, which are produced by interactions of the ^{18}O beam with a small lead impurity in the target, and the fermium activities. There is, however, a large relative enhancement of the activities due to ^{262}Ha and its daughter, ^{258}Lr in the adsorption experiments.

As indicated in table 3, these 26 alpha events contain 5 time-correlated parent-daughter pairs, as well as ~14 uncorrelated events and ~2 background events. A maximum likelihood [28,29] fit to the half-life of the 16 alpha singles events which occurred at times shorter than 140 s from the beginning of the counting together with the 5 parent events of the mother-daughter correlations gives a half-life of 28^{+7}_{-5} s, consistent with the known ^{262}Ha half-life of 34±4 s. [22] The asymmetric error limits represent the interval of equal likelihood chances [29] corresponding to a confidence level of 68%.

It should be noted that in the first correlated pair of alphas, the daughter energy of 8.752 MeV is higher than expected for ^{258}Lr. Because of the very low rate of alpha events in the energy range from 8.0 to 9.0 MeV (~0.25 events/detector*hour) it is extremely unlikely that this is a random correlation between unrelated alpha decays. The most plausible explanation is that the high energy resulted from the summing of the ^{258}Lr alpha particle with a conversion electron which accompanied the alpha decay.

From a detector geometry of 30% of 4π, one would expect the ratio of correlated pairs to uncorrelated alpha events to be 0.214. In this work the ratio of correlated pairs to uncorrelated alphas in the energy range from 8.42 to 8.70 MeV was measured to be 0.36. With a one sigma uncertainty of 0.18, this experimental ratio is consistent with the expected ratio. A maximum likelihood fit to the ^{262}Ha half-life based on the decay times of the parents of the correlated alpha events gives 22^{+17}_{-8} s, again consistent with the known ^{262}Ha half-life. Such a fit to the ^{258}Lr half-life based on the time intervals between parent and daughter events gives $2.5^{+1.9}_{-1.0}$ s, which is consistent with the known value of 4.3±0.5 s [22].

Table 3. Alpha-alpha parent-daughter correlations

Alpha-Alpha Correlation Number	Parent Energy (keV)	Parent Time[a] (s)	Daughter Energy (keV)	Daughter Time Since Parent (s)
1	8640	10.03	8752	4.45
2	8533	131.87	8636	0.08
3	8681	10.82	8661	3.40
4	8437	4.12	8603	2.02
5	8681	2.55	8611	7.88

a. Time from the beginning of counting to the alpha event

We also observed a total of 26 SF decays in the first 140 s of counting. From the time distribution of SF events from 140 s to 500 s, we estimate ~3 of the SF events at t<140 s are due to long-lived background, leaving ~23 SF decays due to the decay of ^{262}Ha. A maximum likelihood fit to the decay times of these SF events indicates a ^{262}Ha half-life of 32^{+8}_{-6} s, again consistent with the known 34 s half-life. These SF and alpha decay rates, along with an estimated 80% adsorption yield, indicate an overall production cross section of 3.2±0.5 nb and an alpha branch of 51±14%, with the remainder of the decay being either by SF or by electron capture to 60-ms ^{262}Ha which then decays by SF.

This value of the ^{262}Ha SF/alpha branching ratio is consistent with that measured by Ghiorso et al. [16], but the one σ uncertainty on this value does not overlap with those for the values measured by Bemis et al. [17,18] and earlier by our group [21]. A summary of the production cross sections and SF branches for ^{262}Ha is presented in table 4. In all cases, the ^{262}Ha was produced in ^{18}O bombardments of ^{249}Bk. Only in the present work were the measurements done on chemically separated samples. Druin et al. [19] observed this 35-s SF activity with a narrow excitation function, which is characteristic of a compound nucleus reaction rather than a transfer reaction. The maximum cross section of 2.8 nb occured at about 99 MeV.

Table 4. Production cross sections for fission and alpha activities and fission branch for ^{262}Ha

Reference	^{18}O Energy (MeV)	Fission Cross Section (10^{-33}cm^{2})	Alpha Cross Section (10^{-33}cm^{2})	Fission Branch (%)
Ghiorso et al. [16]	92-97	~1.0	~1.0	~60
Bemis et al. [17,18]	100			78±6
Hoffman et al. [20]	102	3-4		
Druin et al. [19]	99	2.8±0.5		
Gregorich et al. [21]	102	4.3±1.0	1.4±0.5	75±10
This work	101	1.5±0.5	1.6±0.5	49±13

The discrepancies in the production cross sections for the fission activity and SF branch measurements between the previous experiments and these chemical experiments may best be explained by postulating another SF activity with a similar half-life, not due to the decay of a hahnium isotope, which is produced in the $^{18}O + ^{249}Bk$ reaction. In light of the narrow excitation function, perhaps the most likely candidate would be an isomer of ^{260}Lr which is produced by the $^{249}Bk(^{18}O, \alpha\text{-}3n)$ reaction. The yield of this activity may have been small in the experiments by Ghiorso et al. because of their lower bombarding energy.

4. Extraction of tantalum and hahnium from fluoride solutions

Extraction Procedure for Tantalum and Hahnium

Other chemical separations attempted on element 105 involved the extraction of anionic fluoride species into methyl isobutyl ketone (MIBK). The extraction system with 3.8 M nitric acid and 1.1 M hydrofluoric acid as the aqueous phase, and MIBK as the organic phase was chosen for the following reasons. MIBK has been found to be an ideal solvent for the rapid preparation of alpha sources by evaporation, which are suitable for pulse height analysis [30]. Nitric acid was chosen because of the ease of phase separation with MIBK and because the phase boundary is easily visible. Higher nitric acid concentrations could not be used because the mutual solubility of the phases increased, and higher concentrations of hydrofluoric acid were not used to prevent deterioration of the glass apparatus and contamination of the sample with silicates. Under the conditions chosen, Werning et al. [14] have shown that tantalum is extracted nearly quantitatively, while niobium is extracted to only a small extent. It was expected, that this trend would continue, and hahnium would be extracted quantitatively.

In these experiments, 90-s accumulations of the activity bearing aerosols were collected on Pt foils. The potassium chloride and the reaction products were dissolved in 20 µl of 3.8 M nitric acid / 1.1 M hydrofluoric acid. This solution was then placed in a 1 ml centrifuge cone containing 20 µl of MIBK. The phases were mixed for 2 s by placing the tip of the centrifuge cone in an ultrasonic bath. The phases were separated in a centrifuge which had been specially modified to reach a maximum speed and return to the stopped position within 4 s. After centrifuging, the MIBK upper phase was pipetted onto a Ni disc which was heated from the edge by contact with an annular piece of copper kept in contact with a hot plate. This edge heating prevented the MIBK from running off during the rapid drying process. After drying, the Ni disc was flamed and then cooled by blowing air on the reverse side, and placed on one of the Si(Au) surface barrier detectors. The average time from the end of the aerosol collection to the start of alpha and SF counting was 50 s.

The chemical efficiency for products which were quantitatively extracted was assumed to be 75%, due to incomplete transfer of the activity from the Pt collection foil to the centrifuge cone, and to incomplete removal of the MIBK phase during the pipetting after centrifuging. In tests performed under similar conditions with ^{172}Ta, the chemical yield was found to be about 75%.

Results of the Hahnium Extraction Experiments

From the production cross sections for the 34-s SF and alpha activities found in the glass adsorption experiments, we calculate that in the 335 extraction experiments performed, we should have observed 14 SF decays and 14 alpha decays, including 2 time-correlated parent-daughter pairs.

In the extraction experiments, no alpha particles in the 8.4-8.7 MeV range, nor any fissions were detected within the first two minutes of counting, demonstrating conclusively that under these conditions hahnium is not behaving chemically like its lighter homolog, tantalum. The separation from actinides was essentially complete, with a contamination of only 0.1% based on the $^{252-255}$Fm seen in the fractions. A histogram of all the alpha events from the first two minutes of counting summed from all 335 experiments is presented in fig.3. Again, fig.2 can be used for comparison with the spectrum of the unseparated mixture. This indicates that, in the extracted organic phase, the peak at 7.43 MeV is much higher than could be explained by ^{250}Fm, and that another nuclide contributes to this intensity. This follows from the relative intensities of the 7.43-MeV peak and the 7.04-MeV peak due to the decay of ^{252,255}Fm in fig.2. This excess is from the 7.43-MeV alpha particles of the 0.52-s ^{211}Po daughter of 7.2-h ^{211}At produced from trace lead impurities in the target.

There are several possible reasons for the absence of ^{262}Ha in the MIBK fractions. Although, based on the behavior of tantalum, the presence of fluoride should prevent the sorption of hahnium on surfaces, we cannot rule out the possibility that hahnium was not observed because it was adsorbed on the glass surfaces used in these experiments. It is presumably the singly charged anionic species such as MF_6^- or MOF_4^- which are extracted into the oxygen containing organic solvents [31]. It is possible that hahnium forms some non-extractable species under the conditions of these experiments. For example, since the tendency to form fluoride complexes is expected to be stronger in hahnium than in tantalum, hahnium may form the non-extractable HaF_7^{2-} under conditions in which tantalum would form the extractable TaF_6^-. Also, since the tendency to hydrolyze is expected to be stronger in hahnium than in tantalum, the formation of oxy-cations, or mixed oxygen-fluoride complexes may prevent extraction of hahnium under the conditions of these experiments. Also, we cannot exclude the possibility that the relativistic stabilization of the 7s electronic orbital could lead to Ha^{3+} which would prevent the extraction of hahnium.

5. Conclusions

a. The alpha and SF decays of ^{262}Ha have been observed in chemical experiments in which the ^{262}Ha was adsorbed on glass surfaces from concentrated nitric acid.

b. The identification of the ^{262}Ha was based on the observation of alpha particles due to the decay of ^{262}Ha and its daughter, ^{258}Lr. Time-correlated pairs of alpha particles from the decay of ^{262}Ha and its daughter were seen.

c. The SF branch for ^{262}Ha has been found to be about three times smaller in the chemical experiments than in measurements done on-line, without any chemical separation. This discrepancy may be due to the production of another SF activity with a similar half-life which is detected in the on-line experiments but is removed in the chemical separations.

d. The adsorption of hahnium on glass from strong nitric acid solution is a chemical property characteristic of the group 5 elements, niobium and tantalum, in the 5+ oxidation state. By analogy to niobium and tantalum, this indicates that the most stable oxidation state for hahnium is also 5+, rather than the Ha^{3+} state that might be predicted by taking into account relativistic effects on the low-spin electronic orbitals.

e. Hahnium did not form extractable anionic fluoride complexes in nitric acid / hydrofluoric acid solutions under conditions in which tantalum was extracted nearly quantitatively. This non-tantalum like behavior may be explained by extrapolation of group 5 chemical properties: The tendency to hydrolyze or form high coordination number fluoride complexes in hahnium may be much stronger than in tantalum, leading to non-extractable species.

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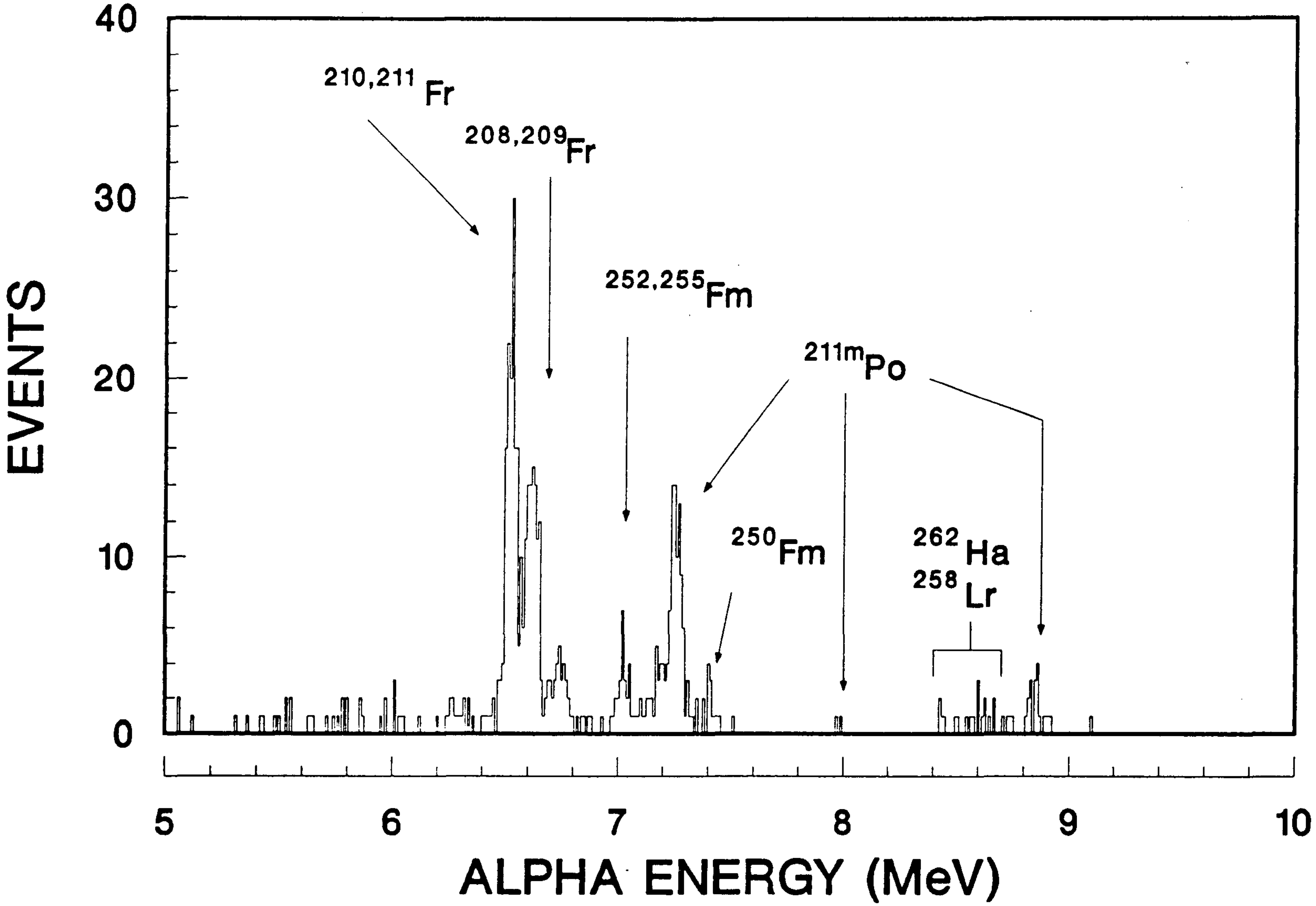
Figure captions

Figure 1. A summed spectrum containing all of the alpha data from the first 30 s of counting from the 801 experiments involving the adsorption of ^{262}Ha on glass from concentrated nitric acid solutions.

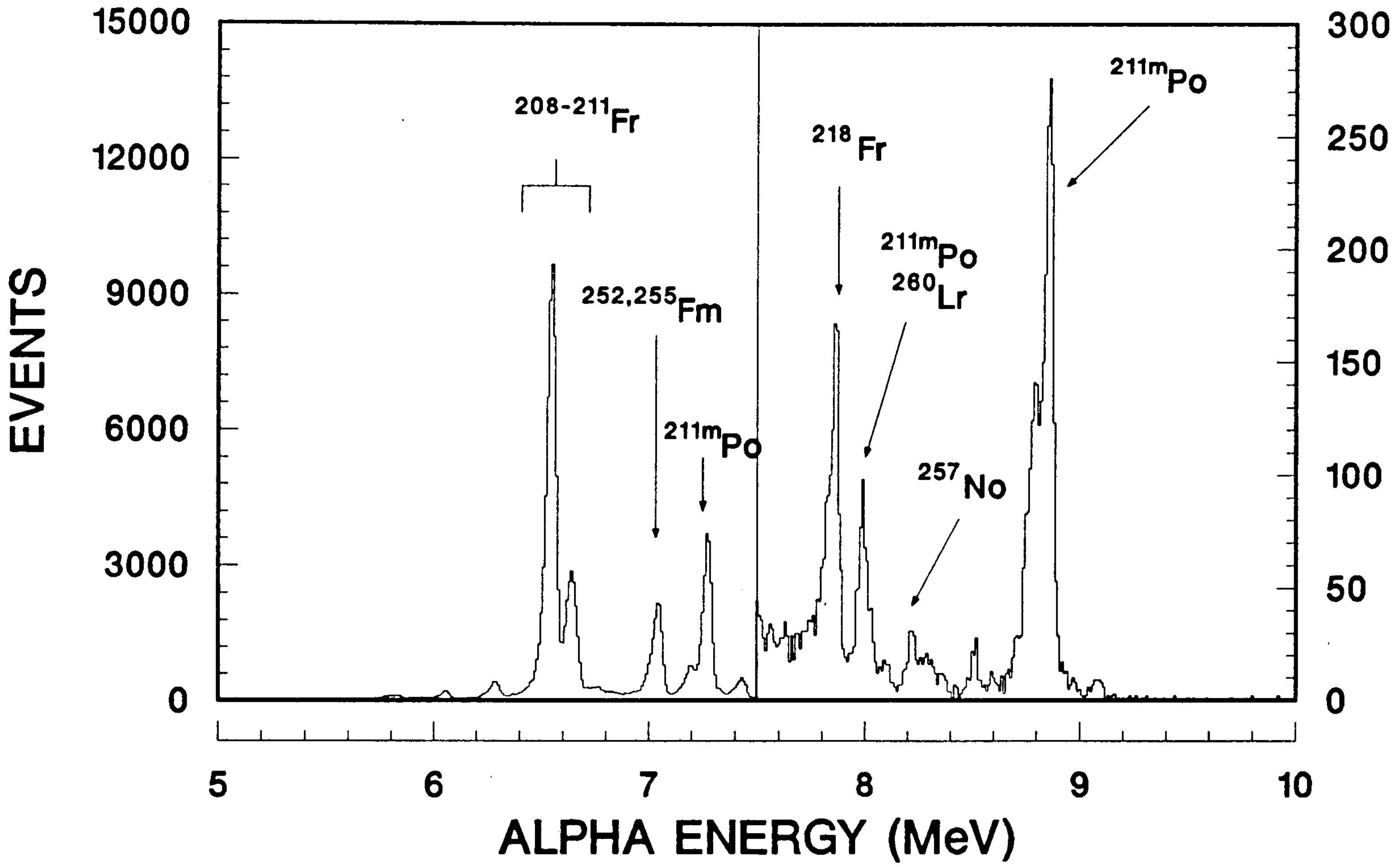
Figure 2. A representative spectrum of the unseparated product mixture from 101 MeV ^{18}O + ^{249}Bk bombardments taken on a rotating wheel system. These data were recorded over a 20 s time interval starting 60 s after the end of collection. One should note the change of vertical scale at the center of the spectrum.

Figure 3. A summed spectrum containing all of the alpha data from the first 120 s of counting from the 335 experiments involving extraction of anionic complexes from a nitric acid / hydrofluoric acid solution into MIBK.



XBL 877-3315

Fig. 1



XBL 877-3316

Fig. 2

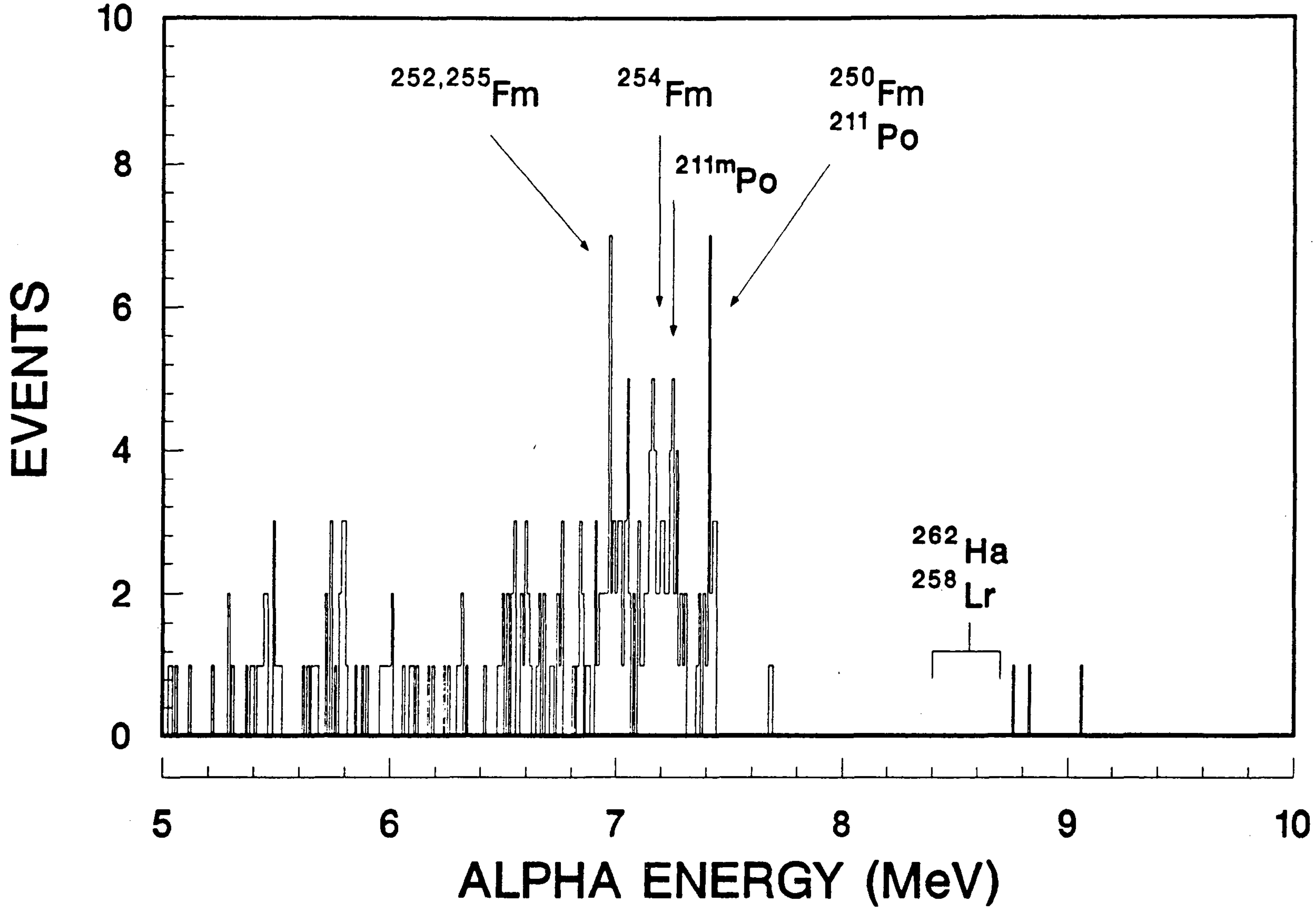


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Fig. 3