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Transactinide superheavy elements: isolation and chemical properties in solution †

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Abstract. Data on the isolation of transactinide elements and their homologues and investigation of their chemical properties in solutions, which were obtained by chromatographic extraction and other methods, are generalised for the first time. Particular attention is given to model experiments on the prediction of the chemical properties and investigation of the relativistic effects of these elements on the basis of the behaviour of homologous elements in solutions containing various complexing ligands. The results and prospects for future research are discussed. The bibliography includes 105 references.

I. Introduction

In recent years, considerable progress has been made in the synthesis of new transactinide elements (TAEs) or, as they are also called, superheavy elements (SHEs). The elements with atomic numbers $Z = 114$, 115, 116 and 118 and the longest-lived (of the presently known) isotopes of element 106 (^{265}Sg and ^{266}Sg) have been synthesised for the first time in the Flerov Laboratory of Nuclear Reactions of the Joint Institute for Nuclear Research (FLNR JINR, Dubna, Moscow region, Russian Federation).[1–4] The element with $Z = 113$ was observed in the decay chain of element 115.[2] High stability to various types of nuclear radioactive decay in the vicinity of deformed ($Z \approx 108$, $N = 162$) and spherical ($Z = 114$, $N = 184$) nuclear shells was observed experimentally and established by calculations. This fact is indicative of the occurrence of the so-called 'islands of stability' among superheavy elements, which has been predicted as early as in the mid-1960s.

During production of new elements, their nuclear physical characteristics ($T_{1/2}$, the radioactive decay mode, *etc.*) are generally determined by measuring α decay or spontaneous fission of the nucleus that formed and the correlations between the decay of parent and daughter radionuclides. However, the exact position of a new element in the Periodic Table should be confirmed by its chemical identification. Investigations of the chemical properties of superheavy elements provide deeper insight into their electronic structures.

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Fourteen transactinide elements and ~70 their isotopes have been produced. In 1997, IUPAC approved the names and chemical symbols of TAEs with $Z = 104 – 109$. In 2003 – 2004, the names and chemical symbols of elements 110 and 111 (Table 1) were approved. Other TAEs have no names. The chemical properties of only two TAEs, *viz.*, rutherfordium and dubnium, were studied in solution. Two experiments on the isolation and chemistry of seaborgium and one investigation of the chemistry of hassium have been carried out. Table 2 lists the isotopes of TAEs, which were studied by chemical methods in solution. The longest-lived ^{261}Rf isotope ($T_{1/2} = 78$ s) was discovered in 1970. However, detailed investigations of the chemical properties of rutherfordium in solution were started only in the early 1990s, which was associated with the development of new approaches to the isolation of TAEs. Investigation of the chemistry of transactinide elements and, particularly, of elements with $Z \geqslant 106$, is a complicated and laborious process. The difficulties are associated with very short lifetimes and low production cross-sections of TAEs in reactions with multicharged ions. These experiments are carried out only in a few research centres in the world (see Table 2).

Table 1. Names and symbols of transactinide elements.

Atomic number (Z)	Name	Symbol
104	Rutherfordium	Rf
105	Dubnium	Db
106	Seaborgium	Sg
107	Bohrium	Bh
108	Hassium	Hs
109	Meitnerium	Mt
110	Darmstadtium	Ds
111	Roentgenium	Rg

To find the optimum conditions for the isolation and investigation of the chemical properties of these elements, it is necessary to perform preliminary experiments with homologous elements in various systems. In addition, these experiments are required because the relativistic effects in the chemical behaviour of heavy elements can lead to considerable deviations from the general regularities.

The chemical properties of TAEs are studied both in the gas and liquid phases. Studies in the gas phase have the advantage that

† The review is dedicated to the blessed memory of Academician Georgii Nikolaevich Flerov, who has initiated studies on the production and chemical identification of superheavy elements in Russia.

Table 2. Isotopes of transactinide elements studied by chemical methods in solution.

Isotope	$T_{1/2}$ /s	Production reaction	Investigation method	Research centre (year)	Ref.
^{261}Rf	78	^{248}Cm(^{18}O, 5n)	ion-exchange chromatography	LBL (1970)	5
	78	^{248}Cm(^{18}O, 5n)	the same	FLNR JINR (1990)	6
	78	^{248}Cm(^{18}O, 5n)	"	FLNR JINR (1998)	7
	78	^{248}Cm(^{18}O, 5n)	"	PSI (2000)	8
	78	^{248}Cm(^{18}O, 5n)	"	JAERI (2002)	9
	78	^{248}Cm(^{18}O, 5n)	"	JAERI (2004)	10
	78	^{248}Cm(^{18}O, 5n)	"	GSI (2004)	11
	78	^{248}Cm(^{18}O, 5n)	extraction chromatography	LBL (1980)	12
	78	^{248}Cm(^{18}O, 5n)	the same	PSI (1998)	13
	78	^{248}Cm(^{18}O, 5n)	liquid – liquid extraction	LBL (1994)	14, 15
	78	^{248}Cm(^{18}O, 5n)	the same	LBL (1996)	16, 17
	78	^{248}Cm(^{18}O, 5n)	adsorption	LBL (1996)	18
			the same	FLNR JINR (2001)	19
^{257}Rf	3.5	^{208}Pb(^{50}Ti, n)	extraction (on-line)	LBL (2002)	20
^{262}Db	34	^{249}Bk(^{18}O, 5n)	adsorption, extraction	LBL (1988)	21
	34	^{249}Bk(^{18}O, 5n)	extraction chromatography	LBL (1989)	22, 23
	34	^{249}Bk(^{18}O, 5n)	the same	LBL (1992)	24
	34	^{249}Bk(^{18}O, 5n)	"	LBL (1999)	25
^{263}Db	27	^{249}Bk(^{18}O, 4n)	ion-exchange chromatography	LBL (1992)	26
		^{248}Cm(^{19}F, 5n)	the same	IN2P3-UPS (2002)	27
^{262}Db	27	^{249}Bk(^{18}O, 4n)	"	GSI (2003)	28
	34	^{248}Cm(^{19}F, 5n)	"	JAERI (2004)	29
^{265}Sg	7.4	^{248}Cm(^{22}Ne, 5n)	"	GSI (1997)	30
	7.4	^{248}Cm(^{22}Ne, 5n)		GSI (1998)	31
^{269}Hs	~ 10	^{248}Cm(^{29}Mg, 5n)	CALLISTO	GSI (2004)	32

Note. The following abbreviations are used: LBL is Lawrence Berkley Laboratory (Berkley, USA), PSI is Paul Sherrer Institute (Villigen, Switzerland), JAERI is Japan Atomic Energy Research Institute (Tokai-Mura, Japan), GSI is Gesellshaft für Schwerionenforschung (Darmstadt, Germany), IN2P3-UPS is Institut de Physique Nucleaire, Radiochimie (Orsay, France), CALLISTO is Continuously Working Arrangement for Clusterless Transport of In-situ Produced Volatile Oxides.

TAEs with very short lifetimes can be investigated. Pioneering experiments on the chemistry of TAEs have been carried out by gas chromatography.[33] However, investigations in the gas phase are limited to volatile compounds. Besides, the electronic structures of the valence shells of elements in the gas phase can differ from those in the liquid state, which is reflected in their chemical behaviour.

Model experiments on the isolation and investigation of TAEs in solutions by ion-exchange chromatography in the on-line mode demonstrated the possibility of studying the physicochemical properties of radionuclides with half-lives of $\sim 5-10$ s.[34,35] Short-lived radionuclides with half-lives of $\leqslant 1$ s were isolated and detected using the super fast SISAK III (Short-lived Isotopes Studied by the AKUFVE Technique) extraction system.[36]

In the last decade, investigations of the chemical properties of TAEs have attracted considerable interest. In 2000 – 2001, studies on the synthesis of TAEs were started in the world-famous Orsay (France) and JAERI (Japan) nuclear research centres, in particular, with the use of ion-exchange chromatography. The number of publications, including relativistic quantum-chemical calculations of the atom states of TAEs in different systems, sharply increased.[37]

In several reviews, experiments on the isolation and the chemical behaviour of TAEs in the gas and liquid phases were analysed (in solutions, the behaviour of only Rf, Db and Sg and their homologues was considerated).[38–41] Data on model experiments aimed at studying TAEs in solutions containing various complexing ligands[42–54] are virtually lacking, although these experiments are required to search for the optimum conditions of isolation, prediction of the chemical properties of TAEs and elucidation of the relativistic effects.

The present review provides an overview of the general approaches to the development of procedures for isolation and investigation of the chemical properties of trace amounts of short-lived TAEs in solutions. The possibility of studying the chemical properties of TAEs (speciation of elements in solution, hydrolysis, complexation, valence states, *etc.*), including elements with $Z \geqslant 106$, was demonstrated by investigations of the homologous elements in various systems. The results of the isolation of short-lived isotopes of Hf, Ta, W, Re, Os, Hg, Pb as homologues of Rf, Db, Sg, Bh, Hs and elements 112 and 114, respectively, and studies of their chemical behaviour are considered. Experimental data on the isolation and the chemical properties of Rf, Db and Sg in solution obtained by chromatographic, extraction and other methods are summarised. In the review, it was shown that the relativistic effects can be revealed by performing comparative studies of the behaviour of TAEs and their homologues in solutions containing various complexing ligands. The results of studies and prospects for the use of different methods for the isolation and investigation of the chemical properties of TAEs in solution are discussed.

II. Principles of production and isolation of transactinide superheavy elements

1. Production of heavy and superheavy elements

The first artificial actinide elements were produced primarily by successive neutron capture in high-flux nuclear reactors or underground nuclear explosions in high neutron fluxes. The last element prepared by this method was ^{257}Fm ($T_{1/2} \approx 100$ days, $Z = 100$). Heavier nuclei are impossible to produce by this method because of short lifetimes. Transfermium elements have been synthesised

by reactions with multicharged ions at accelerators.‡ The elements with $Z = 101-105$ were prepared by so-called 'hot-fusion' reactions using bombardment of targets containing heavy isotopes of transuranium elements (from U to Es) with the accelerated ^{11}B, ^{13}C, ^{14}N, ^{15}N, ^{16}O, ^{18}O, ^{20}Ne, ^{22}Ne and ^{24}Mg ions. The elements with $Z = 106-112$ were produced by the 'cold fusion' reactions of the ^{208}Pb and ^{209}Bi nuclei with the ions varying from ^{54}Cr to ^{70}Zn. Longer-lived isotopes of Sg, Bh and Hs were synthesised by the reactions $^{248}Cm(^{22}Ne, 4.5n)$, $^{249}Bk(^{22}Ne, 4n)$ and $^{248}Cm(^{24}Mg, xn)$, respectively. The elements with $Z = 114$, 115, 116 and 118 were prepared using heavy isotopes of actinides (^{242}Pu, ^{244}Pu, ^{243}Am, ^{248}Cm and ^{249}Cf) as the targets and nuclei of the rare ^{48}Ca isotope as the bombarding particles.

In model experiments, the behaviour of carrier-free short-lived homologous elements is generally studied. These isotopes are also produced by nuclear reactions with multicharged ions at a cyclotron or by uranium fission. With the aim of studying the chemical properties of element 114 using its homologue (lead), a radioisotope generator was constructed to produce the short-lived ^{211}Pb isotope.[54]

2. Specificity of operations with short-lived elements at the tracer scale

Experiments with trace amounts of TAEs bring up the question about the reliability of the results obtained by studying the behaviour of several or even single atoms. The question arises as to whether the behaviour of trace amounts of elements is analogous to their behaviour in macroamounts. The classical law of mass action, which is used for the description of equilibria in chemical reactions, cannot be applied to reactions with single atoms, because one and the same atom cannot exist simultaneously in different species. To solve this problem, an expression equivalent to the law of mass action was proposed.[55,56] In this expression, the concentration (activity, partial pressure) is replaced by the probability of the existence of the species of the element in the corresponding phase (solid, liquid, gas). Therefore, the equilibrium constant (distribution coefficient) between two phases is determined by the probability of the existence of an atom (ion) of the element in a particular phase. Evidently, chromatographic systems, in which transitions of the substance from one phase to another are repeated many times, can be reliably used to study the chemical behaviour of elements at the tracer scale. The classical example supporting this fact is the use of chromatography in experiments on the isolation of 17 ^{256}Md atoms ($T_{1/2} = 75$ min). The chemical identification of mendelevium was carried out from the peak position on the elution curve from a cation-exchange column with a solution of ammonium α-hydroxyisobutyrate. The peak of mendelevium exactly coincides with the peak of thulium, which is its chemical analogue.[57] The behaviour of the element in trace amounts was demonstrated [58] to be identical to its behaviour in macroamounts in the absence of additional factors, for example, the influence of loading the resin with a macrocomponent in the chromatographic separation of elements. In my opinion, studies of the chemistry at the microamount level provide the most reliable insights into the chemical properties of elements, because in this case no side processes (polymerisation, disproportionation, *etc.*), which are often observed in experiments with macroamounts, occur.

3. Techniques for isolation and determination of short-lived radionuclides formed in reactions with multicharged ions

The techniques for isolation and determination of TAEs and short-lived isotopes of homologous elements, which are produced by nuclear reactions with multicharged ions at accelerators, have been described in detail in the literature.[38–41] The transport of nuclear reaction products from the irradiated target to the corresponding chemical apparatus is generally performed through a thin capillary using an aerosol gas jet (KCl/H_2, *etc.*). Transactinide elements are isolated and their chemical properties are studied using both the cyclic and continuous (on-line) modes. The former mode involves repeated cycles of isolation, separation and determination of TAEs by correlating the α–α decays of the parent and daughter radionuclides. The second mode is based on the on-line isolation of short-lived TAEs and separation from radionuclides, which hinder the detection, during their production followed by the long-lived decay product determination.

When isolating TAEs and investigating their behaviour by liquid extraction in the cyclic mode, all chemical operations are carried out manually. The optimum time for one experiment is several minutes. The extraction method was used to isolate ^{261}Rf and study its chemical properties.[14–17] The process involving chromatographic methods was automated. The Automated Rapid Chemistry Apparatus (ARCA), which includes microcolumns and microprocessor computers, was used to isolate and study Rf,[8–10] Db (see Refs 22, 23, 25 and 26) and Sg.[30,31] This high-precision and expensive apparatus was described in detail in the studies.[38,39,59] The central part of the apparatus consists of an aerosol collector and two magazines each containing twenty 1.6×8 mm microcolumns. The columns are packed with the necessary sorbent (ion-exchange resin, extractant on an inert support, *etc.*). A solution in which aerosol is dissolved is delivered to the collector. The resulting solution containing radionuclides (sorbate) is fed to one of the moving microcolumns. The column moves further and another solution (eluate, desorbate) is fed. Then the second column takes the place of the first column, and a new portion of the sorbate containing radionuclides is delivered, *etc*. Solutions eluted from each column are collected on individual supports, dried and directed to α-spectrometric measurements. The minimum time for each cycle (dissolution of the aerosol, adsorption, elution, desorption and preparation of a source for radiometric measurements) is 45–90 s; 2/3 of this time is spent on the preparation of the source. The automated system makes it possible to perform repeated cycles of isolation of short-lived radionuclides; the number of cycles can be several thousand. However, the possibilities to use the ARCA apparatus for studying the chemistry of SHEs are limited due to very low yields of radionuclides in a unit time and the unreliability of the statistics.

The isolation and determination of short-lived isotopes of TAEs in the continuous (on-line) mode holds the most promise. This approach involving ion-exchange chromatography was developed in FLNR JINR.[6,60] The scheme of the apparatus is shown in Fig. 1. The nuclear reaction products are directed to an absorber using an aerosol gas jet. The aerosol is dissolved in the

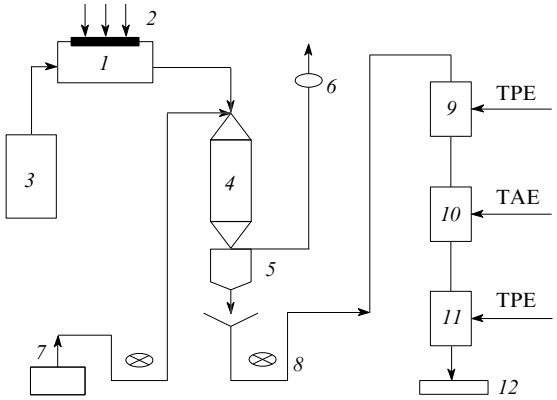


Figure 1. Scheme of the continuous radiochemical isolation of TAEs.[6,60] (*1*) An irradiated target, (*2*) a heavy ion beam, (*3*) an aerosol generator (KCl), (*4*) an absorber, (*5*) a degasser, (*6*) a filter, (*7*) the solution under study, (*8*) peristaltic pumps, (*9*) the first cation-exchange column, (*10*) an anion-exchange column, (*11*) the second cation-exchange column, (*12*) an eluate.

‡ The $^{254-258}Md$ isotopes were produced in the reactions $^{253,254}Es(\alpha, xn)$.

solution under study, which is continuously fed to the absorber. Then the solvent containing TAEs and other radionuclides is passed through three ion-exchange columns connected in series. The first (cation-exchange column) is used to separate transactinide elements from actinide (primarily transplutonium) elements (TPEs), which are strongly retained on the cation-exchange resin, whereas TAEs remain in the solution and are sorbed on the second (anion-exchange) column. The decay products of TAEs, *viz*., late TPEs (No, Fm, Es), are sorbed on the third (cation-exchange) column. Transactinide elements are identified by long-lived decay products after their desorption from the third column and preparation of one sample (source) for α-spectrometric measurements. Therefore, this method allows one to perform continuous isolation and separation of short-lived TAEs from TPEs produced in nuclear side reactions followed by their detection by long-lived decay products, which are accumulated throughout the experiment. The latter fact is of considerable importance for the isolation of trace amounts of radionuclides (single atoms) with a low production cross-section in nuclear reactions. The method of continuous isolation of TAEs was successfully used to isolate and investigate ^{261}Rf (see Refs 6, 7, and 60; in the cited studies, the element is called Kurchatovium, Ku) and ^{262}Db (see Ref. 27) in dilute solutions of hydrofluoric acid. This approach was also used in model experiments on the isolation and investigation of the behaviour of short-lived isotopes of transition d elements (homologues of TAEs). These radionuclides were also determined in the on-line mode using high-resolution HPGe detectors connected to a computer.[34, 35, 43, 44, 46, 48, 52, 61–64]

The super fast SISAK III system, which includes mixers, minicentrifuges and a liquid scintillation detector, was designed for isolation of TAE by extraction and its determination in the on-line mode. Radionuclides are determined in a flowing organic phase. The system was successfully used to separate short-lived radionuclides, including homologues of TAEs.[36, 50, 65–67] The short-lived ^{257}Rf isotope ($T_{1/2} \simeq 4$ s) was isolated for the first time (in 2001) and chemically identified with the use of the SISAK system.[20]

III. Isolation and chemical properties of transactinide elements with $Z = 104-118$ and their homologues

1. Rutherfordium

a. Theoretical prerequisites

Rutherfordium is the first element in the series of d-transition elements in the seventh period of the Periodic table.§ Relativistic calculations by the Dirac–Fock method demonstrated [68] that the electronic configuration of an isolated atom of element 104 in the ground state is $[Rn]5f^{14}6d^27s^2$. Therefore, Rf belongs to Group IVB and its chemical properties would be analogous to the properties of Hf and Zr. It was also hypothesised [38] that the electronic configurations $5f^{14}6d7s^27p^1$ or $5f^{14}7s^27p^2$ (after the filled radon shell) can exist. In this cases, rutherfordium can exhibit chemical properties similar to those of p elements (for example, of Pb). However, the lead atom has a completely filled d shell: $[Xe]4f^{14}5d^{10}6s^26p^2$. If only the outer electron shells are taken into account, thorium is also an electronic analogue of rutherfordium: $[Rn]f^06d^27s^2$. Hence, thorium can be considered as a pseudohomologue of rutherfordium. Plutonium is also considered as a pseudohomologue, because Pu(IV) involved in certain systems behaves analogously to Group IVB elements.

§ Hereinafter, the groups of elements are denoted by Roman numerals (I–VIII), which are used in the 'short-period' form of the Periodic table. In the 'long-period' form of the Periodic table, the groups of elements are denoted by Arabic numerals (1–18).

b. Behaviour of Group IVB elements in solution

To isolate rutherfordium and study its chemical properties by ion-exchange chromatography, the behaviour of its homologues and pseudohomologues, *viz*., Hf, Zr, Th and Pu, was investigated in solutions containing inorganic and organic complexing ligands (upon their sorption on cation- and anion-exchange resins).[6, 8, 42–45, 47, 60, 62, 69]

Use of cation-exchange resins. Figure 2 illustrates the influence of the nature and concentration of an acid on the distribution coefficients (K_d) of hafnium, thorium, some TPEs, rare-earth elements and strontium upon sorption on Dowex-50 × 8 cation-exchange resin. In these experiments, strontium was studied as a homologue of element 102 (No) produced in the decay chain

$$^{261}\text{Rf}\ (\alpha,\ 65\ \text{s}) \longrightarrow {}^{257}\text{No}\ (\alpha,\ 27\ \text{s}) \longrightarrow {}^{253}\text{Fm}\ (\text{e.c.},\ 3\ \text{days}) \longrightarrow {}^{253}\text{Es}(\alpha,\ 20\ \text{days})$$

(e.c. is electron capture).

A knowledge of the behaviour of No, as well as trivalent TPEs (REEs), which are produced in substantial amounts in the synthesis of TAEs, is of particular importance if the latter are identified from daughter decay products.

Hafnium is virtually not sorbed by the cation-exchange resin from HF, H_3PO_4 and $H_2C_2O_4$ solutions but exhibits high adsorbability in H_2SO_4 solutions at a concentration of $\leqslant 0.1$ mol litre^{-1}. Thorium is much more strongly (compared to Hf) sorbed on the cation-exchange resin, this difference being most pronounced in dilute HF and H_3PO_4 solutions. Transplutonium elements, REEs and strontium have large distribution coefficients ($\geqslant 10^4-10^6$) in acids at concentrations of $\leqslant 0.1-0.5$ mol litre^{-1}. The degree of sorption of the elements sharply decreases with increasing concentration of the acid due to competitive sorption of H^+ on the cation-exchange resin.

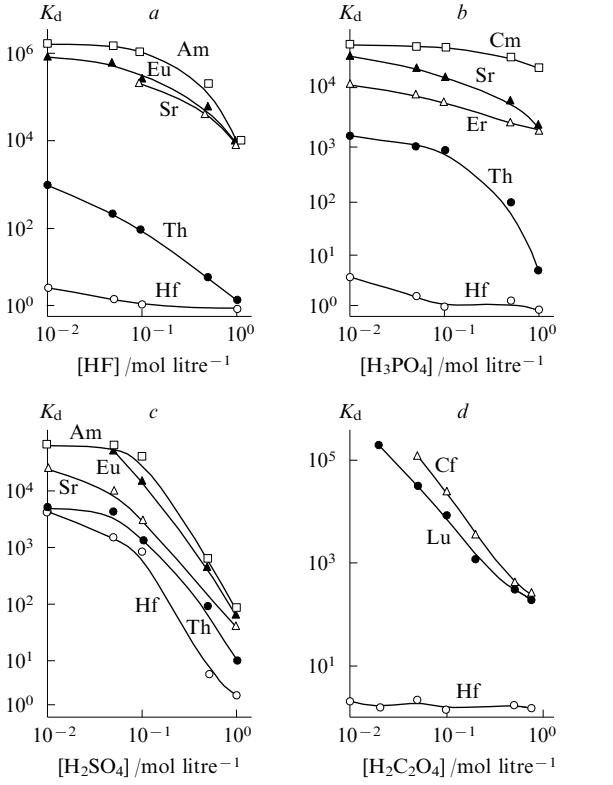


Figure 2. Plots of the distribution coefficients of elements *vs*. the acid concentration in solutions for sorption on Dowex-50 × 8 cation-exchange resin.[43, 45, 47]
Acid: (*a*) HF, (*b*) H_3PO_4, (*c*) H_2SO_4, (*d*) $H_2C_2O_4$.

The order of elution of the elements from the cation-exchange resin reflects their tendency to form complexes in solution. The low adsorbability of Hf on the cation-exchange resin is attributable to the fact that transition d elements are more prone to form neutral and negatively charged complexes with F^-, $H_2PO_4^-$ and $C_2O_4^{2-}$ than with the HSO_4^- ions. The presence of F^- anions in H_2SO_4 solutions leads to a sharp decrease in the distribution coefficients of hafnium already at the HF concentration higher than 5×10^{-4} mol litre^{-1}, whereas the distribution coefficients of strontium and TPEs (REEs) remain virtually unchanged (Fig. 3).[45] An analogous behaviour of hafnium and zirconium is observed upon their sorption on the cation-exchange resin from mixed HNO_3/HF solutions. An increase in the HF concentration from 5×10^{-4} to 5×10^{-2} mol litre^{-1} in 0.1 M HNO_3 solution leads to a decrease in the distribution coefficients of zirconium and hafnium by approximately three orders of magnitude.[8] These data are indicative of the formation of stable neutral and negatively charged complexes of these elements with F^- ions in solutions containing HF at concentrations of $\geqslant 10^{-3}$ mol litre^{-1}. At lower HF concentrations, cationic complexes and various hydrolysed forms adsorbed on the cation-exchange resin can exist. Therefore, the ability of inorganic ligands to form complexes with Hf and Zr increases in the following series $OH^- > F^- > H_2PO_4^- > HSO_4^-$.

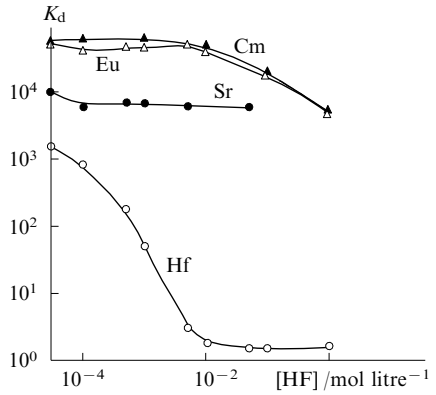


Figure 3. Plots of the distribution coefficients of elements *vs.* the HF concentration in a 0.05 M H_2SO_4 solution for sorption on Dowex-50 × 8 cation-exchange resin.[45,47]

The difference in the distribution coefficients of Hf, Zr, TPEs (REEs) and Sr is responsible for the high separation factors of these elements on the cation-exchange resin in dilute HF, H_3PO_4, $H_2C_2O_4$ and H_2SO_4/HF solutions. Hence, these systems can be used to separate Hf and Zr (Rf) from TPEs from large volumes of solutions with purification factors of $\geqslant 10^5 - 10^6$ on small cation-exchange columns in the on-line mode.[6,42–45,47] In this case, weakly adsorbed elements (Hf, Zr, Rf) are continuously washed out, whereas TPEs, REEs and Sr (No) remain on the column.

Use of anion-exchange resins. The plots of the distribution coefficients of Hf, Sr and TPE (REEs) *vs.* the concentration of acids upon their adsorption on Dowex-1 × 8 anion-exchange resin from HF, H_2SO_4, H_3PO_4 and $H_2C_2O_4$ solutions are shown in Fig. 4. The distribution coefficients of hafnium and zirconium are rather high ($> 10^2 - 10^4$), whereas TPEs (REEs) and strontium are virtually not sorbed on the anion-exchange resin from HF, H_3PO_4 and H_2SO_4 solutions but have high adsorbability in dilute $H_2C_2O_4$ solutions. Sorption of TPEs (REEs) and Sr in $H_2C_2O_4$ solutions sharply decreases in the presence of small amounts of HCl (Fig. 5). Therefore, anion-exchange columns can be used both to concentrate Rf, Hf and Zr and separate these elements from the daughter radionuclides (TPEs, REEs) in dilute HF, H_2SO_4, H_3PO_4, $H_2C_2O_4$/HCl and H_2SO_4/HF solutions.[5,43–47]

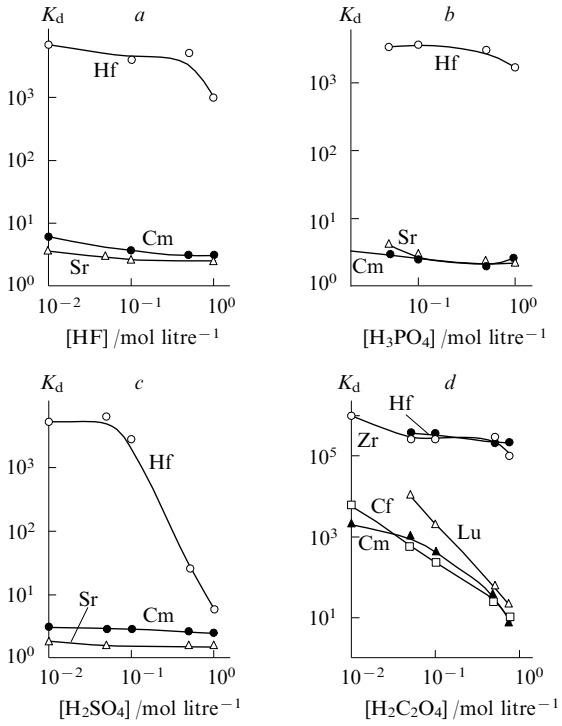


Figure 4. Plots of the distribution coefficients of elements *vs.* the acid concentration in solutions for sorption on Dowex-1 × 8 anion-exchange resin.[43–45,47]
Acid: (*a*) HF, (*b*) H_3PO_4, (*c*) H_2SO_4, (*d*) $H_2C_2O_4$.

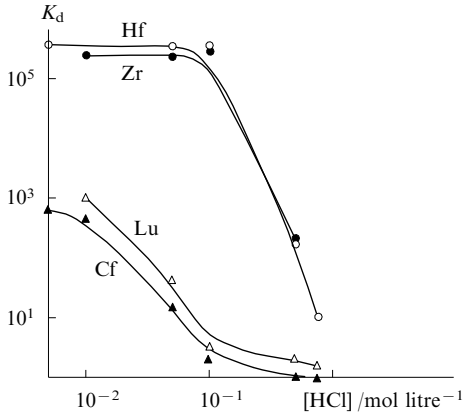


Figure 5. Plots of the distribution coefficients of elements *vs.* the HF concentration in a 0.05 M $H_2C_2O_4$ solution for sorption on Dowex-1 × 8 anion-exchange resin.[44]

c. Model experiments

The possibility of using various systems for the isolation of TAEs in the on-line mode was examined in model experiments on the isolation of short-lived hafnium isotopes and investigation of their chemical behaviour under conditions simulating isolation of Rf.[34,43,44,46,61,62,70] The hafnium isotopes were produced by the nuclear reactions ^{144}Sm(^{20}Ne, *x*n)Hf and Gd(^{18}O, *x*n)Hf at the U-400 cyclotron (FLNR JINR). The scheme of isolation was analogous to that presented in Fig. 1. The solution under study containing nuclear reaction products was continuously passed (at a flow rate of ~ 2 ml min^{-1}) through three 0.4 × 4 cm columns, which were connected in series and filled with Dowex-50 × 8 cation-exchange resin, Dowex-1 × 8 anion-exchange resin and Dowex-50 × 8 cation-exchange resin, respectively. γ-Spectrometric measurements of the columns were carried out in turn both in

Table 3. Sorption (from 0.5 M H_3PO_4 solutions) of hafnium isotopes produced in the reactions Gd(^{18}O, *x*n) and radioactive decay products of hafnium on ion-exchange columns.[43]

First column, Dowex-50 × 8			Second column, Dowex-1 × 8			Third column, Dowex-50 × 8		
radionuclide	$T_{1/2}$ /min	sorption (%)	radionuclide	$T_{1/2}$ /min	sorption (%)	radionuclide	$T_{1/2}$ /min	sorption (%)
^{167}Lu	54	23	^{165}Hf	1.7	100	^{167}Lu	54	77
^{168}Lu	6	2	^{166}Hf	6.8	100	^{168}Lu	6	98
^{167}Yb	17.5	10	^{167}Hf	2.05	100	^{167}Yb	17.5	90
			^{168}Hf	25	100	^{169}Yb	2.7	100
			^{169}Hf	3.2	100			
			^{170}Hf	960	100			

the on-line mode (the solution containing radionuclides was passed through the columns) and in the off-line mode (the flow of the solution was discontinued). Radionuclides of hafnium and its daughter decay products, which were detected on three ion-exchange columns by passing a 0.5 M H_3PO_4 solution containing the radionuclides, are given in Table 3.[43] The hafnium radionuclides were completely sorbed on the anion-exchange column, whereas its radioactive decay products, REEs (Lu, Yb), were detected primarily on the last column (> 90%), and substantially smaller amounts of the latter products were detected on the first column. Rare-earth elements, which are the daughter radionuclides of Hf, were sorbed on the first cation-exchange column; these radionuclides were produced in the system before the solution was passed through this column. The second cation-exchange (third in order) column sorbed radionuclides produced by the decay of Hf isotopes, which were retained on the anion-exchange column, for example,

$$^{167}\text{Hf}(\beta^+,\ 2\ \text{min}) \longrightarrow {}^{167}\text{Lu}(\beta^+,\ 54\ \text{min}) \longrightarrow {}^{167}\text{Yb}(\beta^+,\ 17.5\ \text{min}).$$

Analogous results were obtained in model experiments on the isolation of short-lived Hf isotopes from 0.2 M HF and 0.05 M $H_2C_2O_4$/0.1 M HCl solutions.[44,46] These experiments demonstrated that the above-mentioned systems can be used for the continuous, on-line, isolation of ^{261}Rf and its determination by the long-lived decay products, *viz*., ^{253}Fm and ^{253}Es.

A procedure was developed for the determination of the distribution coefficients of Rf between anion-exchange resins and HNO_3/HF solutions in the on-line mode in the study of short-lived Hf isotopes.[62] The conditions of sorption (the amount and the nature of the anion-exchange resin, the elution rate) were chosen so that the retention time of Hf (Rf) on the column corresponds to the half-life of the radionuclide. Hafnium was found to be sorbed on the anion-exchange resin as the negatively charged HfF_6^{2-} complex.

d. Isolation of rutherfordium and investigation of its chemical properties

Chromatographic methods. As mentioned above, pioneering experiments on the isolation of ^{261}Rf and investigation of its chemical behaviour in solution were carried out by ion-exchange chromatography, which had been used earlier for the identification of TPEs (LBL, Berkley, USA, 1970).[5] Like zirconium and hafnium, rutherfordium was eluted from a cation-exchange column with a solution of α-hydroxyisobutyric acid (α-HIBA) much more rapidly than TPEs. In the experiment, 17 α-decays of ^{261}Rf ($T_{1/2}$ = 65 s) and its daughter radionuclide ^{257}No ($T_{1/2}$ = 25 s) were observed. The second investigation of Rf in solution was published 10 years later, when the first automated apparatus for rapid isolation of short-lived TAEs was constructed.[12]

The behaviour of rutherfordium in HCl solution was studied by the extraction-chromatographic method using columns filled with Aliquat-336 (methyltricapryl ammonium chloride) on an inert support. A 12 M HCl solution containing Rf and Hf radionuclides and trivalent TPEs was passed through a column, which was then washed with a 6 M HCl solution. Transplutonium elements were eluted from the column with a 12 M HCl solution. The main amounts of Rf and Hf were found in the 6 M HCl fraction. In the experiment, only six α-decays of ^{261}Rf and its daughter element (^{257}No) were observed. However, the authors of the study [5] concluded that Rf, like Hf and Zr, forms negatively charged complexes in concentrated HCl solution. More recently, the ability of Rf to form negatively charged chloride complexes in concentrated HCl solution was confirmed by the ion-exchange method (JAERI, Japan).[9] The experiments were carried out on an AIDA apparatus (Automated Ion Exchange Separation Apparatus Coupled with the Detection System for Alpha Spectroscopy), which is an improved modification of the above-described ARCA apparatus. It was demonstrated that sorption of Rf, Hf and Zr on CA08Y anion-exchange resin increases with increasing concentration of HCl from 7.0 to 11.5 mol litre^{-1} (K_d may be as large as $\sim 10^3$), whereas Th is not sorbed on the anion-exchange resin. The adsorbability of the elements decreases in the series Rf > Zr > Hf, which indicates that Rf is more prone to form negatively charged chloride complexes (compared to Hf and Zr) in concentrated HCl solutions.

The chemical properties of Rf in dilute HF solutions were studied by the above-described method for the continuous isolation of short-lived radionuclides followed by their identification by long-lived decay products (FLNR JINR).[6,60] The ^{261}Rf isotope was produced using a combined target consisting of ^{248}Cm and ^{157}Gd, which was bombarded at the U-400 cyclotron with ^{18}O ions with an energy of 97–102 MeV and a beam intensity of 4×10^{12} pps. The scheme of isolation of radionuclides from the irradiated target was analogous to that presented in Fig. 1. A 0.2 M HF solution containing radionuclides was continuously passed at a flow rate of 1.5–2.0 ml min^{-1} through three columns (0.4 × 4 cm), which were connected in series and filled with Dowex-50 × 8 cation-exchange resin, Dowex-1 × 8 anion-exchange resin and Dowex-50 × 8 cation-exchange resin, respectively. The first cation-exchange column was replaced from time to time with a new column (after 300 ml of the solution was passed). The time of aerosol transport to the absorber was 5 s. The time during which the solution was passed through the absorber and three ion-exchange columns was no longer than 30 s. Throughout the experiment, radionuclides that appeared in different parts of the system were monitored by radiometry using Ge/Li detectors. The Hf isotopes, which were produced in the Gd(^{18}O, *x*n) reactions, and isotopes of REEs, which were produced by the decay of hafnium, were detected on the anion- and cation-exchange columns, respectively. The total time of irradiation was 24 h. After completion of irradiation, the cation-exchange columns were washed with 6 M HNO_3 solutions, which were analysed for α and γ activities. The α spectra of radionuclides desorbed from the first and second cation-exchange columns are shown in Fig. 6. It can be seen that curium isotopes were present in large amounts on the first column (see Fig. 6 *a*). This is accounted for by the fact that the target substance appeared in the system. In addition, the peaks characteristic (in energy of α particles) of the Cf isotopes, ^{253}Es, ^{254}Fm and ^{255}Fm are clearly seen. The spectrum of the desorbate from the second cation-exchange column (see Fig. 6 *b*) shows only a small amount of Cm isotopes, whereas Cf isotopes are absent, which is indicative

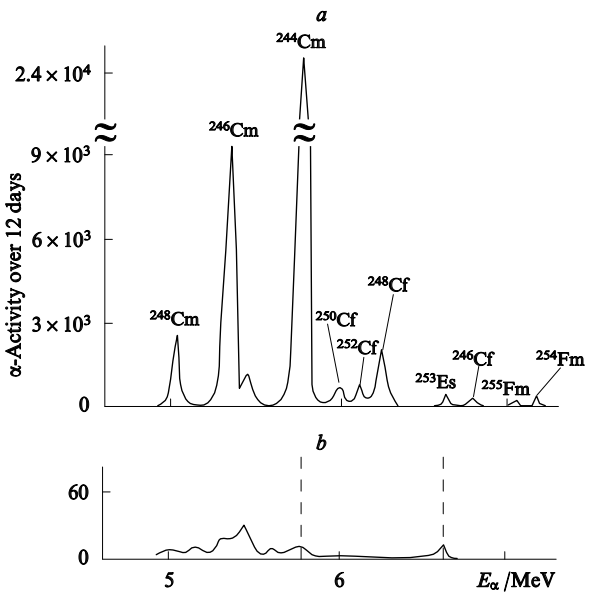


Figure 6. α-Spectra of radionuclides, which were produced in the synthesis of ^{261}Rf.[6, 60]
The desorbates from the first (*a*) and second (*b*) cation-exchange (Dowex-50 × 8) columns.

of a high degree of purification ($K_p \approx 10^5$) from these radionuclides on the first column. There is a peak in the region of ^{253}Es (6.63 MeV), whereas α particles belonging to the ^{254}Fm and ^{255}Fm isotopes are not observed. In the time measurements of the α activity of the desorbate from the second cation-exchange column, the activity first increased and then decreased with $T_{1/2}$ = 20 days, which corresponds to $T_{1/2}$ for ^{253}Es. The initial increase is associated with accumulation of ^{253}Es, which was produced by the β decay of ^{253}Fm that formed in the chain

$$^{261}\text{Rf}\,(\alpha,\ 65\ \text{s}) \longrightarrow {}^{257}\text{No}(\alpha,\ 27\ \text{s}) \longrightarrow$$
$$\longrightarrow {}^{253}\text{Fm(e.c., 3 days)} \longrightarrow {}^{253}\text{Es}(\alpha,\ 20\ \text{days}).$$

The absence of the ^{254}Fm and ^{255}Fm isotopes and the presence of the ^{253}Fm and ^{253}Es isotopes on the second cation-exchange column unambiguously indicate that the latter isotopes are produced by the decay of ^{261}Rf, which is retained on the anion-exchange column. Evidently, Rf, like Group IVB elements (Hf and Zr), forms negatively charged complexes in dilute HF solutions. These complexes are not sorbed on the cation-exchange resin but are strongly retained on the anion-exchange resin. A total of ~500 α particles belonging to ^{253}Es, which was produced by the decay of ^{261}Rf, were detected, which is larger by an order of magnitude than the amount of ^{261}Rf isolated in other experiments. This is evidence that the method under consideration has advantages in isolating TAEs at the tracer scale and providing reliability of their identification.

The anion-exchange behaviour of Rf, Zr and Hf in 1.9–13.9 M HF solutions was studied using an automated AIDA chemical apparatus.[10] Sorption of Zr and Hf was found to decrease sharply at HF concentrations higher than 8 mol · litre^{-1}, whereas sorption of Rf decreases gradually already at HF concentrations higher than 4 mol litre^{-1}. This difference was accounted for by the formation of less stable fluoride complexes of rutherfordium due to the possible influence of the relativistic effects.[19]

The determination of the distribution coefficients of ^{261}Rf between Wofatit HS 36 anion-exchange resin and mixed HNO_3/HF solutions in the on-line mode demonstrated that the coefficients for Rf and Hf in 0.1 M HNO_3/0.27 M HF and 0.2 M HNO_3/0.27 M HF solutions are of the same order of magnitude (~50 and ~15, respectively).[7] However, the investigation of sorption of ^{261}Rf and Hf on Bio-Rad AG1X8 anion-exchange resin (with an ARCA apparatus) showed[8] that the distribution coefficients of Rf and Hf in 0.1 M HNO_3 solutions containing HF at a concentration of 1×10^{-2}–1.0 mol litre^{-1} differ by more than two orders of magnitude. In this case, the degree of sorption of Rf on the anion-exchange resin was very low (K_d < 8). Hence, the authors of the study[8] have cast doubt on the results obtained in the study.[7] Moreover, the behaviour of Rf in HNO_3/HF solutions was demonstrated to be analogous to the behaviour of its pseudohomologue Th both on the anion- and cation-exchange resins. However, it is not quite correct to compare the results of the cited studies,[7, 8] because anion-exchange resins with different functional groups were used. The low distribution coefficients K_d (see Ref. 8) of Rf on the anion-exchange resin cannot serve as an evidence for the absence of anionic fluoride complexes of Rf. The presence of NO_3^- ions, which are strongly sorbed on the anion-exchange resin, leads to a substantial decrease in radionuclide sorption. The decrease in the HNO_3 concentration from 0.1 to 0.01 mol litre^{-1} was demonstrated[8] to cause an increase in the distribution coefficient of rutherfordium by more than an order of magnitude ($\geqslant 10^2$) and it becomes similar to K_d for Hf within the experimental error. Later on, it was found that the presence of HNO_3 in HF solutions has a much stronger effect on the sorption of Rf on the anion-exchange resin compared to the sorption of Hf or Zr.[11]

The anion-exchange behaviour of rutherfordium in concentrated HNO_3 solution was studied with the use of an AIDA apparatus.[9] Irradiation of the combined ^{248}Cm + ^{nat}Ge + ^{nat}Gd target (nat is natural) with ^{18}O ions produced ^{261}Rf along with the ^{85}Zr and ^{169}Hf isotopes. It was found that Rf, like Zr and Hf, is virtually not sorbed on CA08Y anion-exchange resin from 8 M HNO_3 solution. Preliminary experiments showed that Th and Pu have high adsorbability ($K_d \geqslant 10^2$–10^3) under the same conditions.

Extraction methods. *Extraction with triisooctylamine* (*TIOA*). Upon isolation of Rf by extraction from 0.5, 4.0 and 8.0 M HF solutions using a 0.25 M TIOA solution in xylene as the extractant[17] (383 experiments), 14 α–α correlations of the ^{261}Rf–^{257}No were observed in the organic fraction (only upon extraction from 0.5 M HF solutions). Group IV elements were extracted with TIOA from HF solutions in the series Ti > Zr ≈ Hf > Rf, *i.e.*, the order varies inversely with their ionic radii (Rf > Hf ⩾ Zr > Ti), which is indicative of the formation of inner-sphere complexes.

The ^{261}Rf isotope was extracted from 12 M HCl solutions with 0.1 M and 1.0 M TIOA solutions in benzene.[14] In the organic phase, 20 events with energies of α particles belonging to ^{261}Rf and ^{257}No were observed (only upon extraction with 0.1 M TIOA). Under analogous conditions, ^{95}Zr and ^{95}Nb were extracted with $K_d \geqslant 10^2$, whereas ^{152}Eu and ^{228}Th were virtually not extracted. Hence, the data on the extraction confirm the results of chromatographic experiments on the formation of negatively charged Rf complexes in concentrated HCl solutions.[9, 12]

Extraction with tributyl phosphate (*TBP*). With the aim of studying neutral rutherfordium chloride complexes, extraction of ^{261}Rf, ^{95}Zr, ^{169}Hf, ^{228}Th and ^{238}Pu was examined with the use of a TBP solution in benzene as the extractant depending on the concentrations of HCl and the Cl^- and H^+ ions.[15] The Group IVB elements were extracted from 8–12 M HCl solutions with TBP (0.25 mol litre^{-1}) in the following order: Zr > Rf > Hf. In the case of extraction of ^{261}Rf, ^{95}Zr, ^{175}Hf, ^{181}Hf and Ti with a 0.35 M TBP solution in benzene from concentrated HCl solutions, the elements were extracted in another order:[16] Zr > Hf > Rf > Ti. The distribution coefficients of Rf, Hf and Zr in the TBP/HCl system were determined by extraction chromatography (using an automated ARCA apparatus).[13] In 8 M HCl solutions, the distribution coefficients of Rf, Hf and Zr are 150, 53 and 1180, respectively. Therefore, the extractability of Group IV elements and their tendency to form neutral chloride

complexes decrease in the series Zr > Rf > Hf, which was observed experimentally [15] and predicted theoretically.[71]

Rutherfordium was not extracted from 7.75–12 M HBr solutions with the use of a 0.35 M TBP solution in benzene as the extractant.[16] However, the degree of isolation by extraction in the presence of LiBr was ~90%. Extraction of Group IV elements from HBr solutions decreases in the series Zr > Hf > Rf ≃ Ti, which was also observed for extraction from HCl solutions.[16]

Extraction with dibutylphosphoric acid (*DBPA*). The extraction method in the on-line mode with the use of the SISAK system was employed for the first time for the isolation of the short-lived ^{257}Rf isotope ($T_{1/2} \simeq 4$ s) produced in the nuclear reaction ^{208}Pb(^{50}Ti, n)^{257}Rf. Before chemical determinations, Rf was separated from other radionuclides in a gas-filled separator.[20] This made it possible to decrease the amounts of fission products and radionuclides, which were produced in multinucleon transfer reactions, by more than three orders of magnitude and optimize the on-line isolation and determination of ^{257}Rf. The ^{257}Rf isotope was extracted with a 0.25 M DBPA solution in toluene from 6 M HNO_3. The experiment time was ~18 h, and 5 α–α correlations assigned to the ^{257}Rf–^{253}No pair were observed in the organic phase. Under these conditions, the behaviour of Rf is analogous to the behaviour of its light homologues, *viz*., Zr and Hf.

Adsorption methods. The adsorption method combined with extraction by thenoyltrifluoroacetone (TTA) was developed for studying chelate Rf complexes in the investigation of the adsorption of Hf and Zr on a hydrophobised glass surface from 0.01 M and 1 M HCl solutions saturated with TTA.[72] Short-lived Rf and Hf isotopes were synthesised in the reactions ^{248}Cm/^{152}Gd (^{18}O, 5n) and ^{261}Rf/^{165}Hf[19] at the U-400 cyclotron (FLNR JINR). The experiment was carried out for 16 h, during which 600 sorption cycles of radionuclide isolation were carried out and five α decays of ^{261}Rf were observed. All events were observed only for adsorption from 0.01 M HCl solutions with thenoyltrifluoroacetone. The short-lived ^{168}Hf isotope was virtually equally sorbed from 0.01 M and 1.0 M HCl solutions (87% and 82%, respectively). It appeared that the behaviour of Rf^{4+} in the HCl–TTA system differs from the behaviour of its homologues and resembles the behaviour of Po^{4+}, Sn^{4+} and Ti^{4+}, which form neutral complexes with TTA only in weakly acidic solutions.[19]

To study the hydrolysis of Rf, the ability of Group IVB elements to be adsorbed on glasses treated with transition metal ferrocyanides was investigated.[18] Cobalt ferrocyanides show high selectivity to the tetravalent Zr^{4+}, Hf^{4+} and Th^{4+} cations and low selectivity to their hydrolysed $M(OH)_3^+$ or $M(OH)_2^{2+}$ forms. A substantial decrease in the sorption of Rf on cobalt ferrocyanide was observed already at HCl concentrations lower than 3 mol litre^{-1}, whereas sorption of Zr and Hf decreased only at HCl concentrations lower than 1 and 0.5 mol litre^{-1}, respectively. Consequently, hydrolysis increases in the series Hf < Zr < Rf. This behaviour of Rf was accounted for by the influence of the relativistic effect due to which the Rf^{4+} ion in aqueous solution has a coordination number of 6, whereas the coordination number of Zr and Hf is 8. However, this conclusion is inconsistent with theoretical and experimental data,[73] according to which the tendency of Group IVB elements to be hydrolysed increases in the reverse order, Rf < Hf < Zr, *i.e*., in accordance with the change in the ionic radii of the elements.

2. Dubnium

a. Theoretical prerequisites

The electronic configuration of an isolated atom of element 105 in the ground state should be [Rn]5f^{14}6d^{3}7s^2. The Group VB elements Nb and Ta are chemical homologues of dubnium, and Pa is a pseudohomologue. Relativistic calculations by the Dirac–Fock method demonstrated that 7p electrons are absent in the ground state of the atom.[74] Therefore, no substantial deviations in the chemical behaviour of element 105 associated with relativistic effects are expected. In solution, the main oxidation state of Db would be +5, although Db can also exist in lower oxidation states in the presence of strong reducing agents.[75]

b. Isolation of dubnium and investigation of its chemical properties

Pioneering experiments on the isolation of element 105 and investigation of its chemical properties (earlier, this element was called hanium, Ha) in solution were carried out with the ^{262}Db isotope ($T_{1/2}$ = 34 s), which was produced by the nuclear reaction ^{249}Bk (^{18}O, 5n) (LBL).[21] When studying the chemistry of dubnium, sorption on the glass surface from fuming HNO_3 solutions characteristic of Group VB elements and extraction with methyl isobutyl ketone (MIBK) from mixed HNO_3/HF solutions were investigated. Both series of experiments were carried out manually. Dubnium was adsorbed from a 15 M HNO_3 solution. In 800 experiments on glass, 24 α–α decays of ^{262}Db and its daughter element ^{258}Lr ($T_{1/2}$ = 4.3 s) were observed. Under identical conditions, the degree of sorption of Nb and Ta was 42% and 80%, respectively. By contrast, Group IVB elements (Zr, Hf) were not sorbed. However, upon extraction of dubnium with MIBK from 3.8 M HNO_3/1.1 M HF solutions (335 experiments), no events of α decay or spontaneous fission of ^{262}Db or ^{258}Lr in the organic fraction were observed. In the authors' opinion, this behaviour of Db could be associated with the formation of unextractable doubly charged complexes DbF_7^{2-} or mixed oxyfluoride complexes. Under analogous conditions, tantalum forms singly charged TaF_6^- complexes, which are well extracted by MIBK. The possibility of relativistic stabilisation of 7s orbitals and, as a consequence, the formation of Db^{3+}, which is not extracted by MIBK, is also not ruled out.

Extraction chromatography methods. Extraction of dubnium with TIOA from HCl solution in the presence of small amounts of HF was studied using an ARCA apparatus.[22,23] The ^{262}Db isotope was sorbed on a column containing TIOA on an inert support from a 12 M HCl/0.02 M HF solution. Then the column was successively washed with 4 M HCl/0.02 M HF (Pa–Nb fraction) and 6 M HNO_3/0.015 M HF (Ta fraction). The α activity of the ^{262}Db–^{258}Lr pair was found primarily in the Pa–Nb fraction. Therefore, the Group V elements are extracted with TIOA in the series Ta > Nb > Db > Pa. In the studies,[22,23] the 'non-tantalum' behaviour of dubnium was attributed to the fact that this element, like Nb and Pa, forms the oxyhalide or hydroxy halide complexes $[NbOCl_4]^-$ and $[PaOCl_4]^-$ or $[Pa(OH)_2Cl_4]^-$, whereas tantalum forms the purely halide complex $[TaCl_6]^-$ under these conditions. However, this explanation is not fully explicit because the fact that HCl solutions contain the strong complexing ligand (F^- ions) is ignored.

With the aim of examining the similarity between the chemical properties of Db and Pa, a series of experiments on the extraction of Db, Pa and Nb with diisobutylcarbinol, which is a selective extractant for Pa, was carried out.[24] Radionuclides were sorbed on a column with diisobutylcarbinol from a 7 M HBr solution, and the column was then successively washed with a 6 M HCl/0.02 M HF solution (Nb fraction) and a 0.5 M HCl solution (Pa fraction). The investigation revealed the following series: Pa > Nb > Db. This series does not confirm the similarity in the behaviour of Db and Pa observed upon their extraction with TIOA.

The extraction behaviour of Group VB elements on a column with Aliquat-336 from pure HCl, HF and HBr solutions using an ARCA apparatus was studied in detail.[25] It was found that the elements were extracted from 6 M HCl solutions in the series Pa ≫ Nb ⩾ Db > Ta. In a 4 M HF solution, dubnium was sorbed on an anion-exchange column with the distribution coefficients K_d > 570. These coefficients are similar to those for Nb and Ta (⩾ 10^3). By contrast, Pa is sorbed only to a small extent ($K_d \simeq 19$) under these conditions. Therefore, the Group V elements were extracted from 4 M HF solutions with Aliquat in the following series: Ta ⩾ Nb > Db > Pa. The degree of extraction of the Group V elements from solutions of hydrohalic acids decreases in the series HF > HCl > HBr.[25] These characteristic

features are consistent with the results of relativistic calculations on the stability of negatively charged halide complexes of Group V elements.[71,76]

Ion-exchange method. The ion-exchange method in the on-line mode was used to isolate dubnium and study its behaviour in dilute HF solutions.[27] The ^{262}Db isotope was produced by the nuclear reaction (^{248}Cm, *x*n ^{19}F) at the accelerator at the Institute of Nuclear Physics (Orsay, France). A 0.2 M HF solution containing nuclear reaction products was gradually passed through three ion-exchange columns filled with a cation-exchange resin (Bio Rad AG 50W × 8), a macroporous anion-exchange resin (Bio Rad AG MP1) and a cation-exchange resin (AG50W × 8), respectively. A high degree of purification of Db from actinide elements was achieved on the first column, Db was adsorbed on the second column, and its decay products were retained on the third column. The ^{262}Db isotope was identified by the long-lived decay product ^{254}Fm ($T_{1/2}$ = 3.24 h) after its desorption from the third cation-exchange column. It was demonstrated that ^{262}Db, which could be produced by the reaction ^{248}Cm + ^{19}F, was virtually completely (67 atoms) sorbed on the second (anion-exchange) column. A preliminary investigation of the behaviour of Group V elements on AG MP1 anion-exchange resin in HF solutions demonstrated that the elements in the HF concentration range of 0.01–0.3 mol litre^{-1} are sorbed in the series Ta ≫ Pa > Nb with the distribution coefficients of $\geqslant 10^4$. The authors of the study[27] believed that Db, like its homologues Ta and Nb and pseudohomologue Pa, forms negatively charged complexes in dilute HF solutions, and these complexes are strongly sorbed on the anion-exchange resin.

Anion-exchange method. The anion-exchange behaviour of Db and its homologues and also of Pa in concentrated HF solutions was studied[29] with the use of an AIDA apparatus. In 14 M HF solutions, K_d values are 35 for Db, 150 for Nb, 175 for Ta and 18 for Pa. Therefore, the order of sorption is the same as that observed for extraction with Aliquat (reagents containing identical functional groups) from 4 M HF solutions.[25] However, the distribution coefficients for Db on the anion-exchange resin in 14 M HF solutions are closer to those for Pa, whereas the distribution coefficients of Db for extraction from 4 M HF solutions are close to those of Nb and Ta (see above).

Cation-exchange method. The ^{263}Db ($T_{1/2}$ = 27 s) isotope, which was produced in the reaction ^{249}Bk (^{18}O, 4n), was isolated and chemically identified with the use of α-hydroxyisobutyric acid as the eluent. The experiments were carried out on an ARCA apparatus. During elution of radionuclides, dubnium was washed out together with Nb, Ta and Pa from a cation-exchange column with a solution of α-HIBA within the first four seconds, unlike tri- and tetravalent radionuclides. In the authors' opinion,[26] the pentavalent state of dubnium is the most stable in solution.

The cation-exchange method combined with extraction was used to prove a new decay branch of ^{263}Db through electron capture and to identify ^{263}Rf.[28] After elution of ^{263}Db from the cation-exchange column with α-HIBA, the eluate was transferred into a 9 M HCl solution, from which radionuclides were extracted with a TBP–cyclohexane mixture. In the extractant, spontaneous fission of ^{263}Rf ($T_{1/2}$ = 20 min) was observed; the latter isotope could be produced only by the decay ^{263}Db(e.c.) → ^{263}Rf(s.f.).¶

Model experiments demonstrated that dubnium can be isolated by extraction with trioctylamine (TOA) from solutions of α-hydroxyisobutyric and lactic acids in the on-line mode using the SISAK system.[67]

3. Seaborgium

a. Theoretical prerequisites

Calculations by the Dirac–Fock method predicted[68] the $5f^{14}6d^{4}7s^{2}$ electronic configuration for a free neutral atom of element 106 in the ground state, *i.e.*, this element belongs to Group VIB. Tungsten and molybdenum are homologues of seaborgium and U is its pseudohomologue. In aqueous solutions, Sg^{6+} would be expected to be the most stable oxidation state of seaborgium, although the possibility of the existence of the tetravalent state in the absence of complexing ligands cannot be ruled out.[77] The characteristic feature of elements belonging to this group is that they form oxygen-containing compounds in aqueous solutions through strong M–O covalent bonds.

b. Behaviour of Group VIB elements in solutions

To identify seaborgium by chemical methods, it is necessary to separate it from daughter radionuclides, which can be produced both by nuclear reactions in the synthesis and the radioactive decay

$$^{265}\mathrm{Sg}(\alpha,\ 7\ \mathrm{s}) \longrightarrow {}^{261}\mathrm{Rf}(\alpha,\ 78\ \mathrm{s}) \longrightarrow {}^{257}\mathrm{No}(\alpha,\ 26\ \mathrm{s}) \longrightarrow$$
$$\longrightarrow {}^{253}\mathrm{Fm}(\mathrm{e.c.},\ 3\ \mathrm{days}) \longrightarrow {}^{253}\mathrm{Es}(\alpha,\ 20\ \mathrm{days}).$$

With the aim of finding the optimum conditions for the isolation and identification of seaborgium based on its daughter decay products, the ion-exchange behaviour of its homologues, *viz*., W and Mo, and homologues of rutherfordium and nobelium, *viz*., Hf and Sr, respectively, the pseudohomologue U and some TPEs (Cm) and REEs (Eu) in dilute H_2SO and H_2SO_4/HF solutions was studied.[51] The effect of the H_2SO_4 concentration on the distribution coefficients of the elements upon their sorption on cation- and anion-exchange resins is illustrated in Fig. 7. Tungsten is sorbed only to a small extent on cation-exchange resins from solutions containing H_2SO_4 at concentrations lower than 0.1 mol litre^{-1}, whereas the distribution coefficients of U, Hf, Sr, Cm and Eu are $\geqslant 10^3$–10^4 (see Fig. 7 *a*). Tungsten, hafnium and uranium are sorbed on anion-exchange resins with distribution coefficients larger than 10^2–10^3, whereas Sr, Cf and Eu are virtually not sorbed from these solutions (see Fig. 7 *b*). Therefore, cation-exchange columns can be used to separate W (Sg) from daughter elements, *viz*., Hf (Rf), Sr (No) and REEs (TPEs), and from U in the on-line mode. Anion-exchange columns can be used to concentrate Group IV–VI elements and separate them from di- and trivalent elements. Since the presence of small amounts of HF in dilute H_2SO_4 solutions has only a slight effect on the sorption of W, Hf, Sr, TPEs and U,[51] these solutions can also be used to isolate and study seaborgium.

Sorption of Group IV–VI elements on Dowex-50 × 8 cation-exchange resin and Dowex-1 × 8 anion-exchange resin from mixed HCl/HF solutions has been studied in detail.[69] It was demonstrated that Group VI and V elements can be separated from Group IV elements in the on-line mode with the use of 0.05–01 M HCl solutions containing 1×10^{-3} mol litre^{-1} HF.

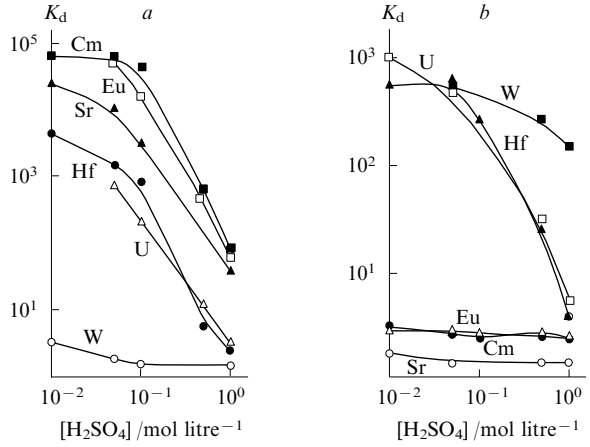


Figure 7. Plots of the distribution coefficients of elements *vs*. the H_2SO_4 concentration for sorption on Dowex-50 × 8 cation-exchange resin (*a*) and Dowex-1 × 8 anion-exchange resin (*b*).[51]

¶ s.f. is spontaneous fission.

The possibility of determining the distribution coefficients of Sg and the compositions of complexes in HCl/HF and HNO_3/HF solutions was examined by studying the sorption of W and Mo on anion-exchange resins containing various functional groups.[63, 78] The sorption selectivity and the separation factor of W and Mo were demonstrated to depend strongly on the composition of the solution and the nature of the functional groups of the ion-exchange resin. The optimum conditions for the separation of the W – Mo pair in the on-line mode were found.

To isolate seaborgium with the use of the SISAK extraction system, extraction of ^{176}W, ^{177}W, ^{99}Mo, U, Th, Am, Cm, La, Ce, Tb, Lu and Hf from HNO_3, H_3PO_4 and H_2SO_4 solutions was studied[79, 80] using Aliquat-336 and TOA. The optimum conditions for the separation of Group VI elements and U from TPEs, REEs and Hf were found. The extraction of elements in different oxidation states decreases in the series $M^{4+} > MO^{2+} > M^{3+}$.

c. Model experiments

Ion-exchange methods. Short-lived tungsten isotopes, which were produced in the nuclear reactions Sm (^{24}Mg, *x*n) at a cyclotron, and Mo, Zr, Ba and REE radionuclides produced by fission of ^{235}U were isolated in model experiments and their chemical behaviour in dilute H_2SO_4, H_2SO_4/HF,[52] HF (see Refs 34, 46 and 48) and HCl/HF solutions[61] was studied. The radionuclides were isolated and determined in the on-line mode using two – three ion-exchange columns. Table 4 lists the tungsten isotopes and products of their radioactive decay, which were determined on columns during elution with a 0.05 M H_2SO_4 solution containing the radionuclides. The Hf and REE isotopes, which were produced by the decay of tungsten before the solution was fed into the column, were sorbed on the first (cation-exchange) column. The tungsten isotopes and products of their radioactive decay, *viz*., the 'daughter' (tantalum) and 'granddaughter' (hafnium) isotopes, adsorbed on the second (anion-exchange) column. The 'great-granddaughter' isotopes (Lu and Yb, respectively) were retained on the third (cation-exchange) column. The ^{168}W, ^{169}W and ^{172}W isotopes were found on the anion-exchange resin, but the shorter-lived ^{167}W isotope ($T_{1/2}$ = 19.3 s) was not detected because of the lack (at that instant) of data on the γ-radiation energies of this radionuclide. However, the presence of the ^{167}Ta, ^{167}Hf, ^{167}Lu and ^{167}Yb radionuclides, which could be produced only by successive β^+-decays of ^{167}W, on the anion-exchange column and the second cation-exchange column, provides evidence that this isotope was also present on the anion-exchange column.

Therefore, the short-lived parent radionuclide was chemically identified based on the genetic relationship to longer-lived decay products. The results of model experiments suggest that ^{265}Sg ($T_{1/2} = 7 \pm 3.3$ s) can be isolated and its chemical properties can be studied in the on-line mode followed by the identification with the longer-lived decay products ^{261}Rf, ^{253}Fm and ^{253}Es, which can be accumulated on anion-exchange or cation-exchange columns.

Table 4. Distribution of tungsten isotopes produced in the nuclear reactions Sm(^{24}Mg, *x*n) and radioactive decay products of tungsten on ion-exchange columns (from 0.05 M H_2SO_4 solutions); the measurements were carried out in the on-line mode.[48, 52]

First column, Dowex-50 × 8 cation-exchange resin		Second column, Dowex-1 × 8 anion-exchange resin		Third column, Dowex-50 × 8 cation-exchange resin	
isotope	$T_{1/2}$	isotope	$T_{1/2}$	isotope	$T_{1/2}$
^{167}Hf	2.05 min	^{168}W	53.0 s	^{167}Lu	–
^{169}Hf	3.2 min	^{169}W	1.3 min	^{168}Lu	–
^{167}Lu	52.0 min	^{172}W	6.7 min	^{167}Yb	–
^{168}Lu	6.0 min	^{167}Ta	1.4 min	^{169}Yb	46 s
^{169}Lu	2.7 min	^{169}Ta	4.9 min		
^{167}Yb	17.5 min	^{170}Ta	6.8 min		
		^{172}Ta	38.8 min		
		^{167}Hf	–		

Extraction method. Tungsten and molybdenum as homologues of Sg were isolated by on-line extraction using the SISAK system.[67] It was demonstrated that the degree of extraction of Group VI and V elements with TOA from solutions of α-hydroxyisobutyric or lactic acids is 80% (or higher), whereas Group IV elements (Hf) and REEs remain in the aqueous phase. The best separation was achieved by extraction from 1 M α-HIBA solutions at pH 1 – 2 with the use of 0.046 M TOA as the extractant.

d. Isolation of seaborgium and investigation of its chemical properties

The first experiments on the isolation of seaborgium and investigation of its behaviour in solution were carried out after the 'long-lived' ^{265}Sg ($T_{1/2} = 7 \pm 3$ s) and ^{266}Sg ($T_{1/2} = 20 \pm 16$ s) isotopes had been synthesised in FLNR JINR,[4] although the $^{263}106$ isotope ($T_{1/2}$ = 0.9 s) was discovered as early as 1974. The ^{265}Sg and ^{266}Sg isotopes were produced in the nuclear reaction $^{248}Cm + {}^{22}Ne$ at the Unilac Accelerator Facility (Darmstadt, Germany).[30] Seaborgium was separated from other radionuclides on the ARCA apparatus using chromatographic columns (1.6 × 8 mm) filled with Aminex A-6 cation-exchange resin (17 μm). A 0.1 M $HNO_3/5 \times 10^{-4}$ M HF solution was used as the eluent. The seaborgium fractions were collected during the first ten seconds. Preliminary experiments showed that, under these conditions, the degree of elution of tungsten from the column was 85%, whereas trivalent actinides, Group IV elements and uranium remained on the column; 4000 cycles of isolation and determination of seaborgium were carried out. Three pairs of α – α correlated decays for ^{261}Rf and ^{257}No, which are the daughter decay products of ^{265}Sg, were observed. The ^{265}Sg isotope ($T_{1/2} \approx 7$ s) was not detected directly because the total time consumed for the chemical operations was 38 – 45 s. These results suggest that seaborgium exists in solution in the stable hexavalent state and, like its light homologues, *viz*., tungsten and molybdenum, forms neutral (SgO_2F_2) or anionic ($SgO_2F_3^-$) oxyhalide complexes. The existence of 'seaborgates' SgO_4^-, by analogy with molybdates and tungstates, cannot be ruled out as well.[30]

Another series of experiments on the isolation of seaborgium was carried out with the use of HF-free 0.1 M HNO_3 solutions as the eluent.[31] The ^{265}Sg and ^{169}W isotopes were produced simultaneously by bombardment of the combined ^{248}Cm + Gd target with ^{22}Ne ions. All other experimental conditions were identical to those used in the earlier experiment.[30] The first portions of the eluate (0.1 M HNO_3) contained ~60% of ^{169}W; only one α – α decay pair corresponding to $^{261}Rf - {}^{257}No$ was observed. However, according to the estimates,[31] five α – α correlated events were expected. Based on this fact, the authors hypothesised that in dilute HNO_3 solution, seaborgium gives the positively charged hydrolysed $Sg(OH)_4(H_2O)_2^+$ or $Sg(OH)_5(H_2O)^+$ species, which are sorbed on cation-exchange resins. In such solutions, the behaviour of seaborgium is similar to that of uranium. Tungsten forms primarily the neutral $WO_2(OH)_2$ compounds, which remain in solution.[31]

4. Bohrium and hassium

a. Theoretical prerequisites

It was predicted[68] that the configurations of the outer electron shells of elements 107 and 108 are $6d^57s^2$ and $6d^67s^2$, respectively. Therefore, Bh and Hs belong to Groups VIIB and VIIIB, respectively. Rhenium and technetium are the chemical homologues of Bh. Osmium and ruthenium are the chemical analogues of Hs. The characteristic feature of elements of these groups is that they can exist in various oxidation states. In particular, the stables states +7, +5 and +3 were predicted for Bh.[77] Since the highest oxidation state within the group is stabilised on going to heavier elements, bohrium, by analogy with rhenium, would be expected to occur in aqueous solution in the heptavalent oxidation state as the BhO_4^- oxy anion. Evidently, hassium, by analogy with

osmium, can exhibit the maximum oxidation state of +8 (volatile tetroxide HsO_4) and a lower valence state in aqueous solution.

b. Model experiments

Ion-exchange methods. Model experiments on the isolation of the short-lived osmium and rhenium isotopes under conditions simulating isolation of Hs and Bh, respectively, were carried out at the U-400 cyclotron in FLNR JINR. Osmium radionuclides were produced in the nuclear reactions $^{nat}Dy(^{20}Ne, xn)^{172-178}Os$. Rhenium and tungsten isotopes were present in the system as decay products of osmium, for example,

$$^{175}Os(\beta^+, 1.4\ min) \longrightarrow {}^{175}Re(\beta^+, 5.9\ min) \longrightarrow$$
$$\longrightarrow {}^{175}W(\beta^+, 35.9\ min) \longrightarrow {}^{175}Ta(\beta^+, 10.5\ h).$$

The isolation was carried out from 0.05 M H_2SO_4 and 0.05 M HCl solutions in the on-line mode with the use of ion-exchange columns connected in series (cation-exchange resin – anion-exchange resin – cation-exchange resin).[53,64] In both systems, Os and Re were not sorbed on the cation-exchange resin, but were strongly retained on the anion-exchange column, which is indicative of the presence of neutral or negatively charged forms of the elements in these solutions. Table 5 lists the nuclear physical characteristics of the radionuclides detected on the anion-exchange column (the on-line mode) when passing a 0.05 M HCl solution through the column.[64] Short-lived osmium isotopes with $T_{1/2} = 16-55$ s were isolated. There is a genetic relationship between the osmium isotopes and the daughter decay products of rhenium and tungsten. Hence, these systems can be used to isolate Hs and Bh in the on-line mode.

The possibility of identifying the valence states and speciation of Hs and Bh in dilute HCl solutions was demonstrated in the study of the sorption of Os and Re on various sorbents (in the on-line mode).[64] Dowex-50 × 8 cation-exchange resin, Dowex-1 × 8 anion-exchange resin, mixed $K_2Ni[Fe(CN)_6]$ ferrocyanide and tri-n-octylphosphine oxide (TOPO) containing a sorbent on an inert support were used in the study. During the experiment, the order in which the columns containing various sorbents were connected was varied. Figure 8 shows the γ spectra of three columns connected in series: the cation-exchange resin, ferrocyanide and the anion-exchange resin. The spectra were measured when a solution of radionuclides in 0.05 M HCl was passed through these columns. Osmium, rhenium and tungsten radionuclides were sorbed only on the anion-exchange column. These radionuclides were not observed on the columns with the cation-exchange resin and ferrocyanide. The radionuclides were also absent in the solutions after they have been passed through the anion-exchange column.[64] Since only the Os^{3+} and $(OsO_2)^{2+}$ cations are sorbed on the cation-exchange resin and ferrocyanide from dilute HCl solutions,[81] Os^{4+} were, evidently, present in the model experiment as the major form, that sorbed on the anion-exchange resin as $(OsCl_6)^{2-}$. When the columns were connected in the cation-exchange resin – TOPO – anion-exchange resin series, the osmium isotopes were also found only on the anion-exchange column, whereas Re was detected primarily on the anion-exchange column and, partially, on the TOPO-containing column.[64] In weakly acidic solutions, Re exists in the stable anionic ReO_4^- form, which is not sorbed on the cation-exchange resin, but is strongly retained both on the anion-exchange resin and the TOPO-containing sorbent to form the $3(TOPO)H_3O^+ReO_4^-$ or $(TOPO)H^+ReO_4^-$ solvates.

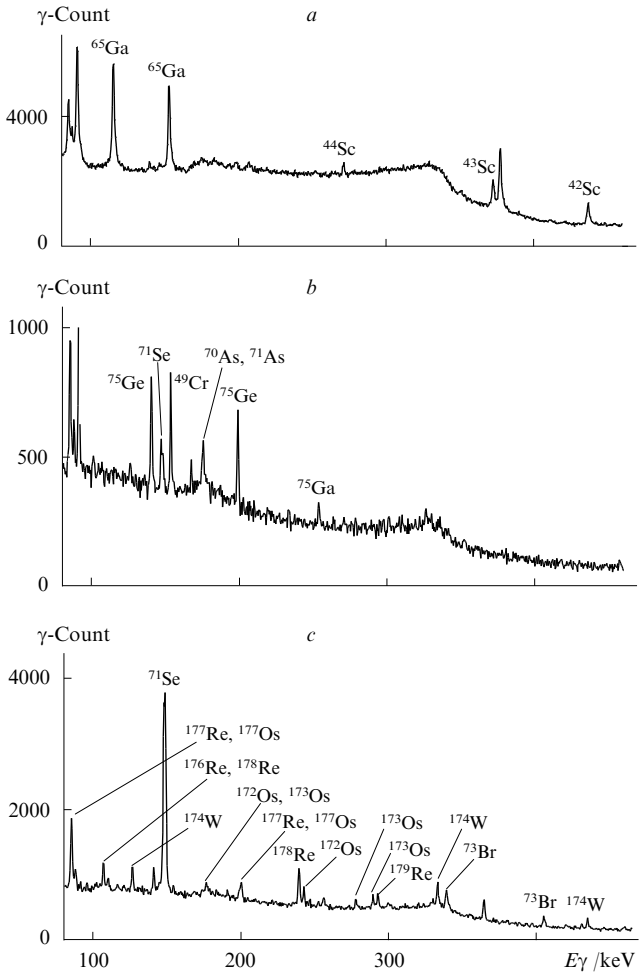


Figure 8. γ-Spectra of three columns connected in series and filled with Dowex-50 (*a*), $K_2Ni[Fe(CN)_6]$ (*b*) and Dowex-1 (*c*), which were measured when passing a 0.05 M HCl solution containing radionuclides (in model experiments with osmium and rhenium isotopes).[64]

Table 5. Nuclear-physical characteristics of osmium, rhenium and tungsten isotopes detected on an anion-exchange column when passing a 0.05 M HCl solution.[64]

Osmium			Rhenium			Tungsten		
isotope	$T_{1/2}$	E_γ /keV	isotope	$T_{1/2}$	E_γ /keV	isotope	$T_{1/2}$	E_γ /keV
^{172}Os	19.0 s	240, 254	^{172}Re	55.0 s	123, 254	^{172}W	6.7 min	154, 175
^{173}Os	16.0 s	285, 187	^{173}Re	1.9 min	181, 373	^{173}W	8.0 min	459, 175
^{174}Os	44.0 s	118, 138	–	–	–	^{174}W	29.4 min	125, 136
^{175}Os	1.4 min	125, 181	^{175}Re	5.0 min	185	^{175}W	34.9 min	166
^{176}Os	3.6 min	776, 857	^{176}Re	5.7 min	109, 240	^{176}W	2.5 h	100.2
^{177}Os	3.0 min	85, 196	^{177}Re	14.0 min	84, 197	–	–	–
^{178}Os	5.0 min	533, 594	^{178}Re	13.2 min	106, 237	–	–	–
^{179}Os	6.3 min	218	^{179}Re	19.5 min	290, 430	–	–	–

In the study, it was shown that Re and Tc (homologues of Bh) can be separated from Nb and Ta on a cation-exchange column with the use of mixed HNO_3/HF solutions (at 75 °C) as the eluent.[49]

Extraction method. The extraction method for the separation of Re and Tc in HNO_3 solution from Nb, Ta, actinides and other elements using a 0.05 M TOA solution in toluene was developed with the aim of isolating Bh in the SISAK system.[50] In the study of Re and Tc, a selective method was developed for the isolation of Bh by extraction with TOA from solutions of α-hydroxyisobutyric acid in the presence of an oxidising agent ($NaBrO_3$).[82]

No experiments on the isolation of Bh from solution were carried out. The ^{267}Bh isotope ($T_{1/2} \approx 17$ s), which was produced by the reaction ^{249}Bk(^{22}Ne, 4n) as the volatile oxychloride BhO_3Cl, was isolated by gas chromatography.[83] The long-lived ^{269}Hs ($T_{1/2} \approx 10$ s) and ^{270}Hs ($T_{1/2} = 2-7$ s) isotopes were isolated for the first time as the volatile tetroxide HsO_4.[84]

In the CALLISTO project, hassium was studied in the liquid phase using a new procedure for the isolation and transport of volatile nuclear reaction products in an aerosol-free gas flow.[32, 85] The ^{269}Hs isotope produced in the nuclear reaction ^{248}Cm(^{26}Mg, 5n) was oxidised to a volatile oxide (apparently, HsO_4) in the gas flow (O_2 + He) and transferred to a special device, in which HsO_4 was trapped and Hs was detected. The device contained a stainless steel plate, which was coated with a thin NaOH film and located a distance of 1 mm from 16 silicon detectors. In the experiment, six 6 α – α correlations were observed in the decay chain of ^{269}Hs. It was hypothesised [32] that octavalent hassium was isolated as sodium hassate $Na_2[HsO_4(OH)_2]$, by analogy with OsO_4, whose dissolution in NaOH affords osmate $Na_2[OsO_4(OH)_2]$.

5. Meitnerium and darmstadtium

Relativistic calculations for elements 109 and 110 [68] predicted the $5f^{14}6d^77s^2$ and $5f^{14}6d^97s^1$ electronic configurations, respectively, for their neutral atoms in the free state. Therefore, Mt and Ds belong to Group VIII platinum elements. Iridium and platinum are the chemical homologues of meitnerium and darmstadtium, respectively. In recent years, the 'long-period' form of the Periodic table has gained increasing acceptance. In my opinion, this form reflects the chemical similarity, in particular, between the platinum-group elements, to a lesser extent compared to the 'short-period' form. In the 'long-period' form, elements 109 and 110 are placed in the ninth and tenth groups, respectively.

The characteristic feature of platinum elements is that they can form complexes with various ligands in solution.

No attempts to study the chemical properties of Mt and Ds in the liquid and gas phases have been reported. Apparently, this is associated with the very short lifetimes of the ^{266}Mt ($T_{1/2} = 5$ ms) and ^{269}Ds ($T_{1/2} = 393$ μs) isotopes, which were produced by the nuclear reactions ^{209}Bi (^{58}Fe, n) and ^{208}Pb (^{62}Ni, n), respectively.

6. Roentgenium and element 112

Theoretical prerequisites

According to the general regularities, elements 111 and 112 can be assigned, respectively, to Groups IB and IIB (or Groups 11 and 12 in the 'long-period form') of the seventh period. Gold and mercury are the chemical homologues of elements 111 and 112, respectively. Group IB and IIB elements have a completely filled d^{10} electron shell. Hence, these elements are characterised by a lower diversity of valence states compared to other groups of transition d elements. The presence of the d^{10} shell is responsible for the chemical inertness of metals and their tendency to form intermetallic compounds. Another specific feature of these elements is the formation of compounds with covalent bonds. Relativistic calculations predicted that the most stable oxidation states of elements 111 and 112 are +3 and +2, respectively. In the metallic state, element 112 may be highly volatile by analogy with noble gases.[86, 87]

Data on the chemical properties of element 111 are lacking.

b. Model experiments

Model experiments on the isolation of element 112 from solution were carried out with the use of short-lived Hg isotopes in the on-line mode.[88] It was demonstrated that Hg is strongly adsorbed from 0.05 M H_2SO_4 solution on a column, which is filled with glass granules treated with silver.

c. Isolation of element 112

Element 112 has only been isolated in the gas phase (FLNR JINR).[89, 90] The ^{283}112 isotope (s.f., $T_{1/2} = 3$ min.) was produced simultaneously with the short-lived ^{185}Hg isotope (α, $T_{1/2} = 49$ s) in the reactions ^{238}U + Nd(^{48}Ca, *x*n) at the U-400 cyclotron. The nuclear reaction products in the gas flow (He) were passed to a counting apparatus consisting of a system of semiconducting detectors with a gold coating and an ionisation chamber, which recorded α decay and spontaneous fission. Compared to Hg, element 112 interacts much more weakly with gold, and its chemical behaviour is more similar to that of Rn under the conditions used.[90]

It was predicted [91] that the α decay of element 112 can occur to form the following chain:

$$^{283}112\ (\alpha,\ 170\ \text{ms}) \longrightarrow {}^{279}110\ (\alpha,\ 50\ \text{ms}) \longrightarrow$$

$$\longrightarrow {}^{275}\text{Hs}\ (\alpha,\ 1.7\ \text{s}) \longrightarrow {}^{271}\text{Sg}\ (\alpha,\ 2.5\ \text{min}) \longrightarrow {}^{267}\text{Rf}(\alpha,\ 7\ \text{days}).$$

In experiments on the synthesis of element 112 by the reaction ^{238}U(^{48}Ca, *x*n) (FLNR JINR, in 2004), a chain of four successive α decays was observed. The chain was terminated to give spontaneously fissionable ^{267}Rf isotope ($T_{1/2} \approx 3$ h) as the final product.[92] The occurrence of such decay chains offers possibilities of isolating element 112, studying its chemistry in solution in the on-line mode and determining it based on long-lived decay products.

7. Elements 113 and 114

a. Synthesis and theoretical prerequisites

Data on the synthesis of element 113 are lacking. However, α activity with $T_{1/2} = 0.5$ s was observed in the decay chain of element 115, and this activity was assigned to element 113.[2]

Element 114 has attracted particular interest because of the theoretical predictions of 'islands of stability' for $Z = 114$ and $N = 184$. Considerable attention has been given to a search for this element in nature, because calculations predicted that the lifetime of this radionuclide may be comparable with the age of the Earth. However, numerous investigations did not give positive results, and studies in this field were terminated. According to the modern concept,[91] even-even isotopes of elements 108 and 110 with a closed spherical shell ($N = 180-184$) should be even more stable. Hence, studies aimed at searching for SHEs in nature will be continued.

In 1998 – 1999, element 114 was synthesised in the reactions ^{244}Pu (^{48}Ca, 3 – 4n) and ^{242}Pu(^{48}Ca, 3n) at the U-400 cyclotron (FLNR JINR).[1] The α decay chain

$$^{289}114(\alpha) \longrightarrow {}^{285}112(\alpha) \longrightarrow {}^{281}110(\alpha) \longrightarrow {}^{277}108(\text{s.f.})$$

and two identical decay chains of the ^{288}114 isotope were observed. These chains afforded finally the spontaneously fissioning ^{280}110 isotope. Therefore, the effect of stabilisation of the neutron-excessive nuclei with $Z = 114$ ($N = 175, 174, 173$) in the vicinity of the closed neutron shell $N = 184$ was established experimentally (earlier, this effect was predicted theoretically).

After filling the d shell of transition elements 111 and 112, the p shell of the subsequent elements begins to be filled. Hence, elements 113 and 114 belong to the so-called 'post-transition' or p elements. The valence electrons of these elements occupy the ns and np sublevels. Thallium and lead are homologues of elements 113 and 114, respectively. It was predicted [93] that 113^{+1} and 114^{+2} are the most stable oxidation states. In addition, due to relativistic effects, element 114^{+2} should exhibit stronger complexing properties than Pb^{+2} and, under particular conditions, would be similar to Hg^{+2}.

No experiments on the isolation of element 113 and investigation of its chemical properties have been carried out.

b. Model experiments

Model experiments on the isolation of element 114 and investigation of its chemical properties were carried out using its homologue, *viz*., Pb.[54,94,95] To produce the short-lived carrier-free ^{211}Pb isotope ($T_{1/2}$ = 36.1 min) a simple and efficient procedure was developed for the on-line isolation of this element from parent radionuclides (based on the same principle as a radioisotope generator).

Construction of the generator. The ^{211}Pb isotope belongs to the main branch of the decay chain of the actinide family

^{227}Ac(β, 21.8 years) ⟶ ^{227}Th(α, 18.7 days) ⟶
⟶ ^{223}Ra(α, 11.4 days) ⟶ ^{219}Rn(α, 3.9 s) ⟶
⟶ ^{215}Po(α, 1.8 ms) ⟶ ^{211}Pb(β, 36.1 min) ⟶
⟶ ^{211}Bi(α, 2.1 min) ⟶ ^{207}Tl(β, 4.8 min) ⟶
⟶ ^{207}Pb(stable).

The repeated isolation of the ^{211}Pb isotope was carried out with the use of a small cation-exchange column on which ^{227}Ac or ^{223}Ra was sorbed, while the short-lived ^{211}Pb isotope was washed out with a solution of an appropriate composition. The scheme of the generator and the elution curves of ^{211}Pb using solutions of various compositions are shown in Fig. 9.

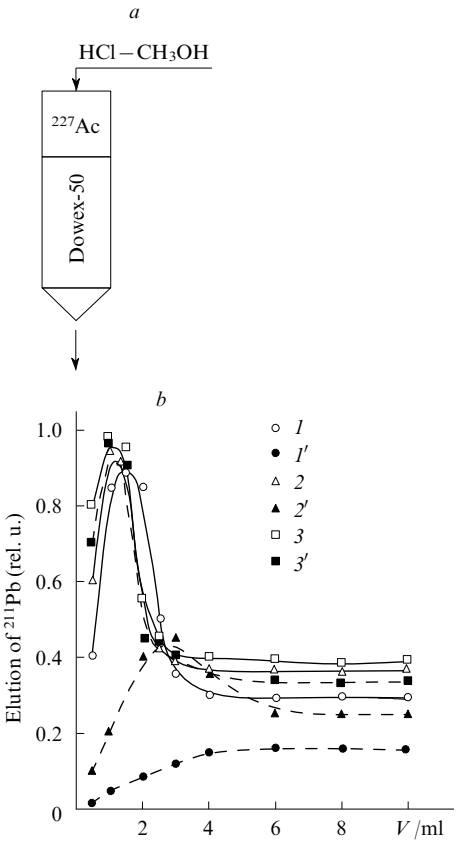


Figure 9. The generator of ^{211}Pb; 0.4 × 5 cm cation-exchange column (*a*) and the elution curves of ^{211}Pb with 1 M and 0.5 M HCl solutions (solid and dashed lines, respectively) containing CH_3OH (*b*).[94]
[CH_3OH] (%): (*1*, *1′*) 0, (*2*, *2′*) 80, (*3*, *3′*) 90.

Investigation of the ion-exchange behaviour of Pb. Cation-exchange resin. With the aim of finding the optimum conditions for elution of ^{211}Pb and stronger retention of the parent radionuclides sorbed on a cation-exchange column, the static and dynamic characteristics of sorption of elements were examined depending on the composition of the solution, the concentration of the acid (HCl, HBr) and the nature of the solvent (alcohols, ketones, *etc*.). The distribution coefficients of actinide elements and Ra were demonstrated to be higher in the presence of an organic solvent, whereas the distribution coefficients of Pb, on the contrary, decrease due to strong complexation in aqueous-organic solutions. In HBr solutions, the distribution coefficients of Pb are lower than those in HCl solutions due to the formation of more stabe bromide complexes. The distribution coefficients of actinide elements in aqueous-organic solutions of HCl and HBr are larger than K_d for lead by four orders of magnitude, which allows the repeated elution of ^{211}Pb from a generator over a long period of time. The purification factors of ^{211}Pb from actinides are $> 10^5 - 10^6$.[54,94,95]

Anion-exchange resin. Lead is characterised by low adsorbability on anion-exchange resins from 1–2 M HCl solutions ($K_d \approx 30$) and high adsorbability from HBr solutions ($K_d \geqslant 10^3$) (Fig. 10). These facts support the conclusion that anionic bromide complexes of lead are more stable than the corresponding chloride complexes. In the presence of organic solvents, the sorption of lead on anion-exchange resins from HCl solutions sharply increases.[54,95] Due to the high distribution coefficients of Pb in dilute HBr solutions and aqueous-methanolic HCl solutions, lead can be concentrated on small anion-exchange columns with simultaneous separation from Hf and actinides, which are not sorbed on anion-exchange resins under these conditions.

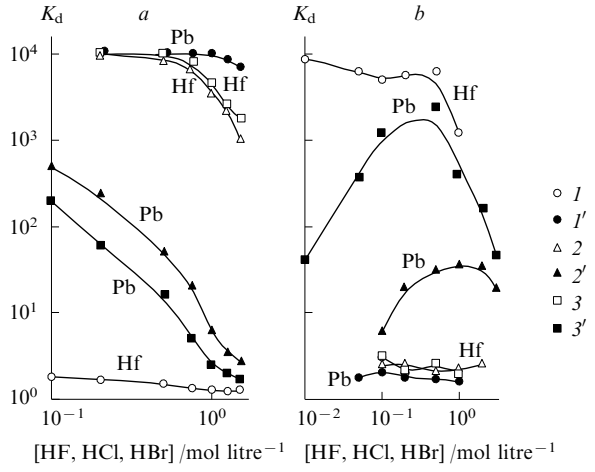


Figure 10. Plots of the distribution coefficients of Hf (*1*, *2*, *3*) and Pb (*1′*, *2′*, *3′*) *vs*. the concentration and nature of acid for sorption on Dowex-50 × 8 cation-exchange resin (*a*) and Dowex-1 × 8 anion-exchange resin (*b*).
(*1*, *1′*) HF, (*2*, *2′*) HCl, (*3*, *3′*) HBr.

Experiments on the isolation of the short-lived ^{211}Pb isotope from a generator and investigation of its chemical behaviour by repeated elution from a cation-exchange column with solutions of various compositions are, in fact, model experiments on the isolation of element 114 and investigation of its chemistry in the on-line mode. In experiments performed in FLNR JINR (in 2004), two chains were observed in the synthesis of element 114 in the reaction ^{242}Pu(^{48}Ca, 3n).[92] These chains consist of four and five successive α decays and are completed by the spontaneous fission of ^{271}Sg ($T_{1/2} = 2.4^{+4}_{-1}$ min) and ^{267}Rf($T_{1/2}$ = 3.3 h), respectively. Evidently, on-line isolation followed by identification of longer-lived decay products can be used for element 114.

8. Elements 115 and 116

Element 115 was synthesised in the nuclear reaction ^{243}Am (^{48}Ca, *x*n)$^{291-xn}$115 at the U-400 cyclotron (FLNR JINR, in

2003).[2] For the $^{288}115$ isotope ($T_{1/2} \approx 87$ ms), which was produced in channels with evaporation of three neutrons, three identical chains of five successive α decays giving finally ^{268}Db(s.f., $T_{1/2} = 16^{+19}_{-6}$ h) were observed. For the $^{287}115$ isotope ($T_{1/2} \approx 32$ ms), which was produced in the reaction upon evaporation of four neutrons, a chain of four successive α decays completed by the spontaneous fission of ^{267}Db (s.f., 73 min) was observed.

Element 116 was synthesised in the same laboratory (in 2000–2001) by the nuclear reaction ^{248}Cm(^{48}Ca, 4n).[3] Three identical decay chains corresponding to the isotope were observed:

$$^{252}116(\alpha) \longrightarrow {}^{288}114(\alpha) \longrightarrow {}^{284}112(\alpha) \longrightarrow {}^{280}110(\text{s.f.}).$$

Therefore, in addition to the discovery of new element 116, the discovery of element 114, which has been synthesised earlier by the reaction ^{244}Pu(^{48}Ca, 4n),[1] was confirmed. More recently (in 2004), three more isotopes of element 116 with masses 290–293 were produced by the reactions ^{245}Cm, ^{248}Cm + ^{48}Ca.[92]

According to the general regularities of the filling of electron shells, elements 115 and 116 can be assigned to p elements, and Bi and Po are, respectively, their chemical homologues. Relativistic calculations demonstrated that element 115 is rather stable in the oxidation state of +1 and the chemical properties of element 115 are to a certain extent similar to the properties of Tl^+. The most stable oxidation state of element 116 is +2.[96]

In the studies,[97,98] ^{268}Db was isolated as the terminal decay product of element 115, which was produced in the reaction ^{243}Am(^{48}Ca, 3n) at the U-400 cyclotron (FLNR JINR). The products of the nuclear reactions were collected in the surface layer of a copper catcher block. Radionuclides were separated from macroamounts of copper by precipitation of $La(OH)_3$ with ammonia. Group V elements were separated from actinides and lanthanides on a cation-exchange column filled with Dowex-50 × 8 with the use of a 1 M HF solution as the eluent. The eluent was evaporated on a polyethyelene film (0.4 μm thick), which was placed between a pair of semiconducting detectors surrounded by ^{3}He counters for measuring α particles, fission fragments and neutrons. Fifteen events of spontaneous fission with $T_{1/2} = 32^{+11}_{-7}$ h were observed, and they were assigned to the ^{268}Db isotope. These results are in good agreement with the results of physical experiments on the synthesis of element 115, where the ^{268}Db isotope was observed for the first time after five successive α decays of the parent nucleus of the $^{288}115$ isotope.[2,92] Therefore, the formation of element 115 in the reaction ^{243}Am + ^{48}Ca and the formation of element 113 in the decay chain of element 115 were confirmed.

The chemical identification of element 116 has not been described.

9. Elements 117 and 118

Data on the synthesis of element 117 are lacking. Element 118 was produced by the reaction ^{208}Pb + ^{83}Kr (LBL)[99] (more recently, these data were not confirmed). In the Laboratory of Nuclear Reactions of the Joint Institutes of Nuclear Research, element 118 was synthesised in the reaction ^{249}Cf + ^{48}Ca.[92,100]

According to the general regularities, element 117 can be assigned to the halides with pronounced metallic properties, and At is a chemical homologue of this element. It was predicted that element 117 is more stable in the oxidation state of +3 than in the oxidation state of +1 due to relativistic effects. In certain solutions, the behaviour of element 117 may be similar to that of Au^{+3}.[77] Element 118 has a completed outer electron shell and should belong to the noble gases. In going from light to heavier analogues, the inertness of noble gases decreases. Hence, the reactivity of element 118 would be expected to be higher. In particular, its solubility in water would be expected to be higher compared to other inert gases.

IV. Conclusion

In the last 10–15 years, considerable progress has been made in isolating TAEs and investigating their chemical properties in solution. A high-precision automated apparatus has been constructed and is being improved. This apparatus allows one to perform repeated isolation, separation and determination of transactinide elements. An efficient method has been developed for the on-line isolation of TAEs and investigation of their chemical properties during the production in nuclear reactions followed by their identification with long-lived decay products. New approaches to the isolation of short-lived isotopes of TAEs (^{257}Rf, ^{269}Hs, elements 112 and 115) on the tracer scale have been devised. These approaches are based on the use of separators, transport of radionuclides from the irradiated target in an aerosol-free gas flow, *etc*.

The behaviour of Rf and Db in solutions of hydrohalic acids has been thoroughly studied by chromatographic and extraction methods. It has been established with a high degree of assurance that Rf and Db form negatively charged complexes in dilute HF solutions and concentrated HCl solutions. It has been demonstrated that the stability of Rf and Db complexes with halide ions increases in the series $Br^- < Cl^- < F^-$, *i.e.*, in the order characteristic of Group IVB and VB elements. However, the results of comparative investigations of the stabilities of halide complexes of elements belonging to the same group by determining the distribution coefficients or the elution (extraction) order of elements are ambiguous and sometimes contradictory. The discrepancies can be attributed to various factors, primarily, to the low statistics and the possible losses of trace amounts of elements in the different steps of their isolation. Hence, conclusions about the behaviour of seaborgium in HNO_3 solutions, which have been made on the basis of the detection of one atom, are unjustified. Short-lived radionuclides are generally determined only in one phase and at one concentration. When operating with a limited number of atoms, errors, for example, in the determination of the distribution coefficients may be larger than 100%.

In studies of the behaviour of homologous elements, the optimum conditions were found for isolation of TAEs with $Z = 104–108$, 112 and 114 and investigation of their chemical properties in solutions containing various inorganic and organic complexing ligands (F^-, Cl^-, Br^-, $H_2PO_4^-$, HSO_4^-, $C_2O_4^{2-}$, TOA, TBP, TOPO, *etc*.) in the on-line mode by chromatographic and extraction methods. The ability of inorganic ligands to form complexes with Group IVB and VB elements increases in the following series $OH^- > F^- > H_2PO_4^- > HSO_4^- > Cl^- > Br^-$. Investigations of the behaviour of short-lived rhenium and osmium isotopes in dilute HCl solutions using various sorbents demonstrated that the species and oxidation states of Bh and Hs can be determined. Homologous elements are widely used to test and construct new systems for the isolation and investigation of the chemical properties of TAE in solution. Model experiments on the extraction of short-lived zirconium and hafnium isotopes (homologues of rutherfordium) with macrocyclic ligands from solutions of mineral acids were carried out.[101] Zirconium and hafnium were separated by extraction with TOA in H_2SO_4 solutions using the SISAK system.[102] A new method for the isolation and identification of superheavy elements by electrochemical deposition in systems containing several working electrodes made of different materials is in the development stage.[103]

An investigation of the relativistic effects in heavy element chemistry is a fundamental problem of modern radiochemistry. The influence of the relativistic effect of the electron shells of heavy atoms on the chemical properties of TAEs remains an open question. First experimental results, in which 'deviations' in the extraction and ion-exchange behaviour of dubnium and rutherfordium compared to the behaviour of their light homologues have been observed and assigned to the influence of the relativistic effects, have been revised and call for further study. The absence of unambiguous evidence for the influence of these effects is asso-

ciated with the difficulty of revealing substantial differences in the behaviour of elements belonging to the same group due to the similarity of their chemical properties and unreliable statistics. Moreover, regularities in the behaviour of elements observed in studies of extraction and ion exchange, *i.e.*, the distribution coefficients, do not always reflect the order in which the stability of the complexes changes. Depending on the nature and concentration of the ligand, the character of the resulting complex (inner- or outer-sphere complexes) and the nature of the sorbent (an extractant, a solvent) and, consequently, the adsorption (extraction) mechanism, an inversion in the behaviour of elements with similar chemical properties can be observed.

In my opinion, investigations of systems in which heavy elements can exhibit substantially different chemical properties (for example, in solutions containing various complexing ligands) have the most promise for revealing relativistic effects. As mentioned above, relativistic calculations predicted that the Rf atom can have the $5f^{14}6d^{2}7s^{2}7p^{1}$ or $5f^{14}7s^{2}7p^{2}$ electronic configuration along with the $[Rn]5f^{14}6d^{2}7s^{2}$ configuration. Evidently, under particular conditions (for example, in the presence of stabilising ligands), Rf can exhibit properties typical of p elements (Pb, Bi). In solutions of hydrohalic acids, Group IVB d elements form complexes whose stability increases from Br to F. For p elements, inverse dependence is observed, *i.e.*, the stability of halide complexes increases in the series F < Cl < Br.[104, 105] Actually, comparative studies of the ion-exchange behaviour of Hf and Pb in dilute solutions of hydrohalic acids demonstrated that Hf is strongly sorbed on cation-exchange resins from HCl and HBr solutions and is not sorbed from HF solutions. In contrast, Pb is more strongly sorbed on cation-exchange resins from HF solutions and is sorbed to a lesser extent from HCl and HBr solutions (see Fig. 10 *a*). An inverse situation is observed for sorption on anion-exchange resins (see Fig. 10 *b*). The results presented in Fig. 10 correlate well with the stability constants of halide complexes of hafnium and lead. As demonstrated above, Rf is not sorbed on cation-exchange resins from solutions containing HF at concentrations higher than 0.1 mol litre^{-1}, but it is strongly retained on anion-exchange resins (*i.e.*, its behaviour is analogous to that of Group IVB d elements). Evidently, investigations of the ion-exchange behaviour of Rf in dilute HBr solutions can reveal the extent to which this element exhibits the properties characteristic of p elements.

Studies of the behaviour of TAEs in different oxidation states in the presence of oxidising (or reducing) agents or by electrochemical oxidation (reduction) in the course of their isolation also hold promise for elucidating the relativistic effects. In this case, the distribution coefficients should be substantially different, due to which the experiments can be performed in the on-line mode.

The relatively long half-lives of some TAEs with $Z \geqslant 106$ allow one to study the chemical properties of these elements in solution. However, the main problem is that SHEs are produced in very low yields in a unit of time (for example, 1 atom h^{-1} for Sg), and the yields sharply decrease with increasing Z (1 atom day^{-1} for element 112). In this connection, methods based on the on-line isolation of TAEs during their synthesis hold the most promise. In the near future, one would expect that new longer-lived isotopes of SHEs in the vicinity of the 'islands of stability' will be discovered. Hence, the development of efficient procedures for the isolation and investigation of such isotopes on the basis of studies of the behaviour of their homologues is of primary importance.

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References

1. Yu Ts Oganessian, V K Utynkov, Yu V Lobanov, F Sh Abdullin, A N Polyakov, I V Shirokovsky, Yu S Tsyganov, G G Gulbekian, S L Bogomolov, B N Gikai, A N Mezentsev, S Iliev, V G Subbotin, A M Sukhov, O V Ivanov, G V Buclanov, K Subotik, M G Itkis, K J Moody, J F Wild, N J Stoyer, M A Stoyer, R W Loughedd *Phys. Rev. C* **62** 041 604 (2000)
2. Yu Ts Oganessian, V K Utynkov, Yu V Lobanov, F Sh Abdullin, A N Polyakov, I V Shirokovsky, Yu S Tsyganov, G G Gulbekian, S L Bogomolov, A N Mezentsev, S Iliev, V G Subbotin, A M Sukhov, A A Voinov, G V Buclanov, K Subotik, V I Zagrebaev, M G Itkis, J B Patin, K J Moody, J F Wild, M A Stoyer, N J Stoyer, D A Shaughnessy, J M Kennelly, R W Loughedd *Phys. Rev. C* **69** 021 601 (2004)
3. Yu Ts Oganessian, V K Utynkov, Yu V Lobanov, F Sh Abdullin, A N Polyakov, I V Shirokovsky, Yu S Tsyganov, G G Gulbekian, S L Bogomolov, B N Gikai, A N Mezentsev, S Iliev, V G Subbotin, A M Sukhov, O V Ivanov, G V Buclanov, K Subotik, M G Itkis, K J Moody, J F Wild, N J Stoyer, M A Stoyer, R W Loughedd, C A Laue, Yu E Karelin, A N Tatarinov *Phys. Rev. C* **63** 011 301 (2001)
4. Yu A Lazarev, Yu A Lobanov, Yu Ts Oganessian, V K Utynkov, F Sh Abdullin, G V Buclanov, B N Gikai, S Iliev, A N Mezentsev, A N Polyakov, I M Sedykh, I V Shirokovsky, V G Subbotin, A M Sukhov, Yu S Tsyganov, V E Zhuchko, R W Loughedd, K J Moody, J F Wild, E K Hulet, J H McQuaid *Phys. Rev. Lett.* **73** 624 (1994)
5. R J Silva, J Harris, M Nurmia, K Eskola, A Ghiorso *Inorg. Nucl. Chem. Lett.* **6** 871 (1970)
6. Z Szeglowski, H Bruchertseifer, V P Domanov, B Gleisberg, L I Guseva, M Hussonnoia, G S Tikhomirova, I Zvara, Yu Ts Oganessian *Radiochim. Acta* **51** 71 (1990)
7. G Pfrepper, R Pfrepper, D Krauss, A V Yakushev, S N Timokhin, I Zvara *Radiochim. Acta* **80** 7 (1998)
8. E Strub, J V Kratz, A Kronenberg, A Nahler, P Throle, S Zauner, W Bruchle, E Jager, M Schadel, B Schausten, E Schimpf, L Zongwei, U Kirbach, D Schumann, D T Jost, A Turler, M Asai, Y Nagame, M Sakama, K Tsukada, H V Gaggeler, J P Glatz *Radiochim. Acta* **88** 265 (2000)
9. H Haba, K Tsukada, M Asai, S Goto, A Toyoshima, I Nishinaka, S Ichikawa, Y Nagame, Y Shoji, M Shigekawa, T Koike, M Iwasaki, A Shinohara, T Kaneko, T Maruyama, S Ono, H Kudo, Y Oura, K Sueki, H Nakahara, M Sakama, A Yokoyama, J V Kratz, M Schadel, W Bruchle *J. Nucl. Radiochem. Sci.* **3** 143 (2002)
10. H Haba, K Tsukada, M Asai, A Toyoshima, K Akyama, I Nashinaka, M Hirata, T Yaita, S Ichikawa, Y Nagame, K Yasuda, Y Miyamoto, T Kaneko, S Goto, S Ono, T Hirai, H Kudo, M Shigekawa, A Shinohara, Y Oura, H Nakahara, K Sueki, H Kikunaga, N Kinoshita, N Tsugura, A Yokoyama, M Sakama, S Enomoto, M Schadel, W Bruchle, J V Kratz *J. Am. Chem. Soc.* **126** 5210 (2004)
11. A Kronenberg, K Eberhardt, J V Kratz, P K Mohapatra, A Nahler, P Thorle, W Bruchle, M Schadel, A Turler *Radiochim. Acta* **92** 379 (2004)
12. E K Hulet, R M Lougheed, J F Wild, J H Landrrum, J M Nitschke, A Giorso *J. Inorg. Nucl. Chem.* **42** 79 (1980)
13. R Gunter, W Paulus, J V Kratz, A Seibert, P Throle, S Zauner, W Bruchle, E Jager, V Pershina, M Schadel, B Schausten, D Schumann, B Eichler, H W Gaggeler, D T Jost, A Turler *Radiochim. Acta* **80** 121 (1998)
14. K B Czerwinski, K E Gregorich, N J Hannink, C D Kacher, B A Kadkhodayan, S A Kreek, D M Lee, M J Nurmia, A Turler, G T Seaborg, D C Hoffman *Radiochim. Acta* **64** 23 (1994)

15. K B Czerwinski, C D Kacher, K E Gregorich, T M Hamilton, N J Hannink, B A Kadkhodayan, S A Kreek, D M Lee, M J Nurmia, A Turler, G T Seaborg, D C Hoffman *Radiochim. Acta* **64** 28 (1994)
16. C D Kacher, K E Gregorich, D M Lee, Y Watanbe, B Kadkhodayan, B Wierczinski, V R Lane, E R Sylwester, D A Keeney, M Hendricks, N J Stoyer, J Yang, M Hsu, D C Hoffmann, A Bilewicz *Radiochim. Acta* **75** 127 (1996)
17. C D Kacher, K E Gregorich, D M Lee, Y Watanbe, B Kadkhodayan, B Wierczinski, V R Lane, E R Sylwester, D A Keeney, M Hendricks, D C Hoffmann *Radiochim. Acta* **75** 135 (1996)
18. A Bilewicz, S Siekierski, C D Kacher, K E Gregorrich, D M Lee, N Stoyer, B Kadkhodayan, S A Kreek, M R Lane, E R Sylwester, M P Neu, M F Mohar, D C Hoffman *Radiochim. Acta* **75** 121 (1996)
19. A Bilewicz *J. Radioanal. Nucl. Chem.* **247** 407 (2001)
20. J P Omttvedt, J Alstad, H Breivik, J E Dyve, K Eberhardt, C M Folden, T Ginter, K E Gregorich, E A Hult, M Johansson, U W Kirbach, D M Lee, M Mendel, A Nahler, V Ninov, B Wierczinski, P A Wilk, P M Zielinski, J V Kratz, N Trautmann, H Nitsche, D C Hoffman *J. Nucl. Radiochem. Sci.* **3** 121 (2002)
21. K E Gregorich, R A Henderson, D M Lee, M J Nurmia, R M Chasteler, H L Hall, D A Bennet, C M Gannet, R B Chadwick, J D Leyba, D C Hoffman *Radiochim. Acta* **43** 223 (1988)
22. J V Kratz, H P Zimmermann, U W Scherer, M Schadel, W Bruchle, K E Gregorich, H I Gannet, R A Hall, D M Henderson, D M Lee, J D Leiba, M J Nurmia, D C Hoffman, H Gaggeler, D Jost, U Baltensperger, Ya Nai-Qi, A Turler, Ch Lienert *Radiochim. Acta* **48** 121 (1989)
23. H P Zimmermann, M K Gober, J V Kratz, M Schadel, W Bruchle, E Schimpf, K E Gregorich, A Turler, K R Czerwinski, N J Hannink, B Kadkhodayan, D M Lee, M J Nurmia, D C Hoffman, H Gaggeler, D Jost, J Kovacs, U W Scherer, A Weber *Radiochim. Acta* **60** 11 (1993)
24. M K Gober, J V Kratz, H P Zimmermann, M Schadel, W Bruchle, E Schimpf, K E Gregorich, A Turler, N J Hannink, K R Czerwinski, B Kadkhodayan, D M Lee, M J Nurmia, D C Hoffman, H Gaggeler, D Jost, J Kovacs, U W Scherer, A Weber *Radiochim. Acta* **57** 77 (1992)
25. W Paulus, J V Kratz, E Strub, S Zauner, W Bruchle, V Pershina, M Schadel, B Schausten, K E Adams, K E Gregorich, D C Hoffman, M R Lane, C Laue, C A McGrath, D K Shaughnessy, D A Strellis, E R Sylweser *Radiochim. Acta* **84** 69 (1999)
26. M Schadel, W Bruchle, E Schimpf, H P Zimmermann, J V Gober, J V Kratz, N Trautmann, H Gaggeler, D Jost, J Kovacs, U W Scherer, A Weber, K E Gregorich, A Tuler, K R Czerwinski, N J Hannink, B Kadkhodayan, D M Lee, M J Nurmia, D C Hoffman *Radiochim. Acta* **57** 85 (1992)
27. D Truber, C Le Naour, F M Guzman *Radiochim. Acta* **90** 127 (2002)
28. J V Kratz, A Nahler, U Rieth, A Kronenberg, B Kuczewski, E Strub, W Bruchle, M Schadel, A Schausten *Radiochim. Acta* **91** 59 (2003)
29. K Tsukada, H Haba, M Asai, A Toyoshima, K Akiyama, I Nishinaka, M Hirata, K Hashimoto, S Ishikawa, Y Nagame, K Yosuda, Y Miyamoto, Y Tani, H Hasegawa, W Sato, A Shinohara, S Goto, M Ito, J Saito, H Ishizu, H Kudo, Y Oura, H Nakahara, K Sueki, N Kinoshita, H Kikunaga, A Yakoyama, in *Extended Abstracts of the 6th International Conference on Nuclear and Radiochemistry (NRC6), Aachen, Germany, 2004* p. 155
30. M Schadel, W Bruchle, B Schausten, E Schimpf, E Jager, G Wirth, R Gunter, J V Kratz, W Paulus, A Seibert, P Thorle, N Trautmann, S Zauner, D Schumann, M Andressy, R Misiak, K E Gregorich, D C Hoffman, D M Lee, E R Sylwester, Y Nagame, Y Oura *Radiochim. Acta* **77** 149 (1997)
31. M Schadel, W Bruchle, E Jager, B Schausten, R Wirth, W Paulus, R Gunter, K Eberhard, J V Kratz, A Seibert, E Strub, P Thorle, N Trautmann, A Waldeck, S Zauner, D Schumann, U Kirbach, B Kubica, R Misiak, Y Nagame, K E Gregorich *Radiochim. Acta* **83** 163 (1998)
32. A Von Zweidorf, W Bruchle, S Burger, H Hummrich, J V Kratz, B Kuczewski, G Langrock, U Rieth, U Rieth, N Trautmann, K Tsukada, N Wiehl *Radiochim. Acta* **92** 855 (2004)
33. I Zvara, Yu T Chuburkov, Z Tsaletka, T S Zvarova, M R Shalaevskii, B V Shilov *At. Energ.* **21** 83 (1966)
34. Z Szeglowski, H Bruchertseifer, V N Brudanin, G N Buklanov, O Constantinescu, Dinh Thi Lien, V P Domanov, L I Guseva, M Hussonnoia, G S Tikhomirova, I Zvara, Yu Ts Oganessian *J. Radioanal. Nucl. Chem. Lett.* **186** 353 (1994)
35. R Dressler, D Schumann, St Taut, S Fischer, R Binder, A V Yakushev, G V Buclanov, Dinh-Thi Lien, V P Domanov, Z Szeglowski, B Kubica, L I Guseva, G S Tikhomirova, H W Gaggeler, H Bruchertseifer *Radiochim. Acta* **77** 241 (1997)
36. B Wierczinski, K E Gregorich, B Kadkhodayan, D M Lee, L G Beauvais, M B Hendricks, C D Kacher, M R Lane, D A Keeney-Shaughnessy, N J Stoyer, D A Strellis, E R Sylwester, P A Wilk, D C Hoffman, R Malmbeck, G Skarnemark, J Alstad, J P Omtved, K Eberhardt, M Mendel, A Nahler, N Trautmann *J. Radioanal. Nucl. Chem.* **247** 57 (2001)
37. V Pershina, in *The Chemistry of Superheavy Elements* (Ed. M Shadel) (Dordrecht, Boston, London: Kluwer Academic, 2003) p. 31
38. O L Keller *Radiochim. Acta* **37** 169 (1984)
39. M Schadel *Radiochim. Acta* **70/71** 207 (1995)
40. Z Szeglowski *Acta Phys. Pol.* **34** 1671 (2003)
41. J V Kratz, in *The Chemistry of Superheavy Elements* (Ed. M Shadel) (Dordrecht, Boston, London: Kluwer Academic, 2003) p. 159
42. L I Guseva, G S Tikhomirova *Radiokhimiya* **33** 101 (1991) [a]
43. Z Szeglowski, L I Guseva, Dinh Thi Lien, V P Domanov, O Constantinescu, G S Tikhomirova, M Hussonnois *Radiokhimiya* **35** 59 (1993) [a]
44. Z Szeglowski, L I Guseva, Dinh Thi Lien, V P Domanov, M Constantinescu, O Constantinescu, G S Tikhomirova, M Hussonnois *Radiokhimiya* **36** 263 (1994) [a]
45. L I Guseva, G S Tikhomirova *Radiokhimiya* **39** 353 (1997) [a]
46. Z Szeglowski, H Bruchertseifer, V P Brudanin, G V Buclanov, O Constantinescu, Dinh Thi Lien, V P Domanov, L I Guseva, M Hussonnois, G S Tikhomirova, I Zvara, Yu Ts Oganessian *J. Radioanal. Nucl. Chem. Lett.* **212** 35 (1996)
47. L I Guseva, G S Tikhomirova *Radiokhimiya* **40** 345 (1998) [a]
48. Z Szeglowski, L I Guseva, Dinh Thi Lien, V P Domanov, B Kubica, G S Tikhomirova, M Constantinescu, O Constantinescu, A V Yakushev *J. Radioanal. Nucl. Chem.* **228** 145 (1998)
49. D Shumann, A F Novgorodov, R Misiak, G Wunderlich *Radiochim. Acta* **87** 75 (1999)
50. R Malmbeck, G Skarnemark, J Alstad, K Fure, M Johansson, J P Omtvedt *J. Radioanal. Nucl. Chem.* **246** 349 (2000)
51. L I Guseva, G S Tikhomirova *Radiokhimiya* **44** 309 (2002) [a]
52. L I Guseva, Z Szeglowski, Dinh Thi Lien, V P Domanov, B Kubica, G S Tikhomirova, A V Yakushev, A G Belov *Radiokhimiya* **44** 313 (2002) [a]
53. Z Szeglowski, Dinh Thi Lien, L I Guseva, S N Timokhin, B Kubica, G S Tikhomirova *J. Radioanal. Nucl. Chem.* **251** 311 (2002)
54. L I Guseva, G S Tikhomirova *Radiokhimiya* **44** 154 (2002) [a]
55. R Guillaumont, J P Adloff, A Peneloux *Radiochim Acta* **46** 169 (1989)
56. R Guillaumont, J P Adloff, A Peneloux, P Delamoye *Radiochim. Acta* **54** 1 (1991)
57. A Giorso, B G Harvey, G R Choppin, S G Thompson, G T Seaborg *Phys. Rev.* **98** 1518 (1955)
58. F J Reischmann, B Rumler, N Trautmann, G Hermann *Radiochim. Acta* **39** 185 (1986)
59. M Schadel, W Bruchle, E Jager, E Schimpf, J V Kratz, U W Scherer, H P Zimmermann *Radiochim. Acta* **48** 171 (1989)
60. Z Szeglowski, H Bruchertseifer, V P Domanov, B Glaizberg, L I Guseva, M Hussonnois, G S Tikhomirova, I Zvara, Yu Ts Oganessian *Radiokhimiya* **33** 90 (1991) [a]

61. D Schumann, R Dressler, S Fischer, St Taut, R Binder, Z Szeglowski, B Kubica, L I Guseva, G S Tikhomirova, O Constantinescu, V P Domanov, M Constantinescu, Dinh-Thi Lien, Yu Ts Oganessian, V P Brudanin, H Bruchertseifer *Radiochim. Acta* **69** 35 (1995)
62. G Pfrepper, R Pfrepper, A V Yakushev, S N Timokhin, I Zvara *Radiochim. Acta* **77** 201 (1997)
63. G Pfrepper, R Pfrepper, A Kronenberg, J V Kratz, A Nachler, W Bruchle, M Shadel *Radiochim. Acta* **88** 273 (2000)
64. L I Guseva, Z Szeglowski, Dinh-Thi Lien, B Kubica, G S Tikhomirova, S N Timokhin *J. Radioanal. Nucl. Chem.* **260** 357 (2004)
65. H Persson, G Skarnemark, M Skelberg, J Alstad, J O Liljenzin, G Bauer, F Haberberger, N Kaffler, J Rogowski, N Trautmann *Radiochim. Acta* **48** 177 (1989)
66. J Alstad, G Skarnemark, F Haberberger, G Herrmann, A Nachler, M Pense-Maskow, N Trautmann *J. Radioanal. Nucl. Chem.* **189** 133 (1995)
67. B Wierczinski, J Alstad, K Eberhardt, B Eichler, H Gageller, G Herrmann, D Jost, A Nachler, M Pense-Maskow, A V Reddy, G Skarnemark, N Trautmann, A Turler *Radiochim. Acta* **69** 77 (1995)
68. B Fricke *Struct. Bond.* **21** 90 (1975)
69. D Schumann, S Fisher, R Dressler, St Taut, H Nitsche, N Trautmann, M Schadel, W Bruchl, B Schausten, A F Novgorodov, R Misiak, B Eichler, H Gaggeler, D Jost, A Turler, H Bruchertseifer *Radiochim. Acta* **72** 137 (1996)
70. H Bruhertseifer, B Eichler, I Estevez, I Zvara *Radiochim. Acta* **47** 41 (1989)
71. V Pershina *Radiochim. Acta* **80** 75 (1998)
72. A Bilewicz *J. Radioanal. Nucl. Chem.* **221** 19 (1997)
73. V Pershina, D Truber, C Le Naour, J V Kratz *Radiochim. Acta* **90** 869 (2002)
74. B Frike, E Johnson, G M Rivera *Radiochim. Acta* **62** 17 (1993)
75. J P Desclaux *At. Data Nucl. Data Tables* **12** 311 (1973)
76. V Pershina, T Bastug *Radiochim. Acta* **84** 79 (1999)
77. J J Katz, G T Seaborg, L R Morss (Eds) *The Chemistry of the Actinide Elements* (London, New York: Capmen and Hall, 1986)
78. A Kronenberg, P K Mohapatra, G Pfrepper, R Pfrepper *Radiochim. Acta* **92** 395 (2004)
79. J P Omtvedt, M Johansson, J Alsted, G Scarnemark *Radiochim. Acta* **89** 619 (2001)
80. M Johansson, J Alsted, J P Omtvedt, G Scarnemark *Radiochim. Acta* **91** 351 (2003)
81. C Brihaye, T A Butler, F F Knapp Jr *J. Radioanal. Nucl. Chem.* **102** 399 (1986)
82. B Wierczinski, K J Volkers, in *Extended Abstracts of the 2nd International Conference on the Chemistry and Physics of Transactinide Elements (TAN 03), Napa, CA, 2003* p. 120
83. R Eichler, W Bruchle, R Dressler, Ch E Dullmann, B Eichler, H W Gaggeler, K E Gregorich, D S Hoffman, H Hubener, D T Jost, U W Kirbach, C A Laue, V M Lavanchy, H Nitsche, J B Patin, D Piguet, M Schadel, D A Shaughnessy, D A Strellis, S Taut, L Tobler, Y S Tsyganov, A Turler, A Vahle, P A Wilk, A V Yakushev *Nature (London)* **407** 63 (2000)
84. Ch E Dullmann, W Bruchle, R Dressler, K Eberhardt, B Eichler, R Eichler, K E Gaggeler, T N Ginter, F Glaus, K E Gregorich, D C Hoffman, E Jager, D T Jost, U W Kirbach, D M Lee, H Nitsche, J B Patin, V Pershina, D Piguet, Z Qin, M Schadel, B Schausten, H J Schott, S Soverna, R Sudowe, P Thorle, S N Timokhin, N Trautmann, A Turler, A Vahle, G Wirth, A V Yakushev, P M Zielinski *Nature (London)* **418** 859 (2002)
85. A Von Zweidorf, R Angert, W Bruchle, S Burger, K Eberhardt, R Eichler, H Hummrich, E Jager, R Jera, H O Kling, J V Kratz, U Krill, B Kuczewski, G Langrock, G Lehr, M Mendel, A Nachler, A Peil, V Persina, U Rieth, M Schadel, B Schausten, E Schimpf, H J Schott, E Stiel, P Thorle, N Trautmann, K Tsukada, N Wiehl, G Wirth, in *Extended Abstracts of the 6th International Conference on Nuclear and Radiochemistry (NRC6), Aachen, Germany, 2004* p. 141
86. L Keller, C W Nestor *J. Phys. Chem.* **77** 1806 (1973)
87. K S Pitzer *J. Chem. Phys.* **63** 1032 (1975)
88. Z Szeglowski, Dinh Thi Lien, S N Timokhin, A V Yakushev, I Zvara *J. Radioanal. Nucl. Chem.* **247** 451 (2001)
89. A V Yakushev, G V Buclanov, M L Chelnokov, V I Chepigin, S N Dmitriev, V A Gorshkov, S Hubener, V Ya Lebedev, O N Malyshev *Radiochim. Acta* **89** 743 (2001)
90. A V Yakushev, I Zvara, Yu Ts Oganessian, A V Belozerov, S N Dmitriev, B Eichler, S Hubener, A Soverna, Z Szeglowski *Radiochim. Acta* **91** 433 (2003)
91. R Smolanczuk *Phys. Rev. C* **56** 812 (1997)
92. Yu Ts Oganessian, V K Utynkov, Yu V Lobanov, F Sh Abdullin, A N Polyakov, I V Shirokovsky, Yu S Tsyganov, G G Gulbekian, S L Bogomolov, B N Gikai, A N Mezentsev, S Iliev, V G Subbotin, A M Sukhov, A A Voinov, G V Buclanov, K Subotik, M G Itkis, J B Patin, J F Wild, M A Stoyer, N J Stoyer, D A Shaughnessy, J M Kenneally, P A Wilk, R W Loughed, R I Il'kaev, S P Vesnovskii *Phys. Rev. C* **70** 064 609 (2004)
93. O L Keller Jr , J L Burnet, T A Carlson Jr, C W Nestor *J. Phys. Chem.* **74** 1127 (1970)
94. L I Guseva, G S Tikhomirova, N N Dogadkin *J. Radioanal. Nucl. Chem.* **260** 167 (2004)
95. L I Guseva, G S Tikhomirova *Radiokhimiya* **46** 155 (2004) [a]
96. O L Keller Jr, C W Nestor, B Fricke *J. Phys. Chem.* **78** 1945 (1974)
97. S N Dmitriev, Yu Ts Oganessian, V K Utynkov, S V Shishkin, A V Yremin, Yu V Lobanov, Yu S Tsyganov, V I Chepigin, E A Sokol, G K Vostokin, N V Aksenov, M Hussonois, M G Itkis, H W Gaggeler, D Shumann, H Bruchertseifer, R Eichler, D A Shaughnessy, P A Wilk, J M Kenneally, M A Stoyer, J F Wild, in *Contribution to the International Symposium on Exotic Nuclei, Petergof, Russia 2004*
98. S N Dmitriev, Yu Ts Oganessian, V K Utynkov, S V Shishkin, A V Yremin, Yu V Lobanov, V I Chepigin, E A Sokol, Yu S Tsyganov, G K Vostokin, N V Aksenov, M Hussonois, M G Itkis *Mendeleev Commun.* 1 (2005)
99. V Ninov, K E Gregorich, W Loveland, A Ghiorso, C Hoffman, D M Lee, H Nitsche, W J Swiatecki, U M Kurbach, C A Loue, J L Adams, J B Patin, D A Shaughnessy, A D Strellis, P A Wilk *Phys. Rev. Lett.* **83** 1104 (1999)
100. Yu Ts Oganessian *J. Nucl. Radiochem. Sci.* **3** 5 (2002)
101. R Sudowe, Ch E Dullmann, L M Farina, C M Folden, K E Gregorich, S E H Gallaher, D C Hoffman, D C Phillips, J M Schwantes, R E Wilson, P M Zielinski, H Nitsche, in *Extended Abstracts of the 6th International Conference on Nuclear and Radiochemistry (NRC6), Aachen, Germany, 2004* p. 144
102. D Polakova, G Skarnemark, J Alstad, L Stavsetra, L Zheng, J P Omtvedt, in *Extended Abstracts of the 2nd International Conference on the Chemistry and Physics of Transactinide Elements (TAN 03), Napa, CA, 2003* p. 105
103. H Hummerich, J V Kratz, in *Extended Abstracts of the 6th International Conference on Nuclear and Radiochemistry (NRC6), Aachen, Germany, 2004* p. 133
104. N G Polyanskii, in *Analiticheskaya Khimiya Elementov. Svinets* (Analytical Chemistry of Elements. Lead) (Moscow: Nauka, 1986) p. 34
105. Yu Yu Lur'e *Spravochnik po Analiticheskoi Khimii* (Handbook on Analytical Chemistry) (Moscow: Khimiya, 1989)

[a] — *Radiochemistry (Engl. Transl.)*