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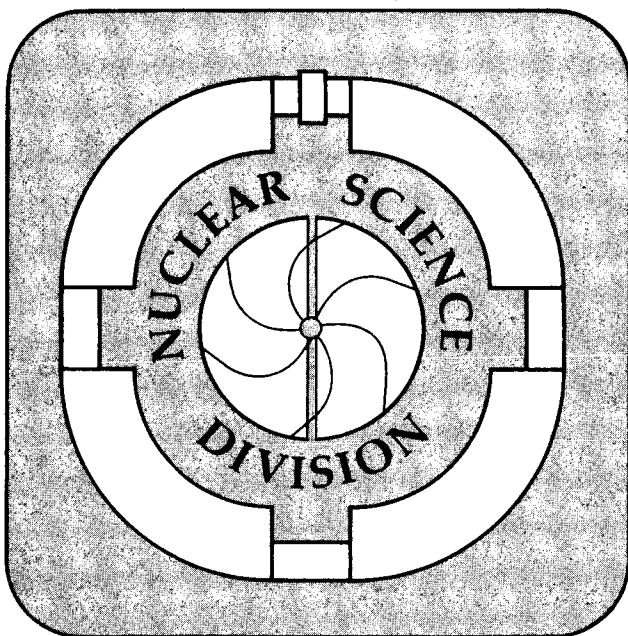# Lawrence Berkeley Laboratory
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CHEMISTRY OF THE TRANSACTINIDE ELEMENTS

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CHEMISTRY OF THE TRANSACTINIDE ELEMENTS

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Introduction

The study of the chemical properties of the transactinide elements (atomic number > 103) is extremely challenging both experimentally and theoretically. It is of special interest and worth overcoming the difficulties involved because of the chance to evaluate the expected increasing influence of relativistic effects at these very high atomic numbers. Increasing deviations from the periodicity of chemical properties based on extrapolation from lighter homologs in the periodic table (Fig. 1) have been predicted for some time (1,2) as a consequence of relativistic effects in this seventh row of the periodic table which may make the periodic properties "non-linear" in Z. The investigation of the chemical properties of the transactinide elements is particularly exciting because of the possibility that relativistic effects may alter the relative stability of the 7s, 6d, 7p valence electrons to such an extent that other oxidation states than those expected from simple extrapolation may be stabilized and the ionic radii may even be affected. In a recent review of relativistic effects in structural chemistry, Pyykkö (3) has stated that for the 6s of Au or the 6p electrons of Tl the relativistic change of the atomic potential is less important than

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the direct dynamical effect on the valence electrons. Further, the p, d, and f electrons (which never come close to the nucleus) will be affected due to more efficient screening from the nuclear charge because of the relativistic contraction of the s and p orbitals. Thus, these orbitals will increase in energy and extend outward radially. In summary, the primary relativistic effects on the atomic orbitals are: 1) contraction of the radius and energetic stabilization of s and p shells; 2) spin-orbit splitting of the $l>0$ orbitals; 3) increased radii and energetic destabilization of the outer d and all f orbitals. All of these effects are believed by Pyykkö to be of the same order of magnitude and will increase approximately as Z^2.

. The comparison of such fundamental chemical properties as the most stable oxidation states and complex formation with those of lighter homologs are invaluable in evaluating the magnitude of the relativistic effects. However, even though elements through 109 are currently known (4), experimental studies of chemical properties have only been performed on elements 104 (rutherfordium, Rf) and 105 (hahnium, Ha). This is because the half-lives of the longest known isotopes are only 0.9 s and 0.1 s for elements 106 and 107, and only a few ms for elements 108 and 109. In addition, the production cross sections drop from about 0.3 nb for $^{263}106$ (5) to only 0.02 nb for $^{265}108$ and $^{266}109$ (6).

In order to study the chemistry of any of these elements, information about their nuclear decay properties is essential. They must be produced an "atom-at-a-time" at an accelerator and

must be identified by measurement of their decay or that of their known daughter products. Obviously, this severely limits the kinds of experiments that can be performed. Techniques such as liquid-liquid extractions, ion-exchange resin separations and other chromatographic methods in which the few atoms or ions undergo many interactions thus ensuring statistical chemical behavior are particularly useful. They can typically give information about oxidation states, complexing ability, and ionic radii. Early studies (1970-71) of the chemistry of Lr (element 103) (7) and of the aqueous and gas-phase chemistry of element 104 (8, 9, 10) showed that, as expected, the actinide series ends at Lr and that a new, 6 d transition series begins with element 104. Hence, the currently known transactinide elements have been placed in the periodic table under their lighter homologs of the 5d transition series, Hf, Ta, W, Re, Os, and Ir. The series should then end at element 112 (eka-Hg) with the filling of the 6d shell.

Since those early studies, computer-controlled automated systems have greatly enhanced our ability to rapidly and reproducibly perform the hundreds or sometimes thousands of successive separations required to obtain statistically significant results. There have been several earlier reviews (11, 12, 13, 14) of measured and predicted chemical properties as well as recent reviews (15, 16) of radiochemical studies of elements 103, 104 and 105. In this paper some new results of both aqueous and gas phase studies of elements 104 and 105 and their lighter homologs will

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be discussed and the prospects for studies of still heavier elements will be considered.

Element 104.

1. Predicted Chemical Properties

Based on multiconfiguration Dirac Fock (MCDF) relativistic calculations, Desclaux and Fricke (17) and Brewer (18) proposed that because of relativistic stabilization of the $p_{1/2}$ orbitals, the electronic structure of atomic Lr is $[Rn]5f^{14}7s^27p_{1/2}$ rather than $[Rn]5f^{14}6d7s^2$ by analogy to Lu which has the electronic structure $[Xe]4f^{14}5d6s^2$. Keller (12) extrapolated from these results to predict that Rf should have the $7s^27p^2$ rather than the $6d^27s^2$ configuration analogous to the $5d^26s^2$ configuration of its lighter homolog, Hf. In this case element 104 might be a "p-element" with properties more similar to Pb whose ground state configuration is $[Xe]5f^{14}5d^{10}6s^2p^2$, than to Hf. (It should be pointed out that Pb does have a closed 5d shell.) In particular, lead and its compounds are much more volatile than the group 4 elements, Ti, Zr, and Hf.

Very early single configuration Dirac-Fock calculations (19) for element 104 had indicated that the ground state of the Rf atom should be $6d^27s^2$. However, recent MCDF relativistic calculations by Glebov et al. (20), using 468 jj-configurations, indicated that it should be a J=2 level consisting of the $6d7s^27p$ configuration (80%) with a level only 0.5 eV higher consisting predominantly of the $6d^27s^2$ configuration (95%) while the $7s^2p^2$ state is 2.9 eV above the ground state. Johnson et al. (21) have

confirmed this result for the ground state and have also computed the first four ionization potentials of element 104 and the other group 4 elements, Ti, Zr, and Hf. They have also calculated the principal maxima in the radial charge density functions for the occupied orbitals having the largest values and that have a significantly large configuration weight for these group 4 elements. Zhuikov et al. (22) have used the MCDF method to calculate the first four ionization potentials of element 104, the promotion energies of the atom, and the atomic and ionic radii. They found that the average radii of valence shells, orbital energies and ground levels of ionized state of element 104 are similar to Hf but different from Pb and its homologs. Since these quantities determine the general chemical properties of an element, they concluded that there is no basis for expecting any distinct "p-character" in the chemical properties of Rf. They further evaluated various experimental approaches for investigating relativistic effects including volatilities in the elemental state, thermochromatography of tetrahalides, and the stability of lower oxidation states. They concluded that distinguishing between "relativistic" and "nonrelativistic" atoms in gas chromatography experiments which depend on Hf or element 104 in the atomic state is not a fruitful approach because of the difficulty in stabilizing the atomic states at the high temperatures of greater than 1500° C required for the chromatography columns. On the other hand thermochromatography of the tetrachlorides or tetrabromides appears very promising. They also believe that

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differences in the ionization potentials (IP) of the lower oxidation states of Rf from those of Zr and Hf should cause differences in the stabilities of their halides and hence in their volatilities. In particular, they calculate that the first IP of element 104 (5.9 + 0.2 eV) is much lower than for Zr and Hf and should result in a greater stability of the lower oxidation state of Rf and a lower volatility of the halide than for Hf.

2. Measured Chemical Properties

The chemical properties of the lighter group 4 homologs Zr and Hf are strikingly similar and Pyykkö (3) has attributed this to the cancellation of nearly equal relativistic and shell-structure effects. Thus, it is of considerable importance to determine whether Rf is similar to Zr or Hf, in order to help assess the relative importance of these effects at higher atomic number. The longest known isotope of element 104 is 65-second ^{261}Rf, discovered via the ^{248}Cm(^{18}O, 5n) reaction in 1970 by Ghiorso et al. (23). In early work by scientists at the Joint Institute for Nuclear Research, Dubna, USSR, the 3-s ^{259}104 produced via the ^{242}Pu(^{22}Ne, 5n) reaction was used in studies (24, 25, 9, 10) of the gas phase properties of the tetrachloride. Element 104 was detected only via spontaneous fission (SF) decay. Based on this, they reported that the volatility of its tetrachloride was similar to that of $HfCl_4$ and much more volatile than the chlorides of the actinides and Sc. In 1970, Silva et al. (8) used the 65-s ^{261}Rf in studies of ammonium alpha hydroxyisobutyrate elutions

from cation exchange resin columns. They found that Rf eluted early, like Zr and Hf, while No and trivalent actinides were retained on the column for more than a hundred column volumes. Since these early studies until rather recently there has been something of a hiatus in the investigation of the chemical properties of the transactinides, except for a study by Hulet et al. (26) in 1980 of the chloride complexing and extraction of the anionic species on columns of trioctylmethylammonium chloride on an inert support. They found that Zr, Hf, and Rf extracted from 12 M HCl while trivalent actinides were not sorbed on the column. The Rf, together with Hf tracer, was then eluted with 6 M HCl. Although only 6 alpha decays from ^{261}Rf were detected in more than 100 experiments this did demonstrate that the chloride complexation of Rf is similar to Hf and much stronger than that of the trivalent actinides. Another notable feature of these experiments is that a computer-controlled automated method was used to carry out the chemical procedure, prepare the sources and perform the alpha spectroscopy.

Since then very little work on Rf has been reported until quite recently. In 1989, Zhuikov et el. (27) examined the volatility of 3-s ^{259}104 relative to Au, Tl, and Pb tracers in "on-line" measurements in a quartz column at 1170° C. Under reducing conditions using Ar/H$_2$ carrier gas, Hf and Rf did not pass through the column while the other elements did. From these data they deduced a lower limit of 370 kJ for the sublimation enthalpy of metallic 104, a value much higher than those for Pb and other

heavy p-elements.

During the last couple years, our group at LBL has studied both the aqueous- and gas-phase chemistry of Rf using the 65-s ^{261}Rf produced at the LBL 88-Inch Cyclotron via the ^{248}Cm (^{18}O, 5n) reaction with a cross section of about 5 nb. Its extraction into tributylphosphate (TBP) and triisooactylamine (TIOA) was compared (28, 29) with that of Zr and Hf in repeated manual separations taking about 1 minute each. The effect of chloride concentration and pH on the extraction of Rf into TBP in benzene and into TIOA in benzene was compared with that of the group 4 homologs Zr and Hf, the pseudo-group 4 element Th, the group 5 homolog Nb, and trivalent actinides. In general, Rf was found to behave as a group 4 element and, unlike the trivalent actinides, extracts efficiently into TBP from concentrated HCl. As shown in Fig. 2(a), Rf extracts better into TBP than does Hf. In Cl$^-$ concentrations above 10 M at constant H$^+$ concentration of 8 M, the extraction of Rf decreases (Fig. 2(b) and becomes lower than that of Hf. Since TBP is believed to extract neutral species, this may indicate that the chloride complexation of Rf is stronger than that of Hf, resulting in formation of the inextractable species RfCl$_6^{2-}$.

We found (29) Rf to be nearly 100% extracted into TIOA from 12 M HCl as are Zr and Nb, while Th and trivalent actinides and lanthanides are not extracted. Our studies of the extraction chemistry of Rf will be extended to a comparison of the distribution coefficients for Rf with those of Zr, Hf, and Th for thenoyltrifluoroacetone (TTA) systems; this should permit calcula-

tion of the radius and some thermodynamic quantities for Rf.

Using the method of isothermal gas-phase chromatography we investigated the volatile bromides and chlorides (30) of Rf and compared their behavior with their lighter homologs in Group 4. Fig. 3 shows a schematic of the apparatus used in these studies. The gases HBr and HCl were used to produce the volatile halides and, in the case of Rf, alpha and SF spectroscopy was performed using surface barrier detectors and our rotating wheel system. The Rf was found to form very volatile bromides compared to those of Hf as shown in Fig. 4. This is in agreement with the results (31, 32) from thermochromatographic column studies and may indicate a relativistic alteration of the electronic structure of Rf. Po and Fr produced in the same experiments as Rf were also measured. Po was found to be somewhat more volatile than Rf while the group 1 element Fr was much less volatile.

Zhuikov et al. (22) have performed relativistic Dirac Slater computations for the tetrachlorides of Rf and its homologs. They used values of the 4+ ionic radii obtained from their atomic calculations. They calculated the effective charge of the central metal ions in the tetrachlorides to be 1.96, 2.36, 2.34, 2.52, and 2.30 and the width of the chlorine 3p valence band to be 0.96, 0.84, 1.04, 0.82, and 1.57 eV for Ti, Zr, Hf, Th, and Rf, respectively. They also calculated the population of electronic levels and noted a slight increase in the population of $s_{1/2}$ orbitals due to relativistic stabilization. From the correlation between the heat of sublimation, ΔH_s, and the deposition

temperature in the thermochromatographic columns, they estimated the value for $RfCl_4$ to be 90 ± 15 kJ/mol compared to 107.6 ± 2.0 for $HfCl_4$ and 108.4 ± 2.0 kJ/mol for $ZrCl_4$. They attribute the higher volatility of the element 104 tetrachloride to the lower effective charge of the atom which leads to more covalent bonding.

Recently, Sgelowski et al. (33) have suggested that the method of measuring the longer-lived decay products of the short-lived isotopes of element 104 can be used to facilitate more detailed studies of its chemical properties. The behavior of perhaps hundreds of atoms of 104, in contrast to tens of atoms of the short-lived 104 isotopes, can be measured by detection of long-lived daughter products which provides a much longer time for purification of the long-lived decay products. They have applied this method to the study of solution chemistry of Rf. The recoiling reaction products were transported from the irradiation site via a gas transport system and collected on a frit. They were removed with 0.2 M HF and sequentially passed through 3 columns containing cation, anion, and cation exchange resins which took about 35 seconds. Trivalent transplutonium elements (TPE's) and lanthanides were retained on the first cation column, Zr and Hf on the anion column, and TPE's again on the final cation column. The 65-s $^{261}104$ was identified by detection of its descendants, 3-day ^{253}Fm and its electron-capture product, 20-day ^{253}Es, which were eluted from the final column. This eluant was extensively purified, and analyzed via alpha spectroscopy. In this way, the behavior of element 104 could be inferred

based on the detection of several hundred ^{253}Es atoms. It was shown that 104 in 0.2 M HF forms strong anionic complexes which, like Hf complexes, sorb on the anion exchange resin colum, but not on the cation exchange resin columns.

Element 105.

1. Predicted Chemical Properties

Based on the placement of element 104 as the heaviest group 4 element, Element 105 would be expected to be the heaviest known member of group 5. By analogy to Ta, the ground state configuration of the neutral atom would be [Rn]$5f^{14}6d^37s^2$. Earlier, Keller (12) postulated that a probable configuration for the neutral atom might be $6d7s^27p^2$ rather than $6d^37s^2$ because of the predicted configuration of $7s^27p$ for Lr rather than $6d7s^2$. With the recent calculations (20, 21) for Rf indicating that the ground state is $6d7s^27p$ with the $6d^27s^2$ only 0.5 eV higher, some contribution to the ground state from the 7p orbital might be expected. However, recent MCDF calculations by Johnson and Fricke (34) indicate that in contrast to elements 103 and 104 the ground state of element 105 is expected to be $6d^37s^2$ with the $6d^27s^27p$ configuration at about 1 eV higher energy. They have also calculated values of 6.9, 16.0, 24.7, 34.2, and 44.6 eV for the first through fifth ionization potentials, respectively.

2. Measured Chemical Properties

Until recently, only studies of the gas-phase chemistry of element 105 had been conducted. From thermochromatographic experiments on the halides of 2-s ^{261}105, Zvara et al. (35, 36)

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concluded that element 105 is a homolog of Nb and Ta, but that its chloride is less volatile than $NbCl_5$ but more volatile than $HfCl_4$. Because only SF activity was measured, it is not certain that the detected fissions belonged only to element 105. Keller and Seaborg (37) and Hyde et al. (38) have interpreted the results for the bromides (36) as showing that Ha behaves more like Hf, a group 4 element, than like the group 5 elements Nb and Ta.

Gäggeler et al. (39, 40) in 1988 and 1990 have investigated the volatility of the bromides of 35-s ^{262}Ha in isothermal gas chemistry experiments in quartz tubes. An automated on-line system was used and alpha particles and SF's were detected. In the 1990 experiments a tape transport system was used to collect the products which were then moved past 450 mm^2 passivated ion-implanted planar silicon (PIPS) detectors for measurement of the alpha and SF activity. A schematic diagram of the on-line gas apparatus (OLGA) and detection system is shown in Fig. 5 and a photograph is shown in Fig. 6 . Reaction products were carried via a helium gas transport system and stopped on a quartz wool plug where they were brominated with HBr or HBr and BBr_3 at 1000° C. The temperature in the isothermal region of the oven was varied between 100° and 700° C in the latest experiments (40). The Ha bromide is somewhat less volatile but otherwise behaves similarly to the bromides of the group 5 elements Nb and Ta and the pseudo-group 5 element Pa investigated under similar conditions. The data are shown in Fig. 7. Surprisingly, $HaBr_5$ appears to be slightly less volatile than $RfBr_4$ (see Fig. 4)

although Ta, Nb, and Pa are all much more volatile than Hf.

The first aqueous chemistry on Ha was conducted by Gregorich et al. (41) in 1987 on 35-s ^{262}Ha produced via the ^{249}Bk(^{18}O, 5n) reaction at the 88-Inch Cyclotron at Lawrence Berkeley Laboratory (LBL). The energy and time distribution of the alpha decay and the detection of time-correlated pairs of alpha particles from the decay of ^{262}Ha and its 4.3-s daughter, ^{258}Lr, provided positive identification of the Ha. The sorption of Ha on glass surfaces after fuming twice with concentrated nitric acid was compared with tracers of the group 4 elements Zr and Hf and the group 5 elements Nb and Ta produced under similar conditions. Some 800 manual separations requiring about 50 seconds each were performed (see Fig. 8) and a total of 26 alpha and 26 SF events was detected. Even after washing with 1.5 M HNO_3, Ha was found to adhere to the glass, a property characteristic of the group 5 elements. Zr and Hf, as well as the trivalent actinides, did not remain on the glass. These experiments confirmed the group 5 character of Ha, as indicated earlier by the gas-phase experiments. Experiments to investigate whether Ha extracted into methylisobutyl ketone (MIBK) under conditions in which Ta extracts but Nb does not were also conducted. It was expected that Ha would behave more like Ta than Nb but, suprisingly, Ha did not extract from mixed nitric acid/hydrofluoric acid solutions although Ta did.

To investigate the unexpected extraction behavior of Ha in more detail, in 1988 and again in 1990, a large collaboration of

German, Swiss, and American scientists used computer-controlled automated techniques to explore the properties of Ha. In the first experiments, some 1600 anion exchange separations were performed using TIOA on an inert support to compare the halide complexation of Ha with the lighter group 5 elements Nb and Ta and the pseudo-group 5 element Pa. The on-line separations were conducted using ARCA-II (42), a miniaturized version of the Automated Rapid Chemistry Apparatus, ARCA. A photograph of ARCA-II is shown in Fig. 9. A diagram of the results is given in Fig. 10. It was found (43) that Ha sorbs on the columns from either (a) 12 M HCl/0.02 M HF or (b) 10 M HCl, as do Nb, Ta, and Pa, indicating the Ha also formed anionic complexes. All of these activities can be stripped from the column along with the TIOA by acetone/0.02 M HF. As shown in the middle part of Fig. 10, after sorbing as in procedure (a), a series of more than 700 collection and separation cycles was performed in which a Nb-Pa fraction was removed from the column with 4 M HCl/0.02 M HF, followed by the stripping of Ta with 6 M HNO_3/0.015 M HF. Most (88%) of the ^{262}Ha/^{258}Lr alpha activity (38 alphas and 4 correlated pairs) was found in the Nb/Pa fraction with the remaining 12% in the Ta fraction, consistent with the approximately 10% of the Nb/Pa activity which tailed into the Ta fraction. This showed that the anionic complexes of Ha are not as strong as those of Ta, but are similar to those of Nb and Pa, indicating a reversal in the trend in going from Ta to Ha. In a final series of more than 500 experiments, the separation scheme shown in the bottom of Fig. 10

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was carried out. As shown, 80% of the Pa was eluted first and then elution of Nb was begun. The Nb fraction contained 20% of the Pa and 80% of the Nb. ^{262}Ha was divided almost equally between these two fractions--25 alphas (5 correlated pairs) in the Pa fraction and 27 alphas (5 correlated pairs) in the Nb fraction.

Additional experiments on the aqueous chemistry of Ha were conducted by the collaboration in August, 1990. It was found (44) that in 0.5 M HCl Ha elutes from the TIOA columns with Pa which elutes first, followed by Nb which elutes later. This shows that Ha is more similar to Pa than to Nb or Ta in the TIOA extractions. (It is interesting to note that Rf, which also extracts nearly quantitatively into TIOA from 12 M HCl behaves differently than the pseudo-group 4 element Th which does not extract under these conditions.) Elutions from cation exchange resin columns with unbuffered 0.05 M alpha-hydroxyisobutyrate solutions showed that Ha, together with Nb and Ta, elutes promptly from the column while tetravalent and trivalent metal ions do not elute under these conditions. This provides additional verification that pentavalent Ha is the most stable state in aqueous solution. The procedure also provides a rapid separation method for Ha from interfering activities produced in the irradiation of ^{249}Bk with ^{18}O and permits definitive studies of its nuclear properties.

In experiments at a lower ^{18}O energy, designed to favor production of ^{263}Ha via the (^{18}O,4n) reaction, preliminary evi-

dence for this new isotope with a half-life of about 30 s, simi-
lar to that of ^{262}Ha, was obtained (45). It decays about 57% by
SF and 43% by alpha emission. Additional experiments will be
needed to confirm this discovery and to obtain additional corre-
lation data between the ^{263}Ha alphas and the decay of its daugh-
ter, 5-s ^{259}Lr. Alpha-alpha correlations were expected, but of
some 10 alphas detected, 2 alpha-SF correlations were observed
but no alpha-alpha correlations. Analysis of earlier data from
our group (46) on the decay of ^{259}Lr produced via the ^{248}Cm(^{15}N,4n)
reaction indicates that it has an SF branch of about 25% which
would make our alpha-SF data consistent with ^{263}Ha decaying to
^{259}Lr, within the statistical errors involved. Data from these
current experiments are still being analyzed and will be pub-
lished later.

Ha continues to provide us with surprises! Its non-Ta-like
behavior and similarity to Pa demonstrate that its chemical
properties cannot be reliably extrapolated from the trends exhib-
ited by its lighter homologs. Additional experimental and theo-
retical work will be needed in order to gain a better understand-
ing of its complex chemistry.

More neutron-rich isotopes of elements 104 and 105 probably
exist which have longer half-lives and could be produced from
transfer reactions between heavy ion projectiles and the large
(40 μg/cm^2) ^{254}Es targets envisioned in the Large Einsteinium
Activation Program (LEAP), proposed by a consortium of four U. S.
national laboratories (47, 48). It might then be possible to

prepare lower oxidation states of these elements and undertake
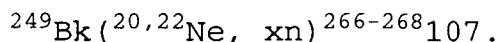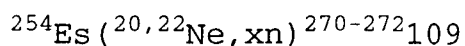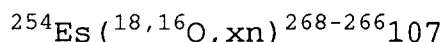studies of their redox potentials.

Element 106

Elements 106 through 112 are expected to complete the 6d
transition series and as such should be chemical homologs of W
through Hg. However, based on our experience with elements 103
through 105, it appears that the relative chemical influence of
the 7p and 6d orbitals will be difficult to predict. Seaborg and
Keller (49) suggest that the orbitals may be close enough in
energy and extension to give a mixed effect similar to that which
occurs for the 5f and 6d orbitals in the U-Pu region. Thus it
will be of particular importance to obtain experimental informa-
tion about the chemical properties of these elements.

It appears possible with existing technology to extend our
studies of the transactinides to element 106, even though the
longest known isotope, $^{263}106$, has a half-life of only 0.9 s.
The microSISAK system (50) can be used to perform chemical sepa-
rations on the second time scale; the only major development
required is the measurement of alpha and SF activity without the
time-consuming step of evaporating the resulting solutions.
Passing the liquids directly over PIPS detectors has already been
demonstrated and can probably be used for alpha spectroscopy of
element 106. Liquid scintillation counting might also be used.
Since by analogy to W the hexahalides of element 106 should be
quite volatile, gas-phase studies should be feasible. These also
have the potential for providing weightless sources for alpha and

SF detection.

Elements 107 and Beyond

Although elements 107-109 have been reported, no chemistry has been performed on any of these elements because of their very short half-lives and small production cross sections. The longest known isotope of element 107, $^{262}107$, has a half-life of only 0.1 s, but it seems probable that heavy ion reactions with ^{249}Bk or ^{254}Es targets can be used to prepare isotopes of both elements 107 and 109 which may be long enough for chemical studies. This is because of the hindrance to SF due to odd proton and odd neutron numbers (51). The recently discovered (52) long-lived isotopes of Lr, 40-min ^{261}Lr and 3.6-hour ^{262}Lr confirm the predicted hindrances. The following reactions which result in products near the postulated region of extra stability (53) around neutron numbers 162 to 164 appear particularly promising:

$$^{254}Es(^{18,16}O,xn)^{268-266}107$$

$$^{254}Es(^{20,22}Ne,xn)^{270-272}109$$

$$^{249}Bk(^{20,22}Ne, xn)^{266-268}107.$$

An on-line separation and condensation apparatus, OSCAR, was built by Dougan et al. (54) to search for $^{272}109$ produced in the $^{254}Es(^{22}Ne,4n)$ reaction and its possible electron-capture daughter, $^{272}108$. It was estimated that the 109 isotope might have a half-life of the order of 25 min and that its daughter might decay by alpha emission with a half-life of up to 1 min. The chemical separation procedure was based on the assumption that

elements 108 and 109 have properties similar to Os and Ir. (The procedure was checked using 15-min ^{182}Ir and its 21.5-hour electron-capture daughter, ^{182}Os.) Element 109 (eka-Ir) is transported via a helium jet system and trapped on a quartz wool plug in a heated quartz tube. A stream of oxygen gas is used to produce volatile oxides, presumably including those of element 108 (eka-Os), which are then carried to a chamber where they are condensed at liquid nitrogen temperatures on a silver disk which was then assayed for alpha activity from element 108. No alpha peaks in the appropriate energy range were observed which could be attributed to element 108. From these results an upper limit of 1 nb was placed on the cross section for production of ^{272}109, assuming that elements 108 and 109 follow the Ir-Os chemistry and that the half-lives are in the appropriate range, i. e., a half-life for SF decay of 108 of at least a few seconds. However, there are large deviations in the predictions of the most stable oxidation state of elements 109. Penneman and Mann (2) predicted a most stable state of I for element 109 and 0 for 110 while Cunningham (55) predicted VI for both elements!

Keller et al. (56) have made detailed predictions of the chemical properties of element 111 (eka-Au) and predict that this noble metal will be most stable in the III oxidation state with a chemistry similar to Au(III), but that its I oxidation state will be less important than for Au. Seaborg and Keller (49) conjecture that the most stable oxidation state of element 112 (eka-Hg) might be the I, but that higher oxidation states will

also be important in aqueous solution. They further suggest that metallic 112 should be quite volatile based on extrapolation from the volatilities of its homologs, Zn, Cd, and Hg.

Whether or not we will be able to investigate the chemical properties of the elements beyond element 106 depends primarily on whether we can devise new methods for the production of species with half-lives long enough to permit even rudimentary chemical investigations. It appears that longer-lived species of these elements probably exist, but the biggest problem now is how to produce them. Thus considerable effort needs to be devoted to investigating and understanding the production mechanisms involved and to devising the best methods for synthesizing these species. Ultimately, perhaps we may even reach the elusive island of superheavy elements predicted in the region of Z=112 to 114 and N=184. Judging from the surprises we have already encountered in our investigations of the chemical properties of the heavy actinides and the transactinides, Rf and Ha, it is a frontier area of chemical research which cannot readily be predicted, but which offers both great challenges and rewards!

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FIGURE CAPTIONS

1. Modern periodic table of the elements (atomic numbers of undiscovered elements are shown in parentheses)

2. (a) Extraction of Rf and Hf into 0.25 M TBP in benzene as a function of molarity of HCl.
   (b) Extraction of Rf and Hf into 0.25 M TBP in benzene as a function of [Cl$^-$] concentration at a constant [H$^+$] concentration = 8 M.

3. A schematic diagram of the arrangement used for gas-phase studies is shown. The recoiling products from the reaction are attached to KCl aerosols and transported in helium gas to the bromination and separation apparatus. After separation, the volatile products are again transported via an aerosol-loaded gas jet and deposited on thin polypropylene films placed on the periphery of a horizontal wheel which is rotated so as to position the foils successively between pairs of surface barrier detectors for alpha and SF spectroscopy.

4. Relative chemical yields of bromides of 65-s ^{261}Rf (solid line with actual data points), 25.5-s ^{211}Po^m (-··-), 38-s ^{162}Hf (---), and 50-s ^{209}Fr (-·-) as a function of the temperature of the isothermal region of the oven. HBr was used as the brominating agent in all cases.

5. Schematic of new on-line isothermal gas-phase apparatus (OLGA) showing tape transport system which moved collected volatile activities into position for alpha and SF-spectroscopy with the PIPS detectors.

6. Photograph of isothermal gas-phase appartus OLGA.

7. Relative chemical yields of bromides of 35-s ^{262}Ha (solid line with actual data points), 78-s ^{167}Ta (---), 15-s ^{99}Nb^g (-··-), and 1.8-min ^{226}Pa (-·-) as a function of the temperature of the isothermal region of the oven. HBr was used as brominating agent for Ha and Nb; HBr and BBr$_3$ were required in order to brominate Ta and Pa.

8. Photograph of simple setup for first aqueous chemistry on element 105.

9. Photograph of ARCA-II (mini-ARCA).

10. Diagram of elution curves for trivalent actinides, Nb, Ta, and Pa from TIOA column (1.6 x 8 mm), under the same conditions as for the Ha experiments (from Ref. 43).

25

Fig. 1

XBL751-2036

26

Extraction into 0.25M TBP in Benzene

Fig. 2 (a)

27

Extraction into 0.25M TBP in Benzene

Fig. 2 (b)

Fig. 3

Fig. 4

XBL 9010-3429
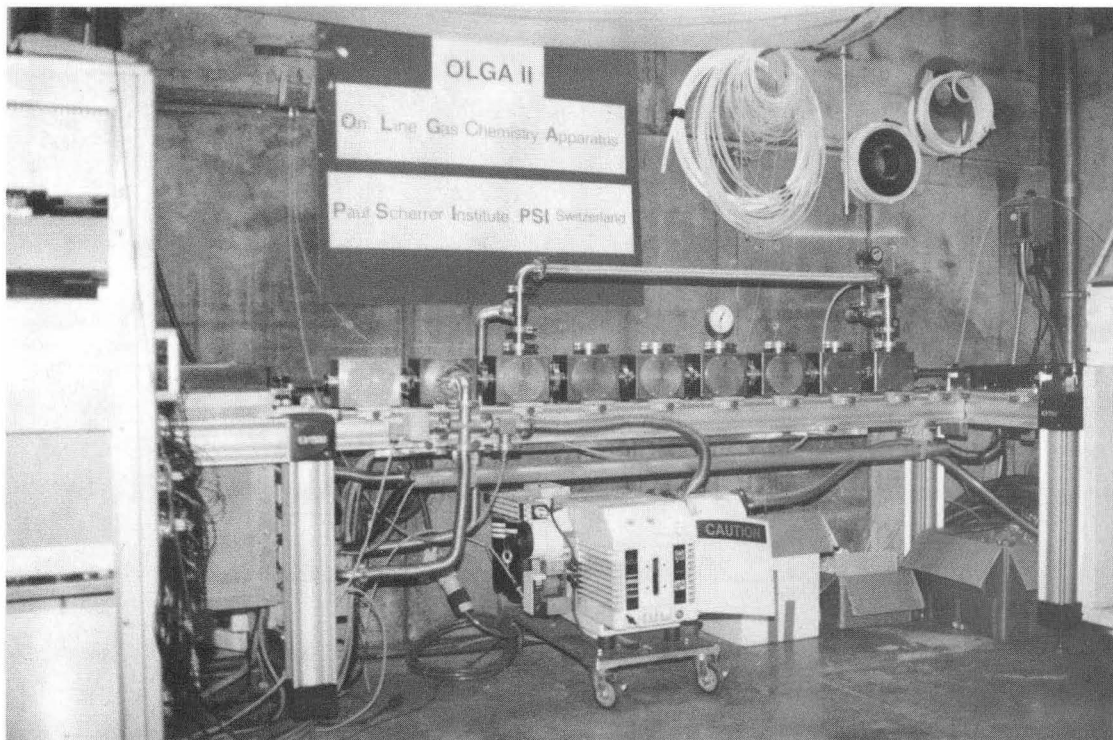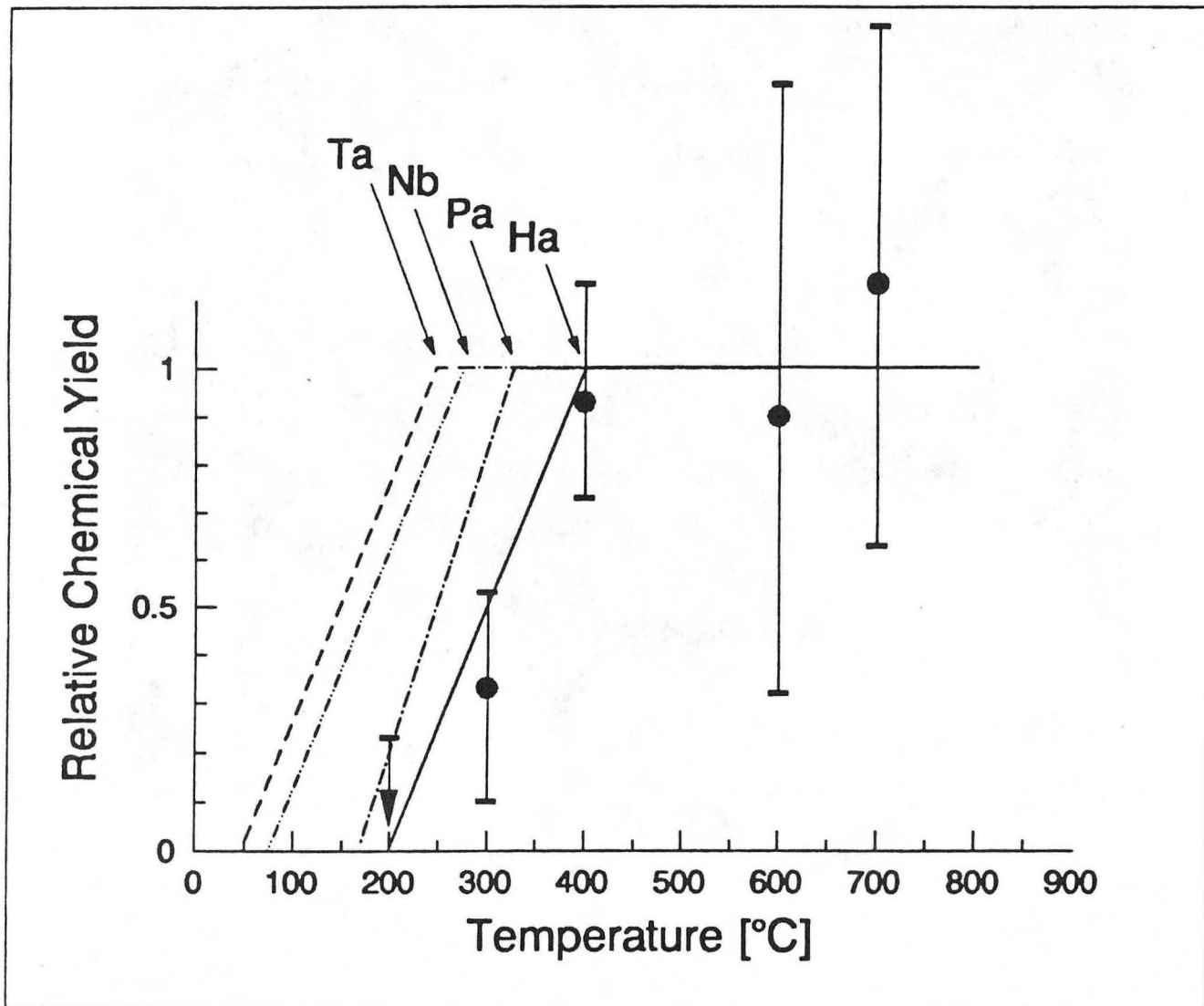
OLGA Tape System

Fig. 5
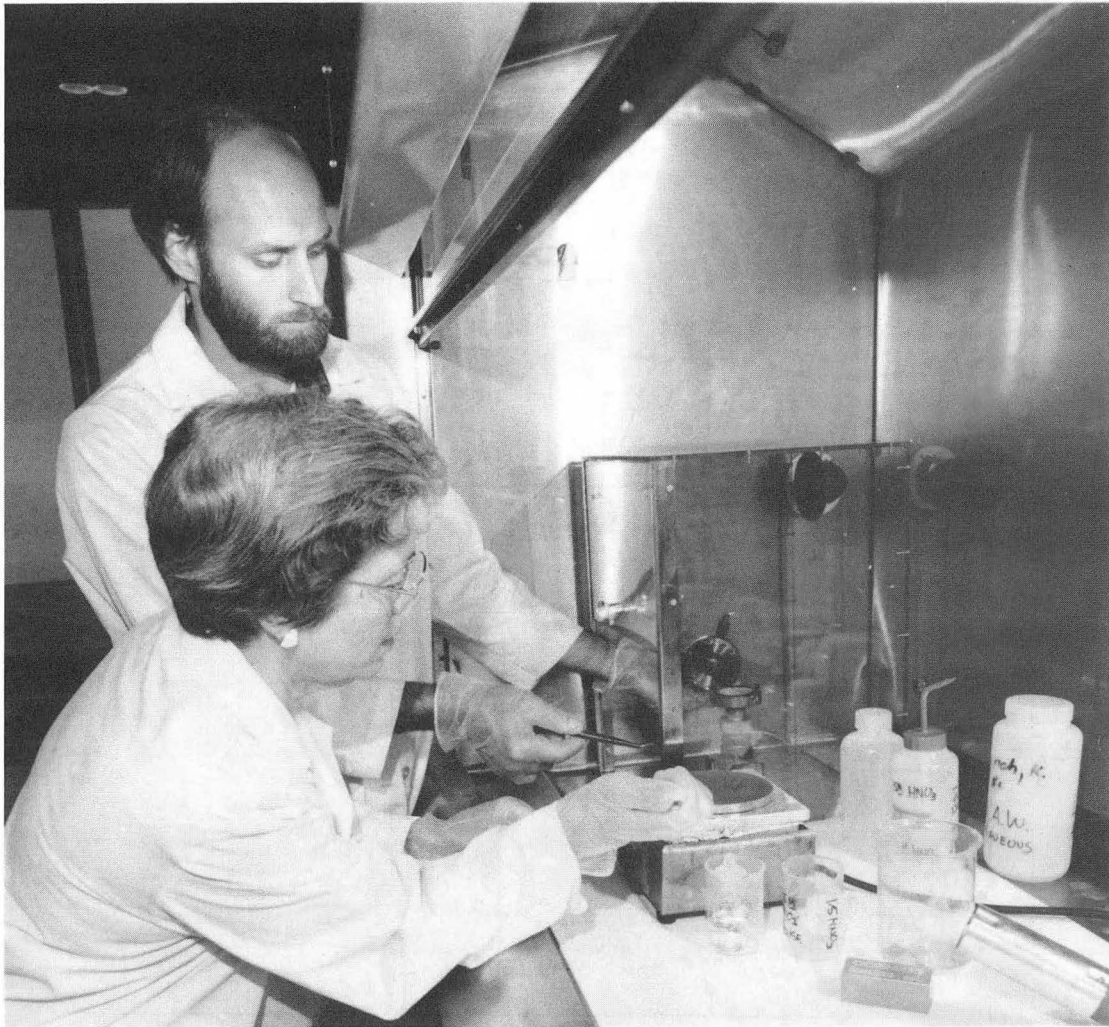
XBL 9010-3430

Fig. 6

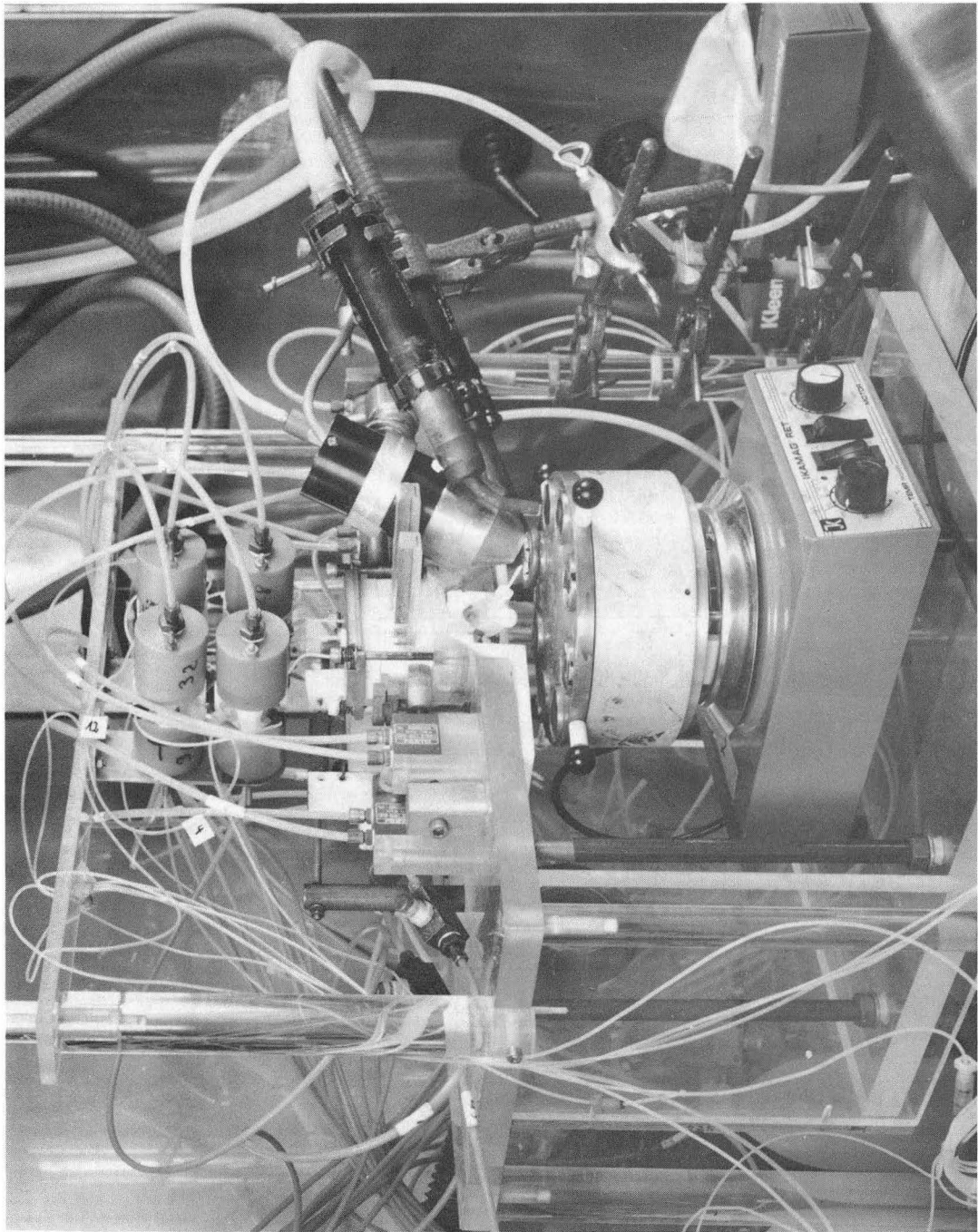XBL 9010-3428
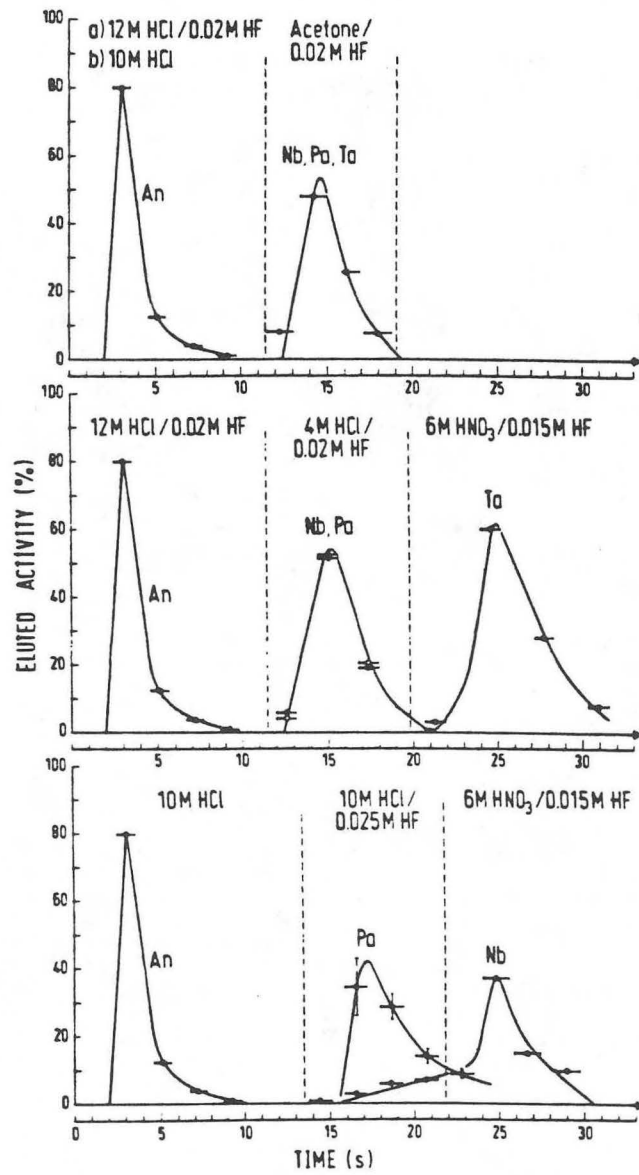
Fig. 7

33

Fig. 8

Fig. 9

Fig. 10

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