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Search for chemical separation of the element 106 homologues in HF and HF-HCl media

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Abstract

In order to study the chemical properties of element 106 in aqueous media, fast, efficient and reproducible chromatographic separations were tested on its assumed homologues : Mo, W and U. Corroborative static and dynamic off-line experiments have shown that after fixation of these three elements on anion-exchange resin in HF medium, selective elution could be achieved by using suitable concentration of HCl - HF and HCl solutions. Separations of short-lived W isotopes, produced through heavy ion irradiation were also performed on-line.

1. Introduction

At the present time, only short-lived isotopes of element 106 are reachable : the longest-lived isotope of this element (^{263}106) is about 0.8 second. However, according to some recent theoretical works [1,2], isotopes of 106 element with half-lives of about one minute or even higher than some ten minutes have been predicted. For example, isotope ^{267}106, near the shell closure at N = 162,

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which is known to enhance nuclear stability to fission and α decays, has been predicted with half-life of about 30 minutes and cross section about 10 picobarns [1,2]. Besides, preliminary experiments which have been performed at JINR (Dubna, Russia), have given evidence of isotopes $^{265,266}106$ whose estimated half-life and cross section are about 2 - 30 s and 80 pb respectively [3,4].

The search of such isotopes of element 106 and the study of its chemical properties in aqueous medium could be achieved by using kinetically fast reactions such as complexation or hydrolysis which allows to carry out, at the same time, fast and efficient separation of element 106 from all other reaction products. As the chemical properties of this element are completely unknown, we need to find probable chemical homologues for comparison purpose, as it was done with element 105. Indeed, experimental studies performed in gaseous and aqueous phases have shown similarities in the chemical behaviour of element 105 with Ta, but mainly with Nb and Pa [5-7], which was recently corroborated by relativistic calculations [8,9]. So, we assume that the closest chemical homologues of element 106 are the hexavalent elements : W or more probably Mo or U, and the purpose of this work is to define operating conditions in order to isolate element 106 and determine its complexation properties comparatively to the supposed chemical homologues Mo, W and U (VI).

Previously, investigations of Zr, Hf (homologues of element 104) Nb, Ta and Pa (homologues of element 105) have been performed by ion exchange chromatography in HCl, HF and HF-HCl media [10,11]. Concerning the behaviour of Mo, W and U, Kraus et al. [12] have published in 1955 results concerning the behaviour of Mo, W, and U in HCl and in HCl - HF solutions. Their work provides a reliable basis for studying the various concentrations which could be used for the individual separation of these elements. It appears that these acid mixtures could be very fruitful for fast and complete separations. However, some data were missing, particularly at low acid concentration, and a part of this preliminary study is devoted to the quantification of distribution coefficients in a chosen range of HF and HCl concentration slighly different from those investigated by Kraus et al. [12].

Since the production of element 106 by nuclear fusion reaction requires ion accelerator, part of our experiments was carried out in classical radiochemistry laboratory, « off-line », that is to say, out of the ion beam, with relatively long-lived isotopes. The second part was conducted « on-line » : short-lived W isotopes were produced by irradiation of a natural Dy target with ^{16}O ion beam.

Two different kinds of off-line experiments were carried out in order to reach a better knowledge of the chemical properties of these homologous elements and thus to define experimental conditions for the elementary separation. All the chosen procedures are based on the adsorption properties of the various complexes involved on macroporous anionic exchangers (BIO-RAD AG MP-1® 200 - 400 mesh), which can be quantified by their distribution coefficient Kd.

i) A first set of experiment was performed under static conditions (batch technique) in order to quantify the Kd values in the range of concentration under interest in HF, HCl and in HF - HCl media.

ii) In the second set of experiments, dynamic procedures (column chromatography in the elution mode) were carried out in order to verify, under dynamic conditions, the retention - elution processes for these elements in the selected media. However, one may notice that such procedures cannot be performed if Kd > 500 cm³/g, owing to the large elution volumes required in view of the resin mass used in these experiments. Moreover, working with elements at tracer scale requires only small quantity of exchanger and therefore small anionic column.

On-line separation experiments were performed using the R.A.C.H.E.L device (Rapid Aqueous Chemistry apparatus for Heavy ELements) described elsewhere [13-15]. Short-lived isotopes of W, continuously collected and dissolved, were separated from the other products, first by fixation on a small anionic column, and secondly, by elution with a suitable HCl or HCl - HF solution, according to the off-line results.

2. Experimental

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2.1. Production and separation of the studied radionuclides Mo, W and U

For the off-line experiments, the behaviour of the elements W, Mo and U were followed using the radioactive tracers ^{178}W ($T_{1/2}$ = 21.6 d), ^{99}Mo ($T_{1/2}$ = 2.75 d) and ^{230}U ($T_{1/2}$ = 20.8 d).

An irradiation of ^{232}Th, at the isochronous cyclotron of Orléans (CERI, France) by a 34 MeV proton beam with an intensity of 20 μA for about 50 hours, led to the production of the radionuclide ^{230}Pa ($T_{1/2}$ ≈ 17 d) through (p, 3n) reaction. After about 15 day decay time, ^{230}U accumulated through β⁻ decay of ^{230}Pa, can be separated [16]. These irradiations lead also to the production of a large amount of fission products generated with large cross sections, and among others, the (β⁻, γ) emitter ^{99}Mo. The radiotracers ^{230}U and ^{99}Mo were stored as a stock solution in 0.2 M HF.

The ^{178}W radioisotope was obtained by 34 MeV proton-irradiation of a natural tantalum foil (0.3 mm thickness). After dissolution of the tantalum target in concentrated HNO_3 - HF mixture, the solution was evaporated to dryness. The obtained residue was treated with concentrated HF solution (succession of dissolution and evaporation) and the final residue dissolved in 1 cm³ 0.2 M HF. Separation of W from Ta was performed by fixation of both elements on anionic resin and elution with 0.5 M HCl - 1 M HF mixture. In these conditions, Ta remains on the column whereas W is eluted. The W fraction was evaporated to dryness, taken with 0.2 M HF and stored as a 1 cm³ stock solution.

For each radioactive tracer, specific activity was about 0.1 μCi / 10 μl.

On-line experiments were performed with short-lived isotopes of W produced at the accelerator MP Tandem 15 MV (Orsay, France) through irradiation of natural Dy target with a 90 MeV ^{16}O^{7+} beam. The dysprosium target (≈ 500 μg cm⁻²) was obtained by molecular plating [17,18] on aluminum of 8 μm thickness. Fusion-evaporation processes (^{16}O, xn) led to the formation of ^{174}W($T_{1/2}$ = 31 min), ^{175}W ($T_{1/2}$ = 35 min) and $^{172, 173}$W ($T_{1/2}$ = 8 min).

Reaction products recoiling from the target are thermalized in helium gaz and adsorbed on KCl aerosols. Continuous transportation of the aerosols together with reaction products is achieved

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in about 3 seconds. Aerosols are dissolved with 0.2 M HF solution in a dissolver-degaser unit. The resulting solution is supplied by a pump to a chromatographic setup of 2 coupled columns. The first column filled with cationic resin (Dowex 50) fixes the trivalent lanthanides (Ln^{3+}) while W and his daughter Ta as anionic complexes pass through. The second one, filled with anionic resin (AGMP1), retains W and Ta isotopes, which can be measured on the column. A more detailed description of the RACHEL setup can be found in ref 15.

After accumulation for about 30 minutes, elution was performed with a chosen medium (HCl or HCl - HF solution) in order to test the feasibility of W separation.

2.2. Chemicals

In all experiments, the resin used was the strong basic macroporous anion exchanger BIO-RAD AGMP-1 (analytical grade, 200-400 mesh, Cl form). For static experiments, the resin was washed thoroughly with distilled water and air-dried in an oven at 70°C for 24 hours, to determine accurately the used masses.

All chemical reagents used were of analytical grade, and deionized water (18 MΩ cm) was used throughout. HF and HCl solutions were titrated with standard NaOH solutions, freshly prepared.

2.3. Determination of the distribution coefficients

Static conditions

Experiments were carried out with 50 to 100 mg of resin (precisely weighed, m_{res}) into a polyethylene vial. After addition of the acid mixture (also weighed), a small weighed quantity of the solution containing the radioisotopes was added (10 to 50 µl). The final volume (V_{sol}) of the solution in contact with the resin was 5 cm³. The vials were then shaken overnight at room temperature in order to reach equilibrium. After centrifugation for 30 minutes, the solutions were decanted and filtered on 0.2 µm micropore filters in order to eliminate the finest particles which could lead to unreproducible results. For each solution, the activity (A_{sol}) of a precisely weighed

aliquot (4 cm^3) was measured under well-defined geometric conditions. Required counting times depended on the distribution coefficients, varying between 1 and 24 hours. Radioactive decay corrections were applied if needed.

Three to four reference solutions were done with weighed quantities of the stock solution and measured in the same geometrical conditions (A_{init}). All measurements were in very good agreement.

Distribution coefficients K_d (in g cm^{-3}) were calculated by comparing the initial activity introduced with the measured activity of the filtered samples, using the classical relation :

$$Kd = \left\{\frac{A_{init} - A_{sol}}{A_{sol}}\right\}\left\{\frac{m_{res}}{V_{sol}}\right\} \qquad (1)$$

Dynamic conditions

Because of short half-life and low production yield of element 106, chemical separations tested with the assumed homologues, must be very fast and efficient. For that purpose, tubings and columns used in our experiments were as short as possible in order to minimize void volumes and dilution of the elements under study in the collected fractions.

All the components in contact with the mobile phase were chemically inert as regard to HF. For that purpose, columns, tubings and vials were made of Teflon or polyethylene. The column (25 mm length and 1.6 mm inner diameter) was filled with a weighed quantity (around 15 mg) of anionic exchanger AGMP-1. Washings of the resin with distilled water were followed by pretreatment with 0.1 M HF.

All experiments are performed in the elution mode process. Elements are adsorbed on the column using a selected medium where they are strong retained (see sub-section 3.2). The medium under investigation is then percolated through the column. Each elution fraction is collected and measured under well defined geometric conditions. The elution curve could then be plotted and a fitting program [19] made possible to determine the chromatographic parameters. These calculations

are based on the Glueckauf's theory of chromatography [20,21] and enabled us to determine accurately the volume ($\overline{V}$) corresponding to the maximum activity of the elution curve (Centroid distribution), the number of theoretical plates (N), the maximum intensity of the peak (A_{max}). The activity ($A(V)$) and therefore the amount of the eluted element is given by :

$$A\,(V) = A_{max}\,\text{Exp}\left\{-\frac{N}{2}\frac{\left(\overline{V}-V\right)^2}{\overline{V}\,V}\right\} \qquad (2)$$

And therefore the corresponding K_d value is defined as :

$$Kd = \frac{\overline{V}-V_i}{m_o} \qquad (3)$$

Where V_i is the void volume of the column and m_o the mass of dry resin.

3. Results and discussion

3.1. Off-line batch experiments

Behaviour in HF media

It is well-known that elements of group 4 (Zr, Hf), 5 (Nb, Ta) and 6 (Mo, W) as well as Pa(V) and U(VI), form strong anionic complexes in fluoride media [10,11,22-27]. The strongest are obtained with pentavent elements but for hexavalent elements the complexes remain still very strong.

The distribution coefficients relative to the adsorption of Mo, W and U are mostly unknown. In our experiments, these parameters were quantified in order to ensure the complete fixation on anionic exchanger.

Fig. 1 shows obviously that Mo and W are strongly retained on anionic exchanger all over the studied concentration range : Kd values higher than 10^4 for Mo and 10^5 for W could be reached at

low HF concentrations. However, the distribution coefficients decrease with increasing HF concentration with a slope of -1 (on logarithmic scale). This phenomenon is in perfect agreement with the behaviour of elements of group 4 and 5 described in previous works [10,11,22,24]. Moreover, the strength of the Mo and W fluoride complexes makes possible to overcome the great tendency of these element towards hydrolysis and formation of polymerized species [24].

Concerning uranium, the Kd values decrease drastically with increasing HF concentration, with a slope of -3. This phenomenon gives evidence of the lower affinity of U towards F⁻ ions in comparison with Mo and W, which could not be interpreted by competition reactions between complexation and hydrolysis. Indeed, in non-complexing media, hydrolysis of U(VI), under UO_2^{2+} form, is known to start at pH higher than 3, with a great tendency towards dimerization [26]. In our experiments (otherwise carried out in complexing media), the HF concentrations under study correspond to pH values between 1.3 and 2. Moreover, the estimated formation constants of the most probable hydrolysis species and fluoride complexes [26], even if they do not take into account medium effects (since extrapolated to I=0 in non-complexing media), enable us to assume, like in the case of Mo and W, that complexation of U with fluoride ions prevails over hydrolysis reactions all over the investigated range of HF concentrations.

The first conclusion of this study is that the fixation of these three elements is complete and very efficient in HF, but the concentrations have to be very carefully chosen (around 0.1 M HF) to avoid the partial elution of U (see sub-section 3.2). Moreover, the estimated slopes $\frac{\partial \log Kd}{\partial \log[HF]}$ are only a way to compare the adsorbabilities of the studied elements. They have no chemical meaning because HF is a weak acid and in our experiments, neither the free fluoride concentration nor pH has been kept constant. At HF concentration between 0.3 and 1 M, it appears that adsorbabilities vary in the order U < Mo < W, but Kd values are much smaller than those obtained at lower HF concentration, which allows strong fixation of the three elements on anionic exchanger.

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Behaviour in HCl media

Elements of group 4 (Zr, Hf), 5 (Nb, Ta) and 6 (Mo, W) and Pa form hydrolyzed or polymeric species in HCl media at relatively low concentration, owing to the low complexation capability of chloride anions as compared with fluoride ions. Among the studied elements, U is an exception as regard to its behaviour towards hydrolysis. It is also known that for W, the threshold of HCl concentration in order to avoid hydrolysis is higher than 6 M [24]. At high HCl concentration (> 10 M) anionic complexes could be formed, but their stability constants are much lower than those of the fluoride complexes [24,25].

The distribution coefficients for Mo, W and U have already been studied by Kraus et al. [12], but concerning W, only over a narrow concentration range (6-12 M). Moreover, Kraus' values of Kd, represented as a function of acid concentration on semi-logarithmic scale, are very difficult to determine accurately, especially at low concentrations. We studied the variation of the Kd values in HCl concentrations varying from 0.2 to 5 M for the three elements.

Present results, summarized in Fig. 2, are in good agreement with the data from Kraus et al. [12] all over the overlapped studied concentrations. For U and Mo, these variations present a pronounced minimum at about 1 - 2 M HCl concentration, whereas the distribution coefficient of W remains approximately the same from 1 to 4 M HCl.

Concerning W and Mo, the observed increase of Kd values for HCl concentration lower than 1 M, is probably due to hydrolysis or perhaps to polymerization. However, polymerization reactions are unlikely in our case, since we worked with elements at tracer level (10^{-10} - 10^{-12} M), instead of 10^{-4} M in Kraus' work. Indeed, at very low concentrations, reactions between two microcomponents are excluded : the very small amount of available atoms leads, of course, to a very low probability of such a reaction. Moreover, hydrolysis phenomena of U(VI) seem unlikely, because it is known to start at pH higher than 3, even at tracer level [26]. Although behaviour of uranium remains difficult to explain, one may emphasize that the presence of a minimum near 1M HCl has already been

observed, not only for hexavalent U and Mo, but also tetravalent Pu, Zr and pentavalent Np, Nb and Pa [27].

The Kd values observed for 1 M HCl (Kd ≈ 10 for W and Mo and Kd ≈ 1 to 2 for U) could be used in order to remove these elements, adsorbed on an anionic exchanger.

On the other hand, for high HCl concentrations, a separation of Mo and W seems to be possible. By using 5 M HCl solution, Mo remains held on the column (Kd ≈ 400), while W has only a Kd value of about 10 and thus would be immediately eluted (see sub-section 3.2).

Behaviour in HF- HCl media

The behaviour of W, Mo and U in HF - HCl mixtures are somehow different and the variation of the Kd values depends strongly on the concentration of both acids. The presence of fluoride avoids hydrolysis reactions to occur, but the stability constants of the mixed chloro-fluoride complexes are strongly dependent on the HCl content.

Distribution coefficients for W, Mo and U in mixture HF - HCl were also studied by Kraus et al. [12], only with 1 M HF. In this work, only the variation of the Kd values for HCl concentrations varying from 0.05 to 1 M for two concentrations of HF (0.25 and 1 M) were re-investigated. Results are given on Fig. 3.

Here again, results are in perfect agreement with the work of Kraus et al. [12]. The HF concentrations used in our experiments do not have any effect on the Kd values. Moreover, it is important to note that in this range of concentration, the Kd values decrease drastically with increasing HCl concentration : for W, Kd values decrease of about 2 orders of magnitude when the HCl concentration passes from 0.05 to 0.5 M. These media seem to be very interesting for separation of U from W and Mo.

According to the fact that in fluoride media, the competition between complexation and hydrolysis is in favor of complexation, the use of a mixture 1 M HF - 1 M HCl for complete desorption (Kd ≈ 5 for U and 20-30 for Mo and W) appears to be a better solution than the elution

with 1 M HCl solution. This fact is totally inconsistent with the review of J. Korkish [24], who indicates a strong adsorption in this medium.

3.2 Off-line desorption experiments in dynamic conditions

The dynamic experiments were performed by taking into account the Kd values measured in static conditions. Only acid concentrations where separations between elements appear possible were investigated. It is important to remember that according to the purpose of this work (the chemistry of element 106), only fast and complete separation are of interest. On the other hand, in order to facilitate the final preparation of the source, some mixture of HCl with organic solvents (ethanol and acetone) were also tested.

In all experiments, flow rate is fixed at 1.5 cm^3 min^{-1}. Experimental data, after normalization to 100 %, by adding the activity of each elution fraction which does not refer to the peak integral, have been fitted using eq. 2. However, in the case of small retention volumes (V < 2 cm^3), the number of experimental values (steps of 200 µl) does not allowed a rigourous fitting accuracy. Therefore, for a sharp elution peak, the values of the fitted eluted activity have no physical meaning, whereas the corresponding volume represents truly the centroid of the distribution.

According to eq. 3, $\bar{V}$ is directly related to Kd value. The variations of the centroid distributions (expressed in cm^3) as a function of HCl concentration are expected to vary similarly as those of Kd. They are represented with elution curves on inserted graphs but in that case, lines are included only to guide the eye.

Fixation and elution with HF

Hydrofluoric acid appears to be one of the best candidate as a fixation medium on anionic exchange resins (Sub-section 3.1). Due to the high strentgh of fluoride complexes, hydrolysis and

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polymerization could be avoided, leading to reproducible behaviour. Refering to Fig. 1, elements W, Mo and U in 0.1 M HF are easily adsorbed on a small anionic column.

In the case of W and Mo, in order to check the adsorption strength over a wide volume of eluent (> 50 cm^3), washings were conducted in 0.1 M HF : no activity was detected in the collected elution fractions.

Concerning U, the surprising low Kd values observed at high HF concentrations in the static experiments were checked in the dynamic ones : broadened elution peaks, shown on Fig. 4, appear in 1 and 2 M HF. Moreover in 0.5 M HF, this phenomenon also appears but is characterized by a very wide and flat distribution. These results suggest that the separation of U from Mo and W should be carried out in 2 M HF medium. Moreover, the corroborative static and dynamic experiments show clearly the low affinity of U for fluoride ions contrary to the elements W and Mo.

Elution with HCl

Elutions with HCl solutions were carried out after fixation of the elements in 0.1 M HF and elimination of the excess of fluoride ions by washings the column with distilled water.

Results obtained for the desorption of Mo, W and U using various concentrations of HCl solutions are presented on Fig. 5 to 7.

It could be easily seen on these graphs, that HCl solutions of concentration ranging from 1 to 2 M are suitable to desorb completely and rapidly all the elements retained on the column in less than 1.5 cm^3. Moreover, in those media, 0.5 cm^3 are enough to remove more than 95% of the initial activity ; using 0.5M HCl, the centroid is not shifted but the peak is more broadened.

At lower HCl concentrations, for W and Mo, hydrolysis reactions interfere with weak complexation by chloride ions and the desorption peaks become wider (for Mo in 0.1 M HCl, the required volume for complete elution is greater than 8 cm^3).

For higher HCl concentrations the behaviour of the Mo and W are somehow different. As it was pointed out in the static experiments, the Kd values of Mo increase with an increase of the HCl

concentration, while for W the Kd values behave constant till 4 M and then increase slowly. This fact could be interpreted with the formation constants of the various hydrolyzed forms for both elements (tungsten is still hydrolyzed in 6 M HCl), whereas weak anionic complexes of Mo could be formed with Cl⁻ anions, with larger Kd values, leading to a wide elution peak.

It could be emphasized that dynamic experiments are mostly in agreement with the static ones which could be seen by comparing Fig. 2 with the centroid distribution on Fig. 5-7. For W and U, slight differences are observed, especially at low HCl concentrations. Elutions in dynamic experiments were carried out in a medium different from the fixation medium.

Mecanisms of elution processes involved might be assumed as follows :
- breaking of the fluorides bonds (metal - F) of the initial adsorbed complexes,
- diffusion - adsorption of the new species along the column according to their own affinity.

Under these assumptions, the difference between static and dynamic results at low HCl concentration could be explained in terms of kinetic effects in the destruction of the strong fluoro complexes adsorbed.

Elution with HCl - organic solvent

Some results obtained for the desorption of Mo with HCl together with alcohol solutions are presented on Fig. 8. These elution curves show clearly the influence, on the desorption process, of the well-known tendency of alcohol to increase the elution volume. However, the use of a solution containing 1 M HCl and ethanol (ratio 1/1) is still suitable for a fast and complete desorption (V < 2 cm³).

Similar results were obtained with 0.5 M HCl and acetone in a proportion of 1/1. Once again, this organic agent increases the elution volume but is still reasonable for complete desorption (V ≈ 2.5 cm³).

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The use of HCl - EtOH mixtures with other proportions (5% HCl 1 M / 95% EtOH, 5% HCl 10 M / 95% EtOH) enhanced the broadening of elution peaks so much that a peak shape is not distinguishable anymore.

Same experiments carried out with W have led to similar results : organic solvent (ethanol and acetone) involved broadening of elution peaks. However, the volume $\overline{V}$ corresponding to the maximum activity was less shifted as compared to Mo.

Elution with HCl - HF media

As it was pointed out above, HF - HCl media appear to be very efficient for the separation of U from Mo and W. Elution curves with 1M HF and various HCl concentrations are presented on Fig. 9-11.

From Fig. 11, it could be easily seen that elution processes of U are fast and complete with 0.1 M HCl / 1 M HF, whereas for Mo and W, the retention phenomena are greater (for 0.1 M HCl - 1 M HF, $\overline{V}$ for Mo is about 6 cm^3, and higher than 12 cm^3 for W). However, no fast and complete separation of W from Mo could be achieved by using these media : elution peaks overlap one another all over the studied concentration range.

Applications

It is possible, considering Fig. 5-7 and 9-11, to choose the optimal conditions for individual separations of U, W and Mo. Non exhaustive separations could be proposed : after adsorption of the three elements on anionic exchanger in 0.1 M HF (Fig. 1), selective and fast separations could be achieved as follows.

1) According to Fig. 11, 95 % of U can be quickly removed from the column within 1.1 cm^3 by using 0.1 M HCl - 1 M HF, while Mo and W remain held on the column.

2) Selective elution of W could be performed by using 5 M HCl solution (in 1 cm^3 , Fig. 6).

3) Finally, Mo could be thereafter eluted in 1 cm^3 using 1 M HF - 1 M HCl (Fig. 9).

The proposed procedure to carry out fast and efficient separations of U, W and Mo is presented on Fig. 12.

3.3 On-line experiments

In these series of experiments, only the behaviour of W was checked out, owing to difficulties to produce on-line Mo and U radioisotopes by using an ^{16}O ion beam. Nevertheless, such tests are essential to determine experimental procedures which will be performed for the production of element 106. Indeed, in these experiments, W is really produced at ultra-trace level (about 10^7 atoms min^{-1}). Simultaneously, short-lived isotopes of Ta were generated (through β^+, EC decay), and in particular, the radioisotope ^{174}Ta ($T_{1/2} = 1.12$ h).

Off-line optimal conditions were tested on-line, in order to minimize elution volumes necessary to isolate the elements. Small volumes are an important factor for the very fast preparation of a source for detection of element 106, whose principal decaying mode is α particle emission.

Elution with HCl solutions

Elution curves with respectively 1 and 4 M are presented on Fig. 13. First of all, it could be emphasize that, at these concentrations, elution processes are very fast and efficient : in 500 µl, more than 99 % of the initial activity is eluted from the column. Results obtained in this type of experiments confirmed accurately those obtained in the dynamic conditions for the off-line measurements. So small volumes fit perfectly with the aim of this work.

Concerning the behaviour of Ta, in 4 M HCl, Ta is eluted simultaneously with W, while in 1 M HCl, Ta is eluted after W but the elution peaks overlap.

Elution with 1 M HF - HCl mixtures

Here again, on line experiments corroborate perfectly off-line dynamic measurements. Results summarized on Fig. 14, are consistent with the proposed procedure described in section 3.2 concerning the individual separation of element 106 chemical homologues.

In 2 M / 0.35 M / 0.2 M HCl - 1 M HF media, Ta (not represented on Fig 14) is not eluted and remains strongly adsorbed on the column while in 8 M HCl - 1M HF, elution process appears very slow, resulting in a flat distribution of Ta in the collected fractions.

4. Conclusion

Ion exchange chromatography experiments were carried out off-line (static and dynamic modes) and on-line (dynamic mode) by using macroporous anionic exchanger in order to isolate the most probable chemical homologues of element 106 : the hexavalent Mo, W and U elements. A large range of HCl and HF concentrations as well as HCl - HF mixtures were investigated off-line to determine the optimal conditions of fixation and individual elution of the three elements. Results have shown that fast and efficient separations can easily be achieved and enable us to propose a procedure allowing the very fast isolation of each element in a very small volume with a great efficiency. The off-line and on-line dynamic experiments were in very good agreement. Moreover, obtaining small elution volumes facilitates the fast achievement of thin α sources in very favourable conditions. In a next future, these preliminary experiments will be applied to search and the chemical isolation of long lived isotopes of element 106.

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Figure captions

Figure 1 : Adsorption of W, Mo and U on macroporous anionic exchanger in fluoride media in the range 0.1 to 1M HF. The dotted lines are included to guide the eye.

Figure 2 : Variation of Kd values of W, Mo and U on macroporous anionic exchanger in hydrochloric acid in the range from 0.2 to 5 M HCl. The dotted lines are included to guide the eye.

Figure 3 : Variation of Kd values of W, Mo and U on macroporous anionic exchanger in 1M HF - HCl mixtures. The HCl concentration varies from 0.05 to 1M. The dotted lines are included to guide the eye.

Figure 4 : Elution of element U in HF media. Elution speed was fixed at 1.5 cm^3 min^{-1}.

Figure 5 : Elution of element Mo with various HCl concentration. Elution speed was fixed at 1.5 cm^3 min^{-1}.

Figure 6 : Elution of element W with various HCl concentration. Elution speed was fixed at 1.5 cm^3 min^{-1}.

Figure 7 : Elution of element U with various HCl concentration. Elution speed was fixed at 1.5 cm^3 min^{-1}.

Figure 8 : Elution of element Mo with HCl - organic solvent mixtures. Elution speed was fixed at 1.5 cm^3 min^{-1}.

Figure 9 : Elution of element Mo with HCl - HF mixtures. HF concentration is maintained at 1M. Elution speed was fixed at 1.5 cm^3 min^{-1}.

Figure 10 : Elution of element W with HCl - HF mixtures. HF concentration is maintained at 1M. Elution speed was fixed at 1.5 cm^3 min^{-1}.

Figure 11 : Elution of element U with HCl - HF mixtures. HF concentration is maintained at 1M. Elution speed was fixed at 1.5 cm^3 min^{-1}.

Figure 12 : Proposed procedure for selective elution of W, Mo and U. Elution speed was fixed at 1.5 cm^3 min^{-1}.

Figure 13 : Elution of on-line produced W isotopes with various HCl concentrations.

Figure 14 : Elution of on-line produced W isotopes with HCl - HF mixtures. HF concentration is maintained at 1M. Elution speed was fixed at 1.5 cm^3 min^{-1}.
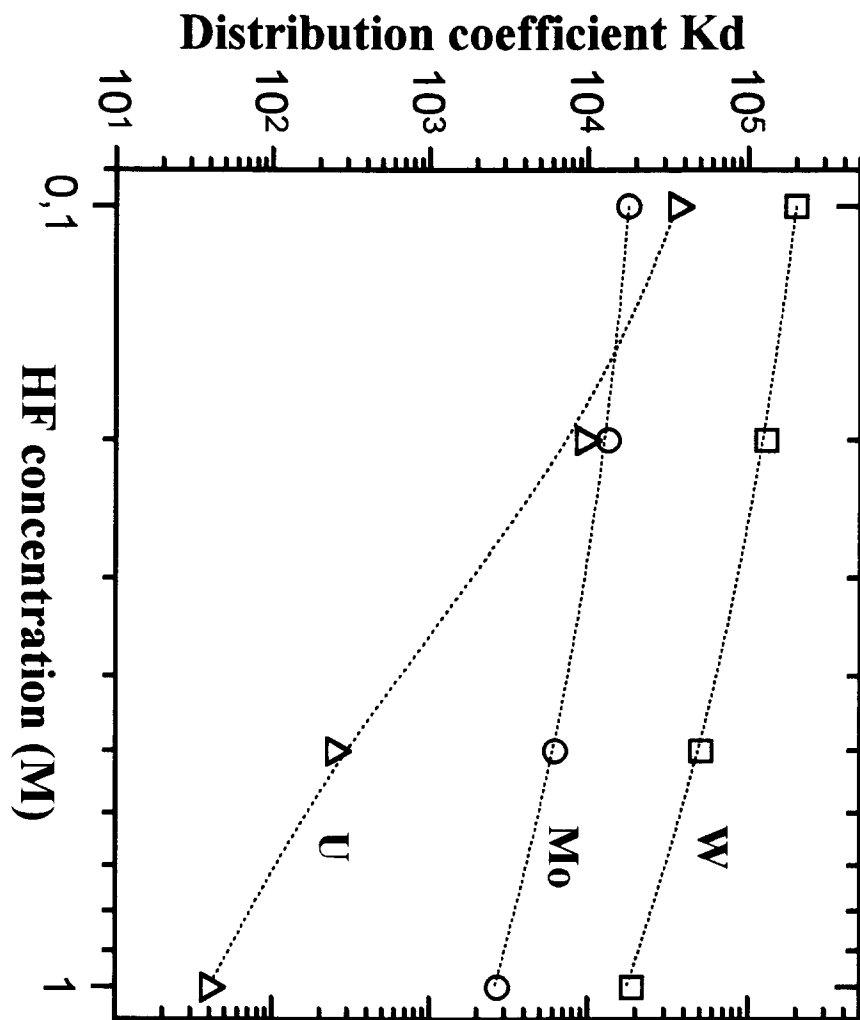
Figure 1 : **D. TRUBERT et. al.** **Search for chemical separations of element 106 homologues in HF and HF-HCl media.**
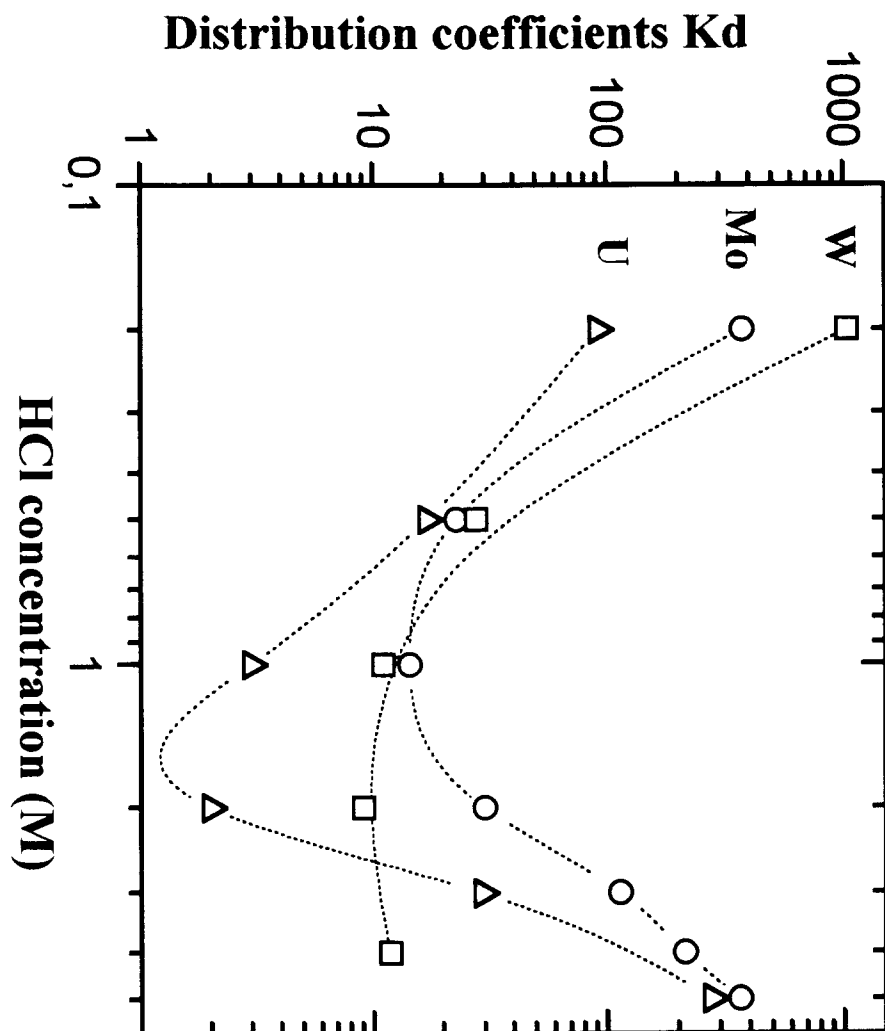
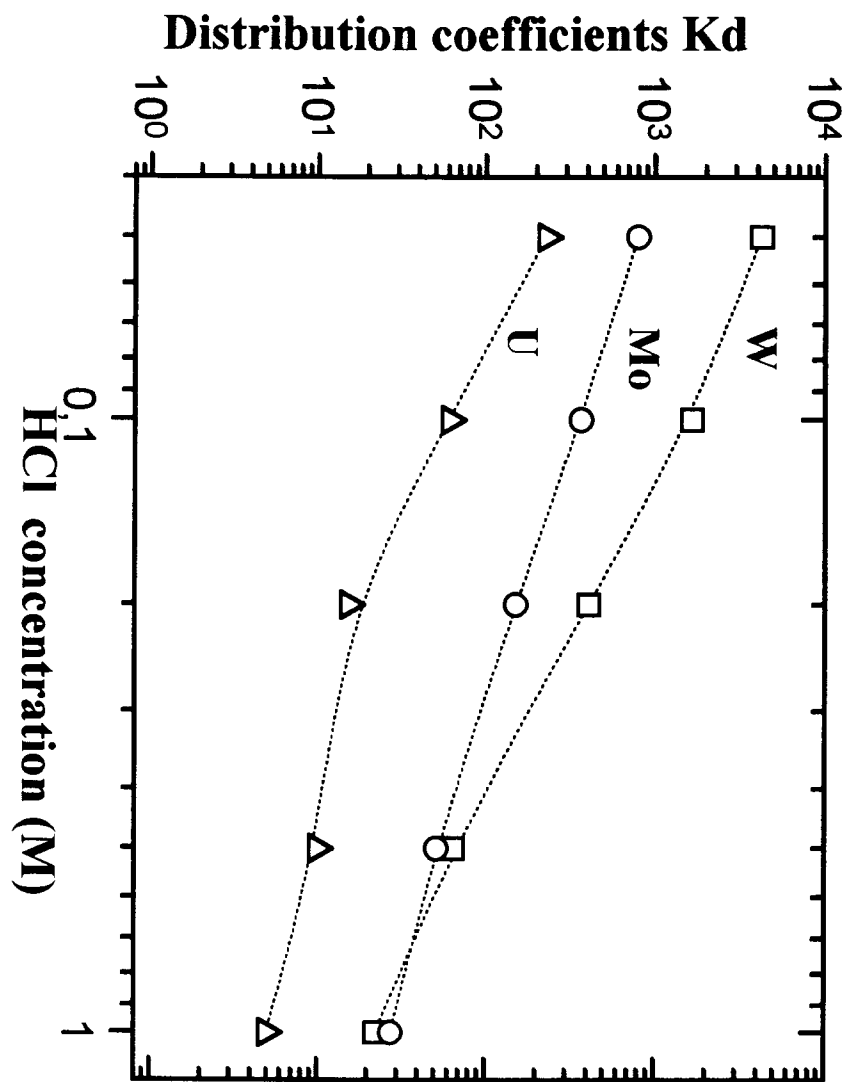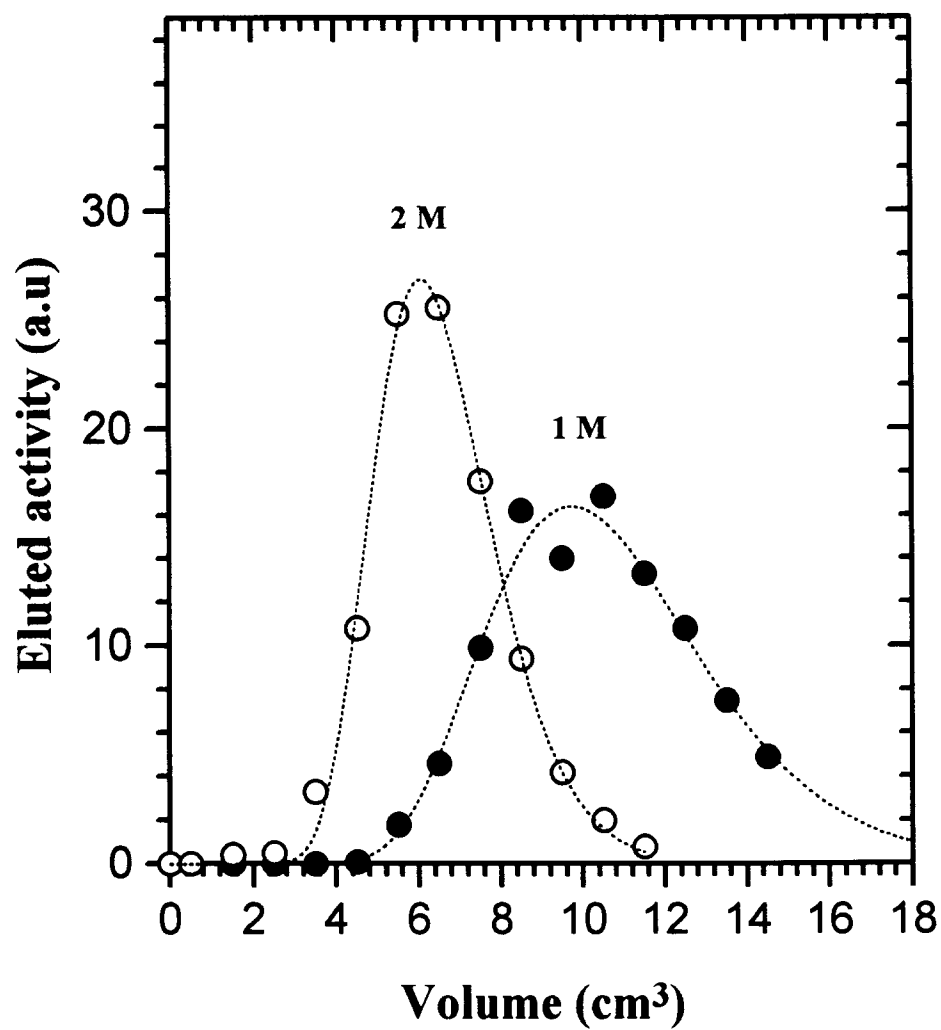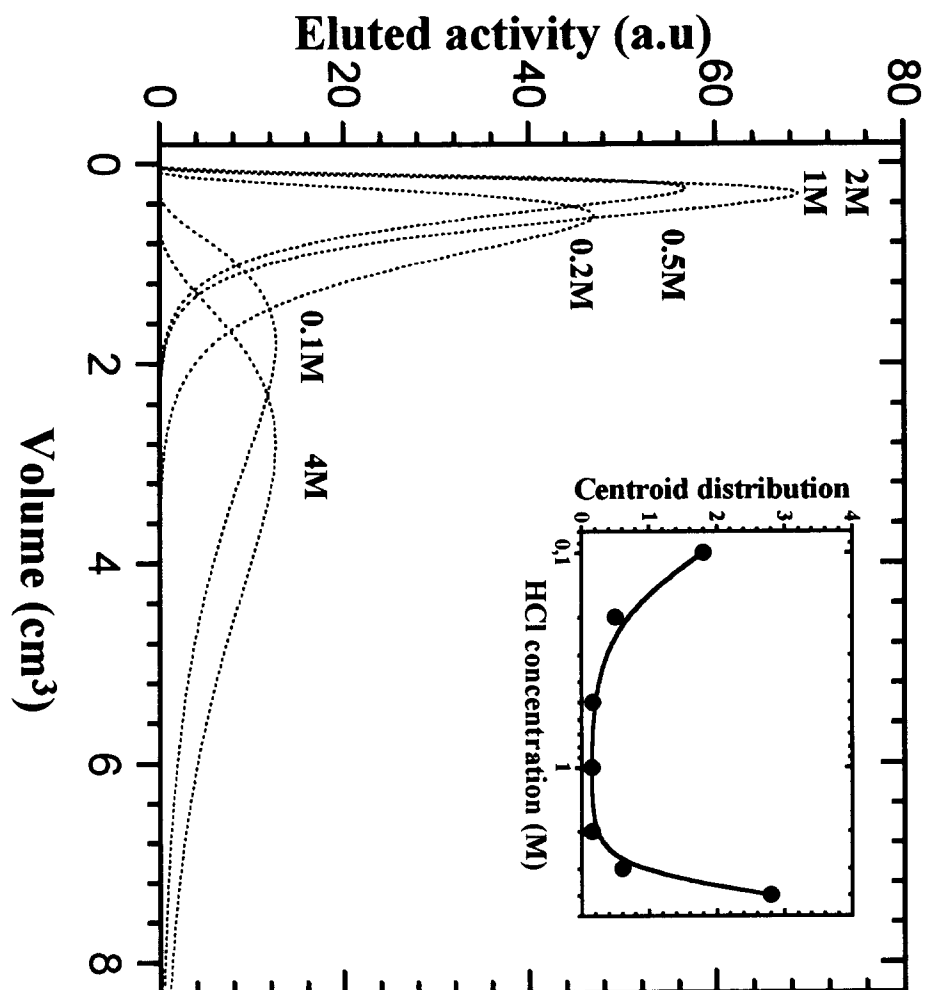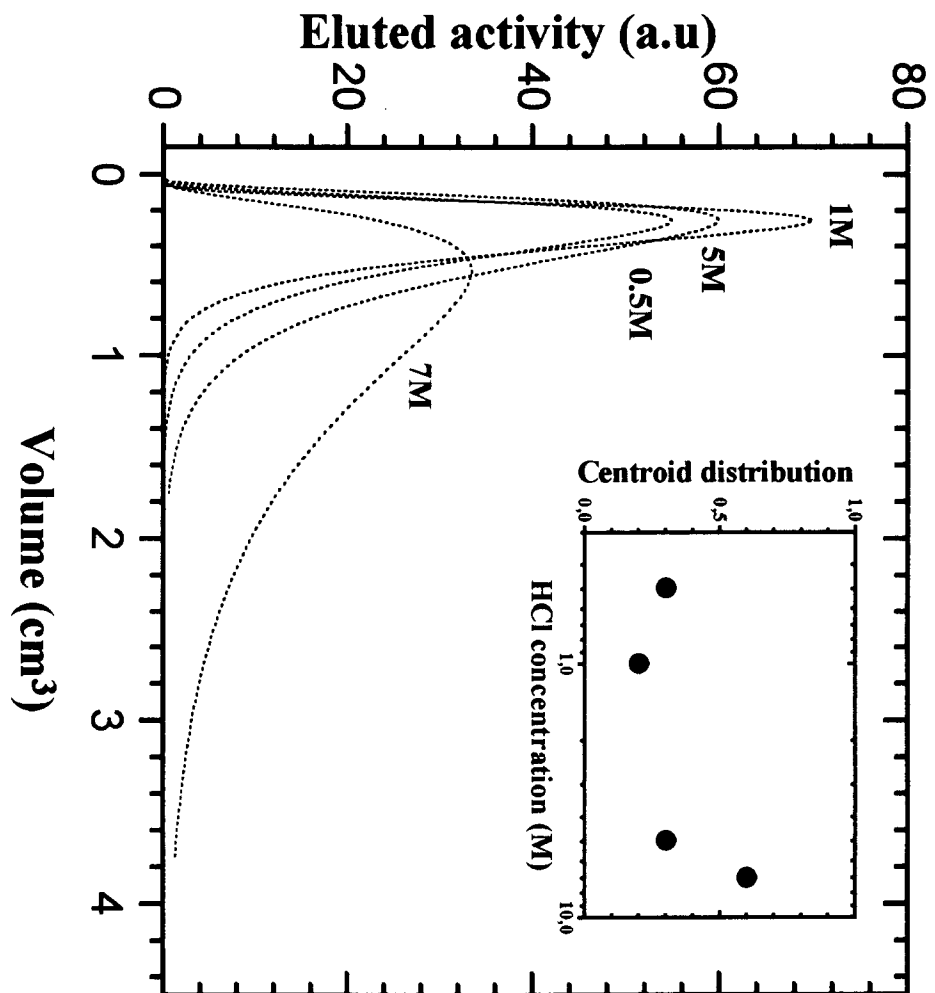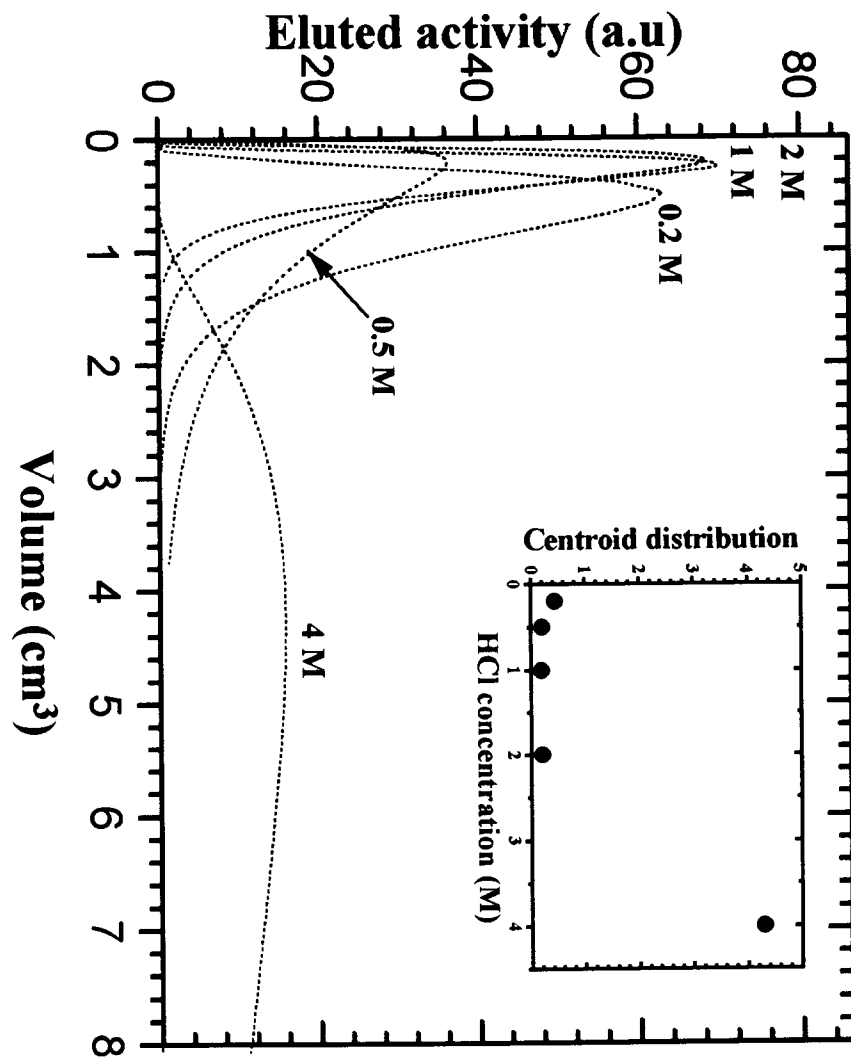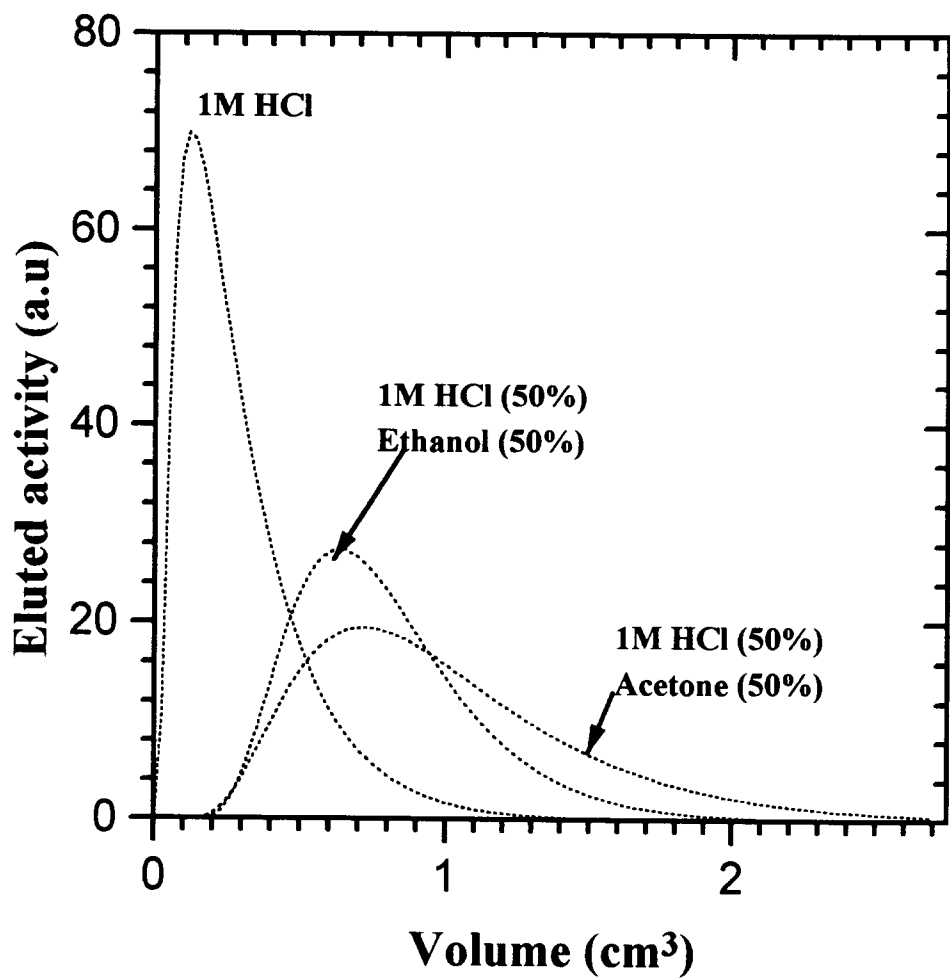**Figure 2 :** **D. TRUBERT et. al.** **Search for chemical separations of element 106 homologues in HF and HF-HCl media.**

Figure 3 :   **D. TRUBERT et. al.   Search for chemical separations of element 106 homologues in HF and HF-HCl media.**

Figure 4 :   D. TRUBERT et. al.   Search for chemical separations of element 106
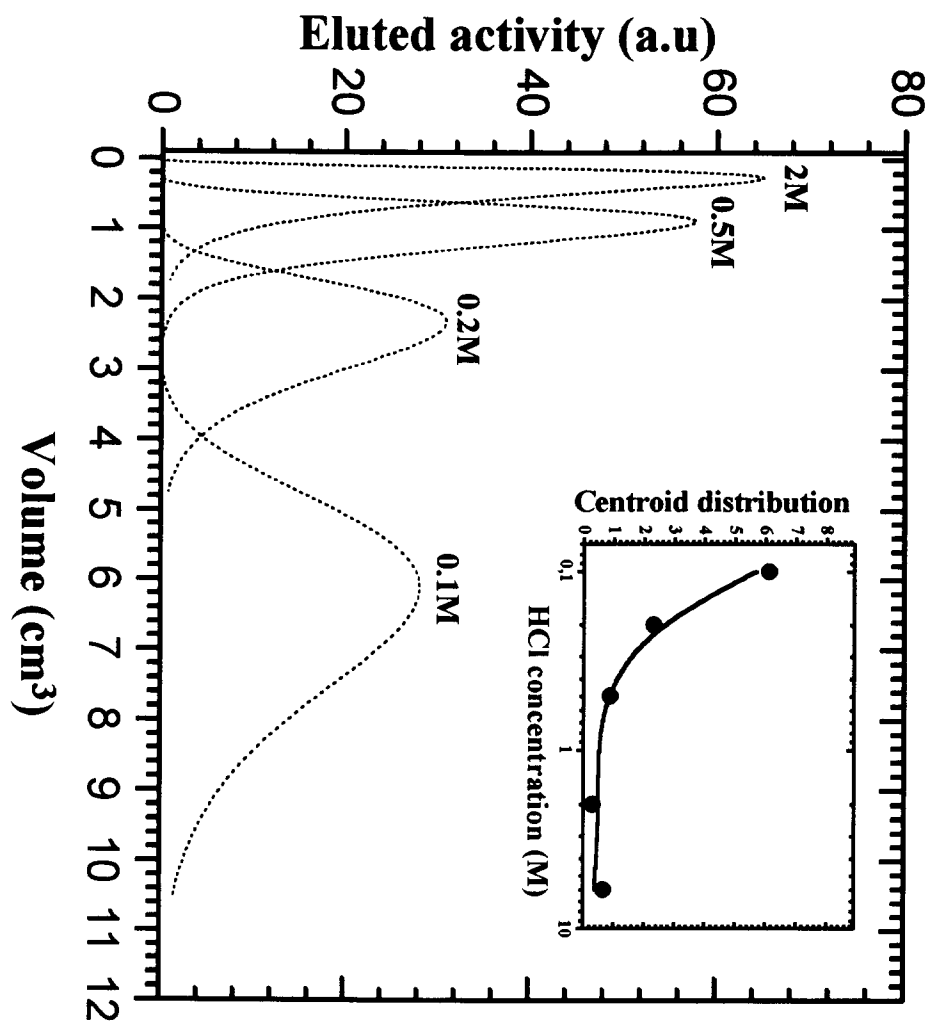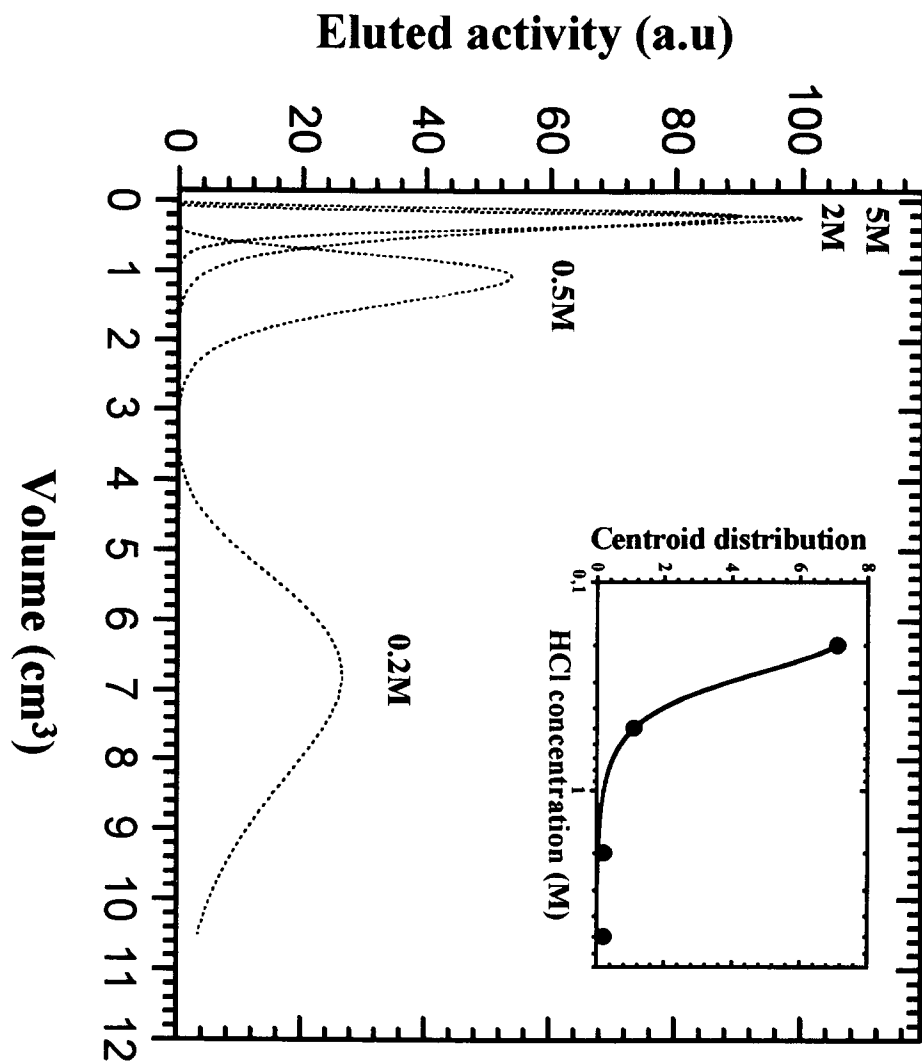homologues in HF and HF-HCl media.

Figure 5 : **D. TRUBERT et. al.** **Search for chemical separations of element 106 homologues in HF and HF-HCl media.**

Figure 6 : **D. TRUBERT et. al.** **Search for chemical separations of element 106 homologues in HF and HF-HCl media.**

Figure 7 : **D. TRUBERT et. al.** Search for chemical separations of element 106 homologues in HF and HF-HCl media.

Figure 8 :   D. TRUBERT et. al.   Search for chemical separations of element 106
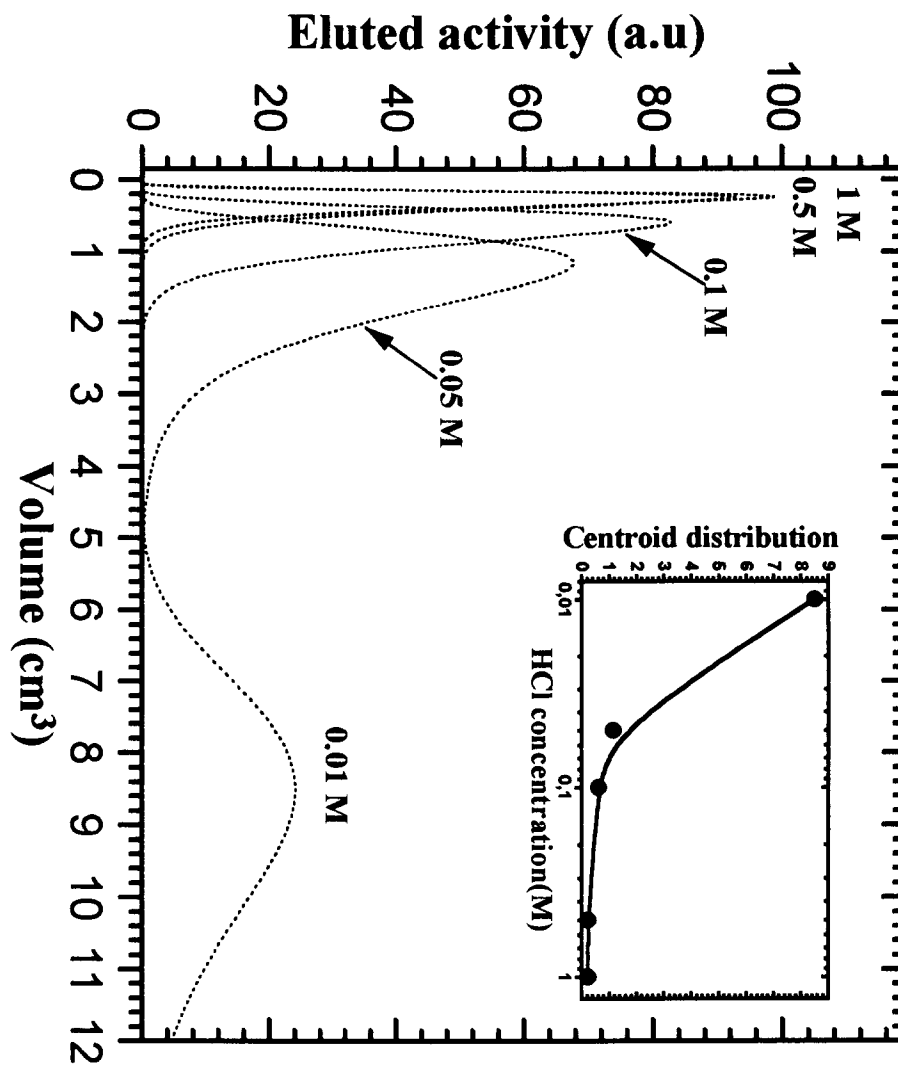homologues in HF and HF-HCl media.

Figure 9 :   D. TRUBERT et. al.   Search for chemical separations of element 106 homologues in HF and HF-HCl media.
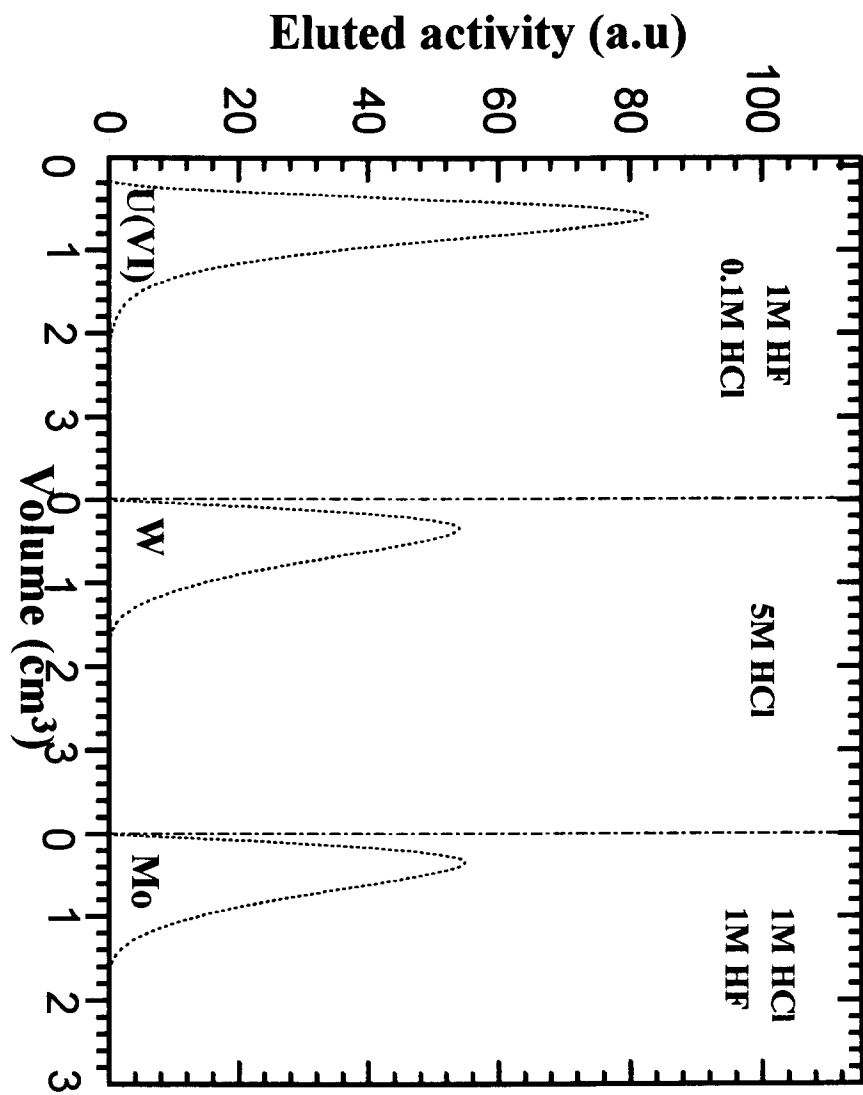
Figure 10 : D. TRUBERT et. al. Search for chemical separations of element 106 homologues in HF and HF-HCl media.

Figure 11 :   D. TRUBERT et. al.   Search for chemical separations of element 106 homologues in HF and HF-HCl media.
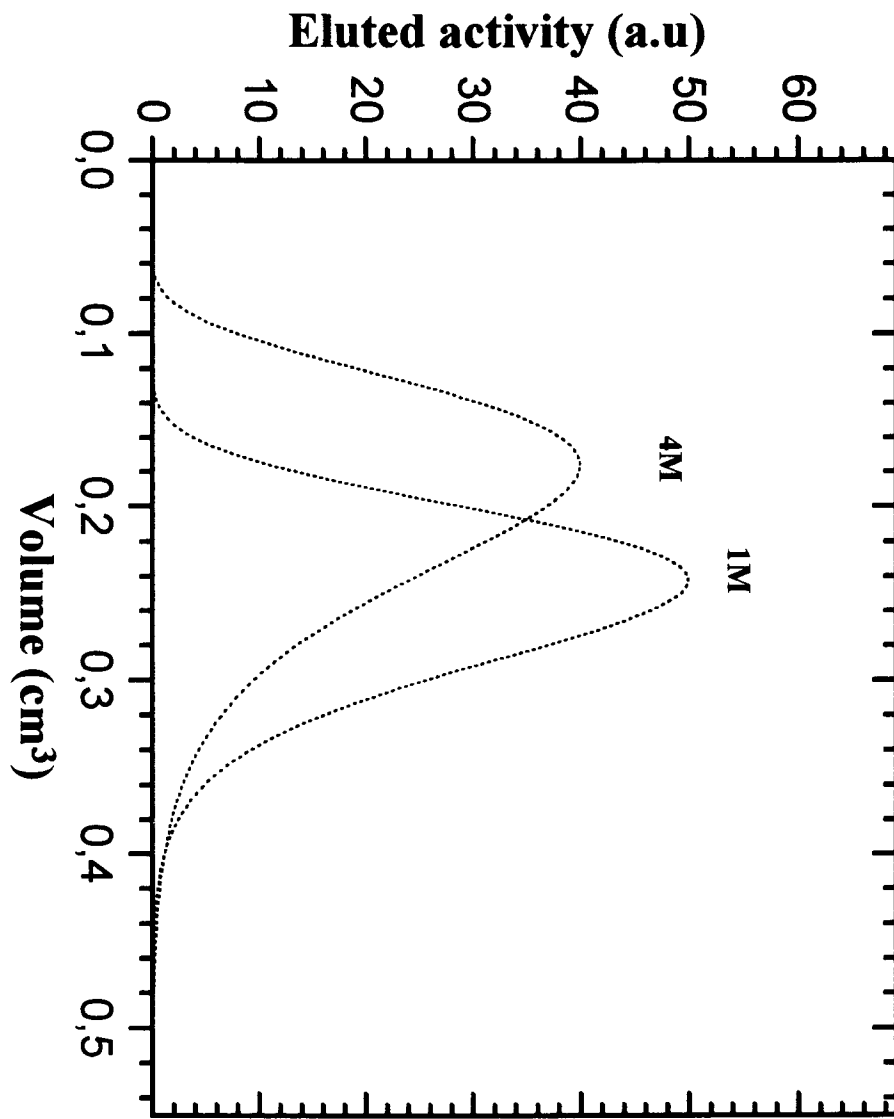
Figure 12 : D. TRUBERT et. al. Search for chemical separations of element 106 homologues in HF and HF-HCl media.

Figure 13 :   D. TRUBERT et. al.   Search for chemical separations of element 106 homologues in HF and HF-HCl media.
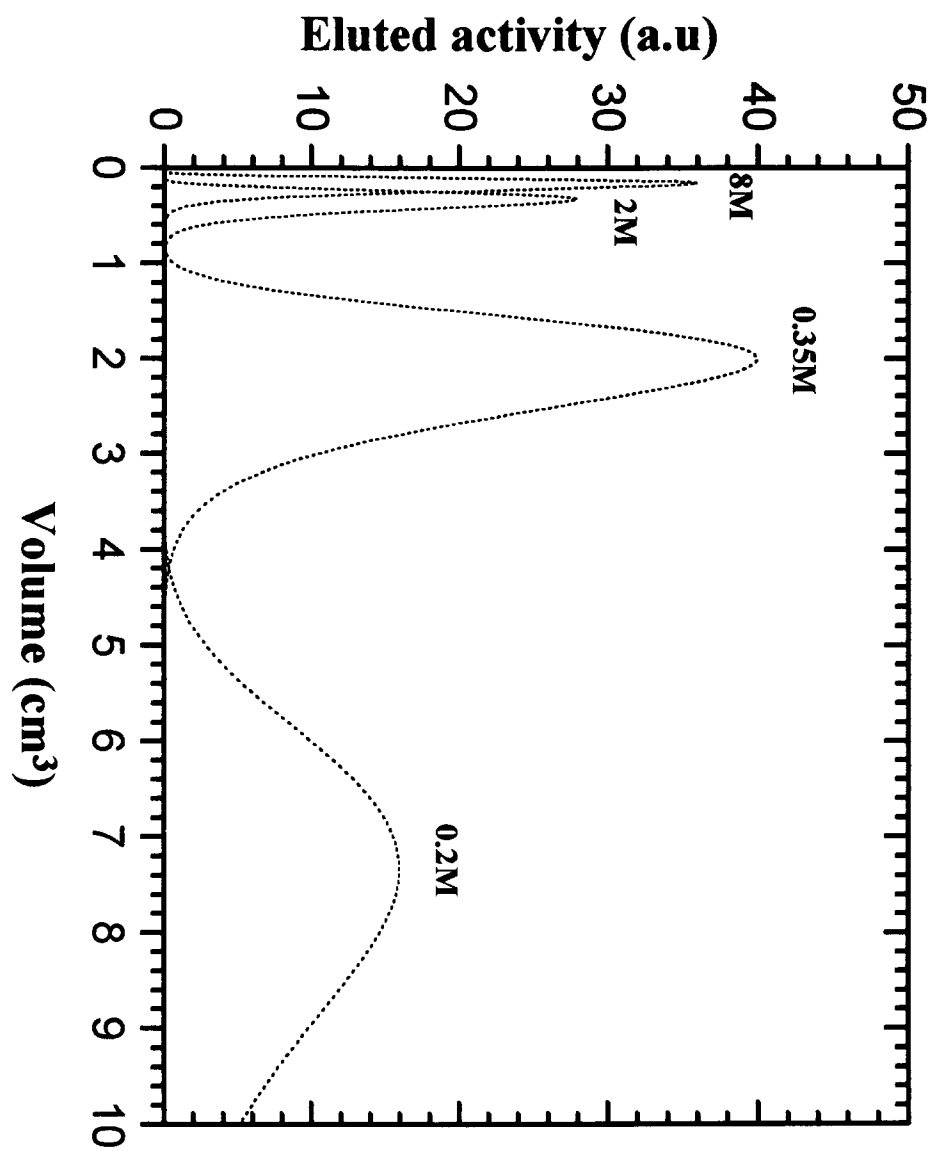
Figure 14 : D. TRUBERT et. al. Search for chemical separations of element 106 homologues in HF and HF-HCl media.