

53 Radiochemical Separations by Thermochromatography

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Abstract: The history, theoretical fundamentals, and practical application of thermochemistry are briefly reviewed. The main advantages of the method – the speed and selectivity of chemical separation of complex mixtures of short-lived radionuclides, including transactinide ones – are analyzed. Prospects of thermochemistry in production of radionuclides widely used in science and technology are considered on the basis of the performed systematic investigations of the thermochemical behavior of volatile compounds of the elements of the periodic table.

53.1 Introduction

The increasing interest in studying short-lived radionuclides, including transactinide ones, in the early 1960s created a demand for improved or newly created methods allowing fast and highly selective separation of various radioelements.

The analysis of the trends in development of analytical and radiochemical methods showed that the simplest and most effective way to satisfy this demand was through high-temperature gas chemistry. The already gained experience in using a variety of gas chromatography versions logically led to the choice of thermochemistry (TC), i.e., stationary non-isothermal gas–solid chromatography based on thermal variation of the interaction between the volatile radioactive species (atoms or molecules) and the adsorbent. In this method, a negative temperature gradient is produced in the direction of the carrier gas flow or, alternatively, in vacuum. It is, consequently, this temperature gradient that retards the transport of species in the column. If the slowing-down is different for different species, they are separated. Thus, it becomes possible to concentrate components of complex mixtures supplied to the thermochemical column even continuously (in contrast to ordinary gas chromatography).

Historically, the term “thermochemistry” was first applied to the method for separation of mainly volatile organic compounds in which the temperature field with a negative gradient moves along the column, so that the outlet temperature gradually increases ousting the separated substances from the column. In this case the thermochemical diagram is a curve expressing the time (t) or temperature (T) dependence of the outlet concentration, i.e., $c = f(t)$ or $c = f(T)$.

In radiochemistry, the most popular version is TC with a stationary temperature gradient, in which the concentration of a substance and its local distribution depend on the distance or temperature, i.e., $c = f(x)$ or $c = f(T)$. This means that the volatile compounds remain in the thermochemical column. In the literature this method was previously referred to by various jargon terms, e.g., “horizontal distillation,” “separation on the gradient tube,” “separation on the temperature gradient,” etc.

It is particularly noteworthy that Marie and Pierre Curie used the method in question as far back as the end of the nineteenth century when they discovered Ra and Po (Curie and Curie 1898). Polonium sulfide was distilled in a carbon dioxide flow into a tube with a negative temperature gradient, where it was precipitated in a narrow zone. Unfortunately, this experience and method has long been forgotten. What may also be considered the first publication on the use of TC in radiochemistry is the paper by Merinis and Bouissieres (1961) on separation of noncarrier-added spallogenic products: radioactive Hg, Pt, Ir, Os, and Re isotopes have been separated from macroscopic gold targets bombarded with medium-energy protons. Another important work of those, which stimulated the further development of TC, was an attempt to

separate and identify the artificial element 104 (now named rutherfordium), an analog of Hf, which clearly showed advantages of the method in the study of short-lived radionuclides (Zvara et al. 1971).

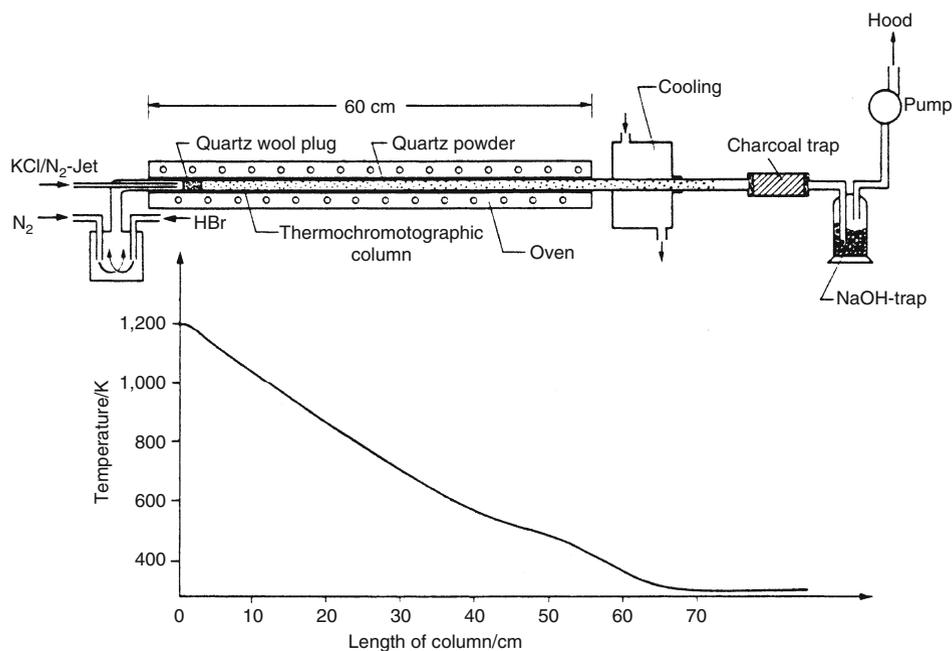
The simple equipment required and the high efficiency of the method stimulated its rapid theoretical and practical development in the 1960s, marked with some outstanding results, as for example, the characterization of previously unknown isotopes of many elements from the periodical system and even more – the discovery of new transactinide elements. Much has been contributed for the increasingly wide use of TC by a group of radiochemists (I. Zvara, B. Eichler, Yu. T. Chuburkov, V. P. Domanov, S. Hübener, A. B. Yakushev, et al.) from the Flerov Laboratory of Nuclear Reactions (JINR Dubna, Russian Federation). This and another group (H.W. Gäggeler, A. Türlér, R. Eichler, et al.) from the Paul Scherrer Institut, Villigen, Switzerland, still successfully continue the development of thermochemistry.

53.2 Equipment and Techniques

Thermochemical set-up: Figure 53.1 displays a typical thermochemical apparatus (Hickmann et al. 1993), the main part representing a gradient oven providing the required temperature field along the column. The oven may be made of a large number of short sections or by winding a heat-releasing wire (nichrome, superkanthal, platinum, etc.) on an insulating tube (quartz, porcelain, alundum, etc.) in a varying mode. To smooth the temperature field of the oven, it has a heat-conducting tube inside and a thermal-insulating

Fig. 53.1

Thermochemical setup and typical profile of temperature along the column (Reproduced with permission from *Radiochimica Acta*, Hickmann et al. 1993)



coating outside. The simplest design is an oven heating at one end of a long heat-conducting tube surrounded with a vacuum enclosure. This design ensures almost linear temperature distribution along the apparatus. The “cold” end of the tube is usually cooled with water or even liquid nitrogen.

The thermochemical apparatus also comprises

- A system for carrier gas (and/or reactant gas) supply, purification, and flow rate control; or, alternatively, an appropriate vacuum system.
- A system for injection of substances to be separated (periodic or continuous).
- A system for trapping outgoing reactant gases and possible radioactive gases or aerosols.

Thermochemical columns (TCC) are usually made of glass, quartz, porcelain, or metallic tubes, chemically resistant to reactant gases. They may be open (hollow) or filled with various substances (metals, oxides, halides, etc.). Probes, containing the radionuclides of interest, are inserted into the TCC at places of maximum temperature (T_S) in a batch mode before the experiments (off-line) or continuously (online) using gas jets with the radionuclides of interest adsorbed on microdisperse aerosol particles (KCl, MoO₃, etc.).

Temperature profiles: A method for determining the profile of the distribution of separated substances in the column is of major importance in thermochemical experiments. Most of them are carried out with radionuclides emitting radiation that penetrates through the column walls (relatively “hard” β and γ rays), which allows the radioactivity within the column sections to be measured off-line either by cutting the column into small parts or by collimating the detector used and screening the column. Mixtures of radionuclides usually require the use of HPGe detectors because of the high-energy resolution. If sufficient activities of radionuclides decaying with emission of high-energy γ -quanta are used, it is in principle possible to monitor the substance distribution in the column online during the thermochemical experiment by using one or several well-collimated movable detectors.

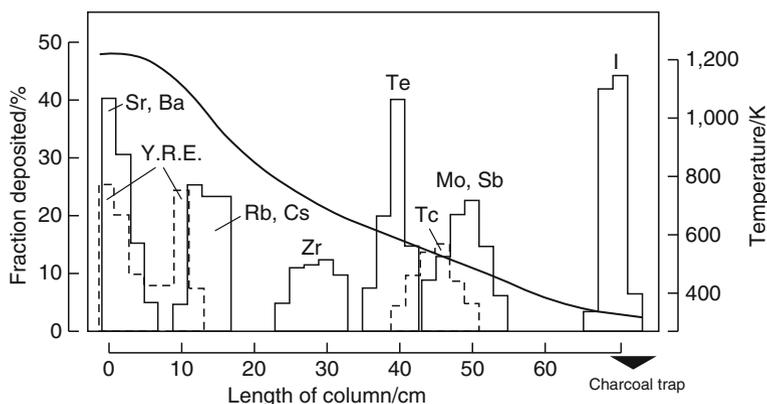
The situation becomes much more complicated when the radionuclides used undergo α decay or spontaneous fission, i.e., if non-penetrating radiation needs to be detected. If these radionuclides are long-lived, the column is cut into small sections, the substances adsorbed on its inner surface are washed off with appropriate solutions, and the resulting solutions are analyzed. In the case of short-lived radionuclides, e.g., transactinide elements, semiconductor or track detectors (mica, quartz) placed inside the column are used. They allow single decays to be determined at each point of the column. In principle, other methods may be used to determine the distribution of substances in the column, e.g., photospectrometry and X-ray fluorescence.

The experiment result is a thermochemical chromatogram. An example is given in [Fig. 53.2](#) (Hickmann et al. 1993), which displays the distribution of bromides of uranium fission products continuously supplied to the column for 15 min. The thermochemical chromatogram for each chemical species allows the determination of the basic parameter T_a , the adsorption temperature (center of gravity of distribution of the substance in the column).

Numerous experiments have shown that this quantity depends first of all on the chemical composition of the volatile substance and on the column material (adsorbate–adsorbent interaction). In addition, it depends on the starting temperature of the column, the period of the thermochemical chromatography procedure, the temperature gradient, the diameter of the column, type and flow-rate of carrier gas (or gas-reagent), and some other parameters. Thus, the adsorption temperature T_a is not a constant and, for example, varies inversely with the duration of the thermochemical chromatography procedure of a particular experiment. Therefore, it is

Fig. 53.2

Element distribution in a thermochemical column with 9 vol% hydrogen bromide as reactive additive to the carrier gas nitrogen, together with the temperature profile along the column. Quartz-powder column, 15 min exposure time (Reproduced with permission from *Radiochimica Acta*, Hickmann et al. 1993)



essential for researchers to try to find ways of transferring the variable T_a to standard constants ΔH_a^0 and ΔS_a^0 , enthalpy and entropy, respectively, used in ordinary gas chromatography.

53.3 Theory

53.3.1 Transport of Volatile Species Along the Column

All theoretical treatments of the thermochemical process (Merinis and Bouissieres 1969; B. Eichler and Zvara 1975; Steffen and Bächmann 1978b; Novgorodov and Kolatchkowski 1979), beginning with papers by Merinis and Bouissieres (1969), are based on the fact that the species' (atom, molecule) transfer time within the TCC breaks into two components – the residence time in the gaseous phase and the residence time on the surface of the column. The latter is governed by the average lifetime of the species in the adsorbed state τ_a (s) related to the temperature by the Frenkel equation (Frenkel 1924):

$$\tau_a = \tau_0 \cdot \exp\left(\frac{Q}{RT}\right), \quad (53.1)$$

where τ_0 is the period of oscillation of the species in the adsorbed state perpendicularly to the surface (s); Q is the adsorption heat ($\text{J} \cdot \text{mol}^{-1}$); R is the gas constant ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$); T is the absolute temperature (K).

The total time of the species transfer (transport) in the column from the starting temperature T_s to the adsorption temperature T_a is most comprehensively described by B. Eichler and Zvara (1975):

$$t = \frac{T_0}{g u_0} \ln \frac{T_a}{T_s} + \frac{s T_0 \frac{V}{A} \exp\left(\frac{\Delta S_a^0}{R}\right)}{v g u_0} \int_{T_s}^{T_a} \frac{1}{T} \exp\left(-\frac{\Delta H_a^0}{RT}\right) dT \quad (53.2)$$

where T_0 is the standard temperature, 298.15 K; g is the gradient of the temperature for its linear distribution along the column ($\text{K} \cdot \text{cm}^{-1}$); u_0 is the linear velocity of the carrier (reagent) gas in the column under standard conditions ($\text{cm} \cdot \text{s}^{-1}$); s and v are the open surface and the open volume of the column per its unit length, (cm) and (cm^2) respectively; V/A is the ratio of the standard molar volume to the standard molar surface (cm); $\Delta\overline{H}_a^0$ is the adsorption enthalpy ($\text{J} \cdot \text{mol}^{-1}$); $\Delta\overline{S}_a^0$ is the adsorption entropy ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$).

This equation is derived on the assumption that the main characteristic parameters of the adsorption interaction ($\Delta\overline{H}_a^0$ and $\Delta\overline{S}_a^0$) are independent of the temperature, that there is no surface diffusion, and that the carrier (reagent) gas adsorption is negligibly small. Solution of this equation, i.e., finding $\Delta\overline{H}_a^0$ is virtually reduced to solution of the integral in expression (53.2). This may be done either numerically or by replacing the integral by the difference of the so-called integral exponential function represented in the tabulated form:

$$\int_{T_s}^{T_a} \frac{1}{T} \exp\left(-\frac{\Delta\overline{H}_a^0}{RT}\right) dT = \left[E_i^*\left(-\frac{\Delta\overline{H}_a^0}{RT_a}\right) - E_i^*\left(-\frac{\Delta\overline{H}_a^0}{RT_s}\right) \right] \quad (53.3)$$

Analyzing Eq. (53.2) B. Eichler and Zvara (1982) considered the effect of various standard state models (V/A) and values of $\Delta\overline{S}_a^0$, calculated on the basis of the molecular-kinetic concepts as the loss of degrees of freedom of the particle (atom) on its transition from the gas phase to the adsorbed state, on $\Delta\overline{H}_a^0$. With given mobile and localized adsorption and five standard states, the theoretically calculated values of $\Delta\overline{S}_a^0$ for adsorption of Po on the Cu surface vary in a very wide range from -31.10 to $-512.27 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ (B. Eichler and Zvara 1982). Naturally, this strongly affects the values of $\Delta\overline{H}_a^0$ calculated by expression (53.2). In the case of polyatomic molecules, when one has to take into account the entropy variation due to variation of internal degrees of freedom, rotation of the molecule, and probably chemical bond of molecules with the surface, a theoretical calculation of $\Delta\overline{S}_a^0$ becomes much more complicated. Thus, the uncertainty in evaluation of $\Delta\overline{S}_a^0$ results in approximate values of $\Delta\overline{H}_a^0$ only. Several attempts have been made to calculate empirically $\Delta\overline{S}_a^0$ and $\Delta\overline{H}_a^0$ for various compounds, e.g., chlorides and oxides (B. Eichler 1976), and to determine experimentally these two main parameters of the adsorption interaction, but their values obtained for a majority of adsorbate-adsorbent pairs are still estimates. Therefore, it is desirable to cite these values together, no matter how they were obtained.

The generally accepted theoretical value of $\Delta\overline{S}_a^0$ is the one obtained for the mobile adsorption model and the standard state $V/A = 1 \text{ cm}$ (B. Eichler and Zvara 1982)

$$\Delta\overline{S}_a^0 = R \cdot \ln\left(\frac{1}{(1 \text{ cm}) \cdot v_B} \sqrt{\frac{kT_a}{2\pi m}}\right) + \frac{1}{2}R, \quad (53.4)$$

where R is the gas constant; v_B is the characteristic adsorbent frequency equal to $5 \times 10^{12} \text{ s}^{-1}$ for quartz; k is the Boltzmann constant; T_a is the adsorption temperature (K) (B. Eichler et al. 2002); m is the mass of the molecule (g).

The key question about the values of $\Delta\overline{S}_a^0$ and $\Delta\overline{H}_a^0$ and, if possible, about their dependence on the temperature may be eventually solved by carrying out quite systematic series of experiments with several experimental conditions, e.g., experiment period, starting temperature, gas composition and velocity, column diameter, etc., varied over a wide range for one and the same adsorbate-adsorbent pair (Steffen and Bächmann 1978b; Chuburkov et al. 1993). Provided that $\Delta\overline{S}_a^0$ and $\Delta\overline{H}_a^0$ are temperature-independent, dependence of $\ln\frac{-\Delta\overline{H}_a^0}{sT_a \cdot (1 \text{ cm})}$ on $\frac{1}{T_a}$

Table 53.1

Values of ΔS_a^0 ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) obtained by various methods

Compound	Experiment (Steffen and Bächmann 1978b)		Empirical dependence (Chuburkov et al. 1993)	Equation 10.4
	Isothermal chromatography	Thermo-chromatography		
ReO ₃	-187.0 ± 5.0	-147.3 ± 17.0	-150 ± 5	-166.3
HReO ₄	-206.4 ± 3.4	-114.8 ± 11.0	-133 ± 3	-168.9
IrO ₃	-191.0 ± 6.2	-137.0 ± 15.3	-150 ± 5	-168.1

(v_0 is the volume gas flow under standard conditions) yields a straight line with a slope $-\Delta H_a^0/R$ and an intercept on the x -axis at $\ln \frac{RT_0}{-\Delta H_a^0} + \frac{\Delta S_a^0}{R}$.

► Table 53.1 illustrates the different approaches of determination of ΔS_a^0 in the case of adsorption of volatile Re and Ir compounds with oxygen-containing carrier gas systems on TCC quartz surfaces. Undoubtedly, experiments are of primary importance in determining the entropy values.

53.3.2 The Potential of Thermochemistry for Radiochemical Separations

In analytical chemistry the quality of separation is characterized by the criterion for separation of two substances ($R_{1,2}$), expressed in TC as:

$$R_{1,2} = \frac{T_{a1} - T_{a2}}{2(\sigma_1 + \sigma_2)} \quad (53.5)$$

where T_{a1} and T_{a2} are the temperatures of the centers of gravity of the distribution of substances 1 and 2 (K); σ_1 and σ_2 are the standard deviations of their distribution (K).

Two theoretical contributions have focused on the distribution of the substance in the course of its motion along the TCC (Novgorodov and Kolatchkowski 1979; Zvara 1985). In one of them the general relations of gas chromatography are adopted. The height equivalency to the theoretical plate (HETP), H (cm), for the laminar flow in an open straight tube column, is (Giddings and Seager 1960)

$$H = \frac{2D_{\text{gas}}}{u_x} + \frac{d^2 u_x}{96D_{\text{gas}}} \quad (53.6)$$

where D_{gas} is the diffusion coefficient of the substance under study in the carrier gas ($\text{cm}^2 \cdot \text{s}^{-1}$); u_x is the linear velocity of the carrier gas defined as

$$u_x = u_0 \cdot \frac{T}{T_0} = \frac{4v_0 T}{\pi d^2 T_0} \quad (53.7)$$

where u_0 is linear velocity of the carrier gas under standard conditions ($\text{cm} \cdot \text{s}^{-1}$); d is the diameter of the column (cm); T is the temperature of the column (K). The diffusion coefficients correlate according to the molecular-kinetic concepts:

$$D_{\text{gas}} = D_{\text{gas}}^0 \left(\frac{T}{T_0} \right)^{3/2} \quad (53.8)$$

where D_{gas}^0 is the diffusion coefficient under standard conditions. Considering (53.7) and (53.8), expression (53.6) takes the following form

$$H = \frac{aT + b}{\sqrt{T}} \quad (53.9)$$

where $a = \frac{\pi D_{\text{gas}} d^2}{2v_0 \sqrt{T_0}}$ and $b = \frac{v_0 \sqrt{T_0}}{24\pi D_{\text{gas}}}$.

For isothermal gas chromatography the dispersion (σ^2) of the substance distribution in the column increases with the coordinate x (i.e., the zone is expanded) as

$$\sigma_{\text{exp}}^2 = xH \quad (53.10)$$

As described above, an advantage of TC over ordinary gas chromatography is that the decrease in the temperature of the column slows down the motion of the zone of the substance to be separated. In addition, the delayed part of the zone meets a higher temperature and is speeded up while the leading part, on the contrary, is slowed down. Thus, the distribution of the substance formed at each moment of the process, i.e., at each individual adsorption temperature, is determined by the fact that the expanding of the zone is equal to its compression

$$d\sigma/dt = (d\sigma/dt)_{\text{exp}} + (d\sigma/dt)_{\text{comp}} = 0 \quad (53.11)$$

As follows from (53.9) and (53.10) and in view of $T = T_s + gx$, the dispersion causing the expanding of the zone is

$$\sigma_{\text{exp}}^2 = \frac{a(T_s + gx) + b}{\sqrt{T_s + gx}} \cdot x \quad (53.12)$$

Differentiation of this expression results in the expression

$$\left(\frac{d\sigma}{dt}\right)_{\text{exp}} = \frac{1}{4\sigma T\sqrt{T}} [a(3T^2 - TT_s) + b(T + T_s)] \cdot w_{\text{zone}} \quad (53.13)$$

where w_{zone} is the velocity of the moving center of gravity of the zone ($\text{cm} \cdot \text{s}^{-1}$). The compression component can be expressed, according to Ohline and Deford (1963), as

$$\left(\frac{d\sigma}{dt}\right)_{\text{comp}} = -g\sigma\Delta\overline{H}_a \frac{w_{\text{zone}}}{RT^2} \quad (53.14)$$

Substituting (53.13) and (53.14) into (53.11) yields

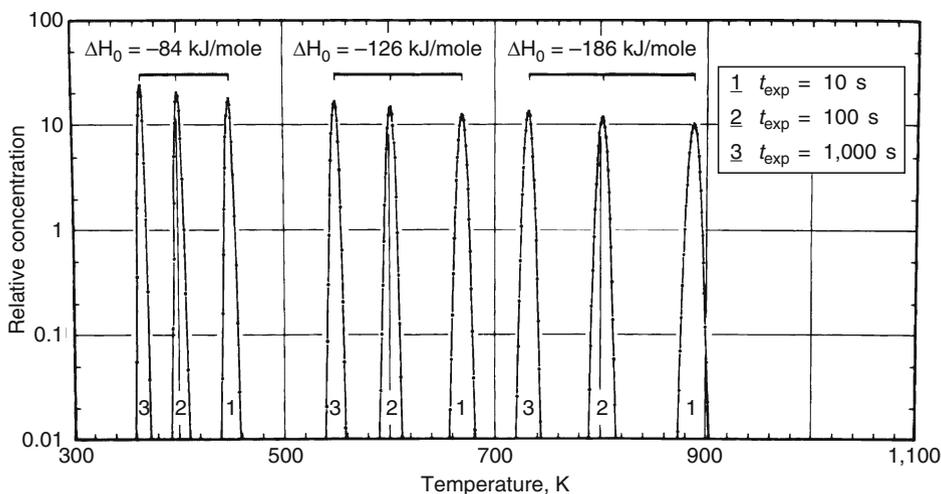
$$\sigma^2 = \frac{R\sqrt{T_a}[aT_a(3T_a - T_s) + b(T_a + T_s)]}{4g\Delta\overline{H}_a^0} \quad (53.15)$$

By using the derived basic equations of TC (Novgorodov and Kolatchkowski 1979), the distribution of a substance along the column was calculated for the simplest case, i.e., when the substance is injected in the column in the form of a δ -function [$c = f(s, t) = \infty$].

Figure 53.3 displays the computed thermochematogram of three hypothetical substances with $\Delta\overline{H}_a^0 = -84, -126, \text{ and } -168 \text{ kJ} \cdot \text{mol}^{-1}$ for three process periods of 10, 100 and 1,000 s. The calculation was carried out with the parameters $d = 0.3 \text{ cm}$; $v_0 = 0.5 \text{ cm}^3 \cdot \text{s}^{-1}$; $D_{\text{gas}}^0 = 0.1 \text{ cm}^2 \cdot \text{s}^{-1}$; $T_s = 1,100 \text{ K}$, and $g = -16 \text{ K} \cdot \text{cm}^{-1}$. Not only retarding but also compression of the zone of the hypothetical substances is obvious. Note that the calculations

Fig. 53.3

Distribution of three hypothetical substances in the TCC for three exposure times (see explanation in the text)



were carried out for the carrier gas velocity close to the optimum velocity, the expression for which was derived from (53.6)

$$v_{0(\text{opt})} = \pi D_{\text{gas}}^0 d \sqrt{\frac{6(T_s + T_a)}{T_0}} \quad (53.16)$$

The standard deviation σ for the substance with $\overline{\Delta H_a^0} = -126 \text{ kJ} \cdot \text{mol}^{-1}$ and $T_a = 500 \text{ K}$ is 3.6 K under the conditions considered.

A slightly different approach to determine the distribution of a substance in no carrier amounts (n.c.a.) was introduced by Zvara (1985). Using the Monte Carlo method and assuming that species leaving the surface of the column with an adopted probability immediately start moving at the carrier gas velocity, the author calculated the extent of the “jump” ($\bar{\eta}$) of the species to the next adsorption event, which is on the average equal to

$$\bar{\eta} = \frac{11 v_0}{48 \pi D_{\text{gas}}} \quad (53.17)$$

The calculations for the case like the one considered above yielded $\sigma = 21 \text{ K}$ for $T_a = 476 \text{ K}$ (Zvara 1985).

The calculations of the standard deviation σ were experimentally checked (Nguyen et al. 1984a) with chlorides of n.c.a. radiolanthanides. The reactant gas was an $\text{H}_2 + \text{HCl}$ (1:1) mixture thoroughly purified of O_2 and H_2O . The starting temperature was 1,373 K. The thermochemical quartz column with the inner diameter of 1.25 mm was thoroughly cleaned and treated with the reactant gas at the starting temperature of 1,373 K. The experiments lasted for 1 h and volatilization of the chlorides was 95% in 2 min, i.e., their injection in the column was close to the “instant” (near to δ -function) mode. The optimum gas flow rate of $0.33 \text{ cm}^3 \cdot \text{s}^{-1}$ was provided. The average value of T_a for the lanthanide (La, Ce, Nd, Sm, Eu, Gd,

Yb, Lu) chlorides was 840 K and $\sigma = 5\text{--}6.5$ K. Calculation by (53.16) for $D_0 = 0.795 \text{ cm}^2 \cdot \text{s}^{-1}$ (Bretshneider 1966) and $\Delta\overline{H}_a^0 = -200 \text{ kJ/mol}$ (B. Eichler 1976) yielded $\sigma = 8.7$ K. A slight discrepancy between experiment and theory is probably due to stronger temperature dependence of D_{gas} : the real exponent in Eq. (53.8) is not 1.5 but 1.8 (Bretshneider 1966).

Gas-thermochromatographic separation techniques found wide application in radiochemistry because here, as pointed out above, the quality of separation is much less dependent on the duration and mode of sample injection in the column than in isothermal gas chromatography. The problems arising from the effect of the size of samples as well as time and mode of their injection in ordinary isothermal gas-chromatographic columns on the separation efficiency are discussed in textbooks and monographs. This issue, however, requires particular consideration in the case of gas TC. On the basis of Eqs. (53.2) and (53.15), substance distributions along the TCC were calculated for a prolonged injection mode, in particular for cork injection (Nogare and Juvert 1962), i.e., in the most often occurring case in radiochemistry, when substances are supplied into column continuously (online operation in conjunction with a reactor or an accelerator). In these computer-aided calculations the injection profile was divided into 100 pseudo- δ -functions. The response, i.e., the distribution of the substance in the thermochemical column, was determined for each of the input models first, and all the responses were summed subsequently. The computing parameters were the same as in the calculation shown in Fig. 53.3.

Figure 53.4 displays the distribution of a substance with $\Delta\overline{H}_a^0 = -84 \text{ kJ/mol}$ via cork injection. The ordinate shows the relative concentration, namely per cent of the injected substance, over the column length corresponding to $\Delta T = 1$ K. Curves 1, 2, and 3 are for the sample injection times t_{in} equal to 0.1, 0.5, and 1.0 of the experiment time t_{exp} . The peaks, which result from the infinite number of divisions (100) of the injection profile, clearly show the motion of the substance in the TCC and the gradual compression (concentration) of the adsorption zone. For example, at the experiment period $t_{\text{exp}} = t_{\text{in}} = 100$ s the extreme right peak corresponds to the transfer time 0.5 s, the next one to 1.5 s, then to 2.5 s, 3.5 s, etc. Accordingly, at $t_{\text{exp}} = t_{\text{in}} = 10$ s the peaks (right to left) correspond to the transfer times 0.05, 0.15, 0.25 s, etc.

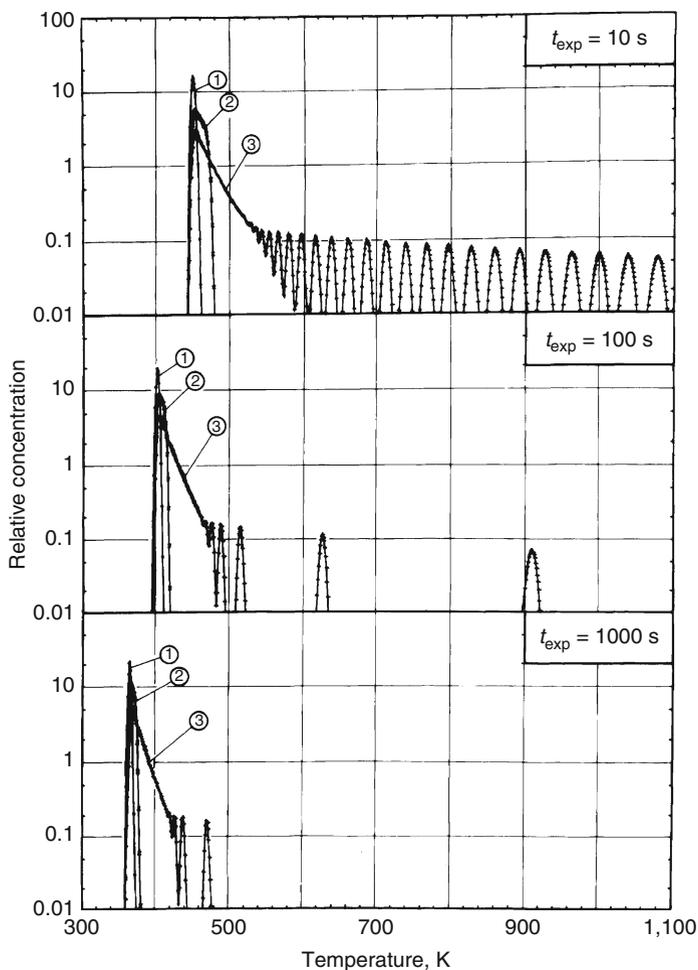
It is also illustrated, that at $t_{\text{exp}} = 10$ s and $t_{\text{in}} = 5$ s the adsorption peak is already formed 5 s after the initiation of the thermochemical process. The calculations were carried out for the optimum carrier gas flow rate (53.16). This flow rate might be appreciably larger, e.g., in the study of very short-lived radionuclides (with $T_{1/2} \approx 1\text{--}3$ s) (Zvara et al. 1998), but this will result in an increased σ , i.e., in worse separation.

The separation criteria in the case of continuous sample injection in the TCC ($t_{\text{in}} = t_{\text{exp}}$) over a period of 10, 100, and 1,000 s for two pairs of substances with $\Delta\overline{H}_a^0 = -84$ and -126 kJ/mol and $\Delta\overline{H}_a^0 = -126$ and -168 kJ/mol are 0.43, 1.05, and 2.26 and 0.84, 1.27, and 1.66, respectively. Hence, satisfactory separation of the hypothetical substances under consideration is attained as soon as after 100 s.

These theoretical considerations of the thermochemical process presume that the adsorption entropy and enthalpy do not depend on the temperature. It was also postulated that the adsorbent was homogeneous, its surface was not saturated with the adsorbate (monolayer or less), and the carrier (reagent) gas was “unsorbable.” Diffusion in the solid phase (adsorbent) and surface diffusion were ignored. Furthermore, in the theoretical considerations the effect of the carrier (reagent) gas pressure on the substance transport was not taken into account, which, however, should be considered in the case of TC at reduced reactant gas pressures and vacuum TC or with densely filled columns.

■ Fig. 53.4

Distribution of a substance in TCC for cork injection: (1) – $t_{in} = 0.1 t_{exp}$, (2) – $t_{in} = 0.5 t_{exp}$, (3) – $t_{in} = t_{exp}$. (see explanation in the text)



53.4 Systematic Experiments

Thermochemical investigations in radiochemistry deal with volatile (as a rule, at temperatures up to 1,500 K) radioactive elements or their compounds. At the above-mentioned temperatures most elements form one or more volatile compounds: hydrides, halides, oxides, sulfides, oxyhalides, hydroxides, organic derivatives, etc. Radionuclides used in TC are produced in various nuclear reactions. They are mainly fission products of uranium and transuranium elements, spallogenic products of reactions involving medium-energy particles, and radionuclides produced at accelerators of low-energy charged particles (p, d, ^3He , α) or of heavy ions (^{18}O , ^{22}Ne , ^{48}Ca , etc.). The latter occupy a prominent place in

thermochemical experiments as they are used for synthesizing atoms of new elements. The rapid development of TC was significantly due to the study and realization of the potency of this method for discovering new elements, the isotopes of which are characterized by half-lives from a few seconds to tens of seconds, too small for “usual” chemical investigations. To attain these objectives and to plan efficient work on synthesis, purification, and detection of new elements, a lot of experiments have been carried out to study the behavior of not only analogues of new elements of the periodic table but also impurity elements.

Hydrogen, air, oxygen, water vapor, halogens, hydrohalogens, CCl_4 , BBr_3 , SOCl_2 , sulfur vapor, and mixtures of some of them were used as reagent gases. The choice of the reagent gas is dictated by the conditions to be created. They must allow domination of only one volatile compound of the element under study for correct interpretation of its behavior. Most experiments were carried out with relatively long-lived radionuclides, whose volatile compounds were injected in the thermochemical column either directly from the pre-irradiated target or from a specially prepared sample. In this case the speed at which the volatile compound is supplied into the column depends on the diffusion speed in the sample and the rate of interaction with the reagent gas, and the injection profile usually has a decreasing exponential form. In some experiments volatile compounds were supplied into the TCC in a continuous mode immediately after production of the desired radionuclide in the reactor or at the accelerator.

Below, a brief review of the volatile compounds of most chemical elements at n.c.a. amounts, which were used in thermochemical experiments, will follow. The adsorption temperature was taken as the volatility criterion, which allows planning of thermochemical separations in preparative radiochemistry. As this quantity is not constant, its variation within traditional duration times of the thermochemical process (15–60 min) shall be taken into account. In addition, this variation applies to the adsorption temperatures of each component of the mixtures under separation. A particular contribution to systematic thermochemical investigations has been made by B. Eichler, who published a remarkable review of mainly his own works more than 30 years ago (B. Eichler 1976).

Group 1: The main compounds of alkali elements relevant for thermochemistry are the chlorides. B. Eichler and Malzeva (1976) separated Cs and Fr chlorides in a column filled with quartz sand is described. The adsorption temperatures T_a at a chlorine flow of $t_{\text{exp}} = 1,800$ s were 670 and 590 K, respectively. According to other authors (Rudstam and Grapengiesser 1973), T_a for NaCl and RbCl are 720 and 680 K, respectively, while Merinis and Bouissieres (1969) give a T_a for CsCl of 620 K. Alkali bromides and iodides show similar behavior. The alkali elements may also be studied in the form of metals, e.g., in vacuum thermochemical columns of high-melting metals (Hübener and Zvara 1979).

Group 2: Ca, Sr, and Ba chlorides were investigated, and their adsorption temperatures turned out to be equal to approximately 1,200 K (B. Eichler and Domanov 1974). For Ra dichloride, T_a is slightly lower (1,130 K) (Merinis et al. 1970). The thermochemical investigations of these metals are described systematically (Hübener and Zvara 1982).

Group 3: The most completely studied compounds in thermochemistry are the lanthanide and actinide chlorides. Their temperatures of adsorption on quartz are presented in [Table 53.2](#). The behavior of bromides is similar to that of the chlorides (Hickmann et al. 1993). The adsorption temperatures of La and Tb trichlorides (Kim et al. 1987b) are 30 K higher than for their tribromides. High-temperature thermochemical investigations of volatile hydroxides of hexavalent U and Pu (probably W analogues) started recently (Hübener et al. 2001). Interesting results were obtained in thermochemical studies

Table 53.2

Volatile compounds of elements of group 3 of the periodic table

Probable compound	Adsorption temperature on quartz, K	Probable compound	Adsorption temperature on quartz, K
EuCl ₂	1,180 (Nguen et al. 1984b)	AcCl ₃	1,120 (Merinis et al. 1970)
YbCl ₂	1,180 (Nguen et al. 1984b)	UCl ₃	820 (Merinis et al. 1970)
ScCl ₃	739 (B. Eichler 1976)	NpCl ₃	850 (Merinis et al. 1970)
YCl ₃	903 (B. Eichler 1976), 1,050 (Hickmann et al. 1980)	PuCl ₃	820 (Merinis et al. 1970)
LaCl ₃	920 (Merinis and Bouissieres 1969), 1,120 (B. Eichler 1976), 846 (Nguen et al. 1984a)	AmCl ₃	850, 880 (Merinis et al. 1970) 900 (B. Eichler et al. 2002) 890 (Adams et al. 1998)
CeCl ₃	893 (B. Eichler 1976), 843 (Nguen et al. 1984a)	CmCl ₃	860 (Merinis et al. 1970)
PrCl ₃	900 (Merinis and Bouissieres 1969)	BkCl ₃	820, 880 (Merinis et al. 1970) 920 (Yakushev et al. 2003)
NdCl ₃	920 (Merinis and Bouissieres 1969), 838 (Nguen et al. 1984a)	CfCl ₃	840, 860 (Merinis et al. 1970)
PmCl ₃	890 (Merinis and Bouissieres 1969)	EsCl ₃	895 (Adams et al. 1998) 920 (B. Eichler et al. 2002) <853 (Yakushev et al. 2003)
SmCl ₃	843 (Nguen et al. 1984a)	EsBr ₃	730 (Graf et al. 1999)
EuCl ₃	890 (Merinis and Bouissieres 1969), 858 (Nguen et al. 1984a)	CeCl ₄	720 (Merinis and Bouissieres 1969)
GdCl ₃	843 (Nguen et al. 1984a)	ThCl ₄	700 (Merinis et al. 1970)
TbCl ₃	790 (Merinis and Bouissieres 1969), 943 (B. Eichler 1976)	UCl ₄	630 (Merinis et al. 1970)
YbCl ₃	903 (B. Eichler 1976), 838 (Nguen et al. 1984a)	NpCl ₄	620, 640 (Merinis et al. 1970)
LuCl ₃	790 (Merinis and Bouissieres 1969), 873 (B. Eichler 1976), 835 (Nguen et al. 1984a)	PuCl ₄	640 (Merinis et al. 1970)
		BkCl ₄	<648 (Yakushev et al. 2003)
		PaCl ₅	370 (Merinis et al. 1970)
		UCl ₆	390 (Gärtner et al. 1997)

of plutonium in moist oxygen (Domanov et al. 2002). Observed adsorption zones with $T_a \approx 720, 520, 400,$ and 170 K were attributed to plutonium compounds $\text{PuO}_2, \text{PuO}_3, \text{PuO}_x(\text{OH})_y,$ and $\text{PuO}_4,$ respectively.

The study of metals or lanthanide and actinide suboxides using thermochemical columns of high-melting metals (Ti, Zr, Ta, Mo, W) is particularly promising. The experiments were carried out in vacuum (Beyer and Novgorodov 1976) or in inert helium atmosphere with Na and Ca vapor added as a reducing agent (Hübener and Zvara 1979). Adsorption of metals on metal surfaces was heretically treated (Roßbach and Eichler 1984), with both the adsorption enthalpy and entropy calculated for 63 adsorbates on 22 adsorbents. Lanthanide (B. Eichler et al. 1985b) and actinide (B. Eichler et al. 1985a) adsorbates were considered analogously. The

potential of vacuum thermochemistry for the separation of lanthanides was demonstrated (Beyer and Novgorodov 1976), where Lu, Yb, and Tm as well as Gd, Eu, and Sm were satisfactorily separated in a tantalum column with no more than 50 theoretical plates. Particularly noteworthy are the experiments with the excellent separation of Cf–Md achieved in a molybdenum TCC (Hübener and Zvara 1982), and Cm–Bk in a niobium TCC (Taut et al. 2000). The behavior of heavy actinides in TCC made of Ti, V, Nb, and Ta has been studied by Taut et al. (1998, 2001).

Group 4: The thermochemical behavior of the elements of this group received special consideration because they are assumed to be lighter analogues of the first transactinide element 104 (Rf). Zr and Hf chlorides and bromides have been studied carefully, but the results were extremely discrepant. While in early investigations the adsorption temperature of the Ti, Zr, and Hf tetrachlorides was found to be 438, 463, and 453 K, respectively (B. Eichler 1976), parallel investigation of T_a for the Zr and Hf tetrachlorides yielded 393 and 373 K, respectively (Kim et al. 1987b). Evidently, the uncontrolled oxygen content of the reactant gas led to very high T_a for ZrCl₄, e.g., 550 K (Bayar et al. 1978a) and even 840 K (Hickmann et al. 1993). This effect was carefully studied (Domanov and Kim 1988; Domanov et al. 1988), who assumed existence of volatile oxychlorides ZrOCl₂ and HfOCl₂, thermally stable in the gas up to the temperature of approximately 700 K. Their T_a values are slightly higher than the T_a of the analogue tetrachlorides (383 and 373 K) and are equal to 423 K (for ZrOCl₂ and HfOCl₂). The behavior of hafnium and zirconium bromides is similar to chlorides. Thermochemistry of Hf and Zr chlorides and bromides have also been performed in columns filled with NaCl, KCl, CsCl, and KBr. The T_a increase considerably (to about 850 K) because of chemical interaction resulting in formation of compounds like (Na,K,Cs)₂(Zr,Hf)(Cl,Br)₆ (Tsalas and Bächmann 1978; Kim et al. 1987a). Stability of these compounds increases in the series Na→Cs.

Group 5: Elements of this group form two well-known types of volatile compounds: halides and oxyhalides. Noteworthy vanadium compounds are VCl₄ (or VOCl₃) with $T_a = 298$ K (B. Eichler and Domanov 1974) and VCl₃ (or VCl₂) with $T_a = 684$ K (Novgorodov et al. 1986a). The adsorption temperatures of Nb and Ta pentachlorides on quartz were found to be 410 and 770 K, respectively (B. Eichler and Domanov 1974). The value of T_a for tantalum is unexplainably overestimated. This is confirmed by the fact that the adsorption temperatures for pentabromides of the two elements are similar and are equal to approximately 330 K (Belov et al. 1974; Zvara et al. 1975). Carefully performed experiments (Domanov and Kim 1988) yielded close T_a values for Nb pentachloride and oxychloride on quartz, 333 and 373 K, respectively. The adsorption temperatures of Nb and Ta pentachlorides in the columns filled with KCl and CsCl increase to approximately 530 and 660 K for the respective adsorbents, which is due to formation of compounds like (K,Cs)(Nb,Ta)Cl₆ (Tsalas and Bächmann 1978).

Group 6: High-melting elements of this group form a variety of volatile compounds whose adsorption temperatures on quartz are listed in [Table 53.3](#). It is, however, difficult to interpret the composition and properties of oxychlorides because of their close T_a values. In TCC filled with KCl or CsCl, molybdenum chloride forms two approximately equal peaks at $T_a = 533$ and 453 K or 653 and 573 K, respectively (Tsalas and Bächmann 1978).

Group 7: The main volatile compounds formed by the elements of this group are halides, oxides, oxyhalides, and hydroxides. [Table 53.4](#) shows that many experiments have been carried out, there is a large difference between the adsorption temperatures of the compounds as, for example, ReO₃ and HReO₄.

Table 53.3

Volatile compounds of elements of group 6 of the periodic table

Probable compound	Adsorption temperature on quartz, K
CrCl ₂	883 (Novgorodov et al. 1986a)
CrCl ₄ (CrO ₂ Cl ₂)	293 (B. Eichler and Domanov 1974)
MoBr ₄	370 (Hickmann et al. 1993), 370 (Belov et al. 1974)
MoJ ₄	680 (Hickmann et al. 1993)
MoCl ₅	358 (B. Eichler and Domanov 1974), 290 (Hickmann et al. 1993), 353 (Helas et al. 1978), 360 (Bayar et al. 1978d), 323 (Chuburkov et al. 1996)
MoOCl ₃	413 (Helas et al. 1978), 378 (Chuburkov et al. 1996)
MoOCl ₄	<300 (Helas et al. 1978), 373 (Bayar et al. 1978d), 310 (Chuburkov et al. 1996)
MoO ₂ Cl ₂	320 (Bayar et al. 1978d), 330 (Helas et al. 1978), 340 (Chuburkov et al. 1996) <440 (Türler et al. 1996)
MoO ₃	1,260 (B. Eichler 1976)
H ₂ MoO ₄	623 (Helas et al. 1978) 700 (Vahle et al. 1995) 650 (Vahle et al. 1997)
WCl ₆	353 (B. Eichler and Domanov 1974), 448 (Helas et al. 1978)
WOCl ₄	328 (Helas et al. 1978), 400 (Belov et al. 1972), 373 (Chuburkov et al. 1996)
WO ₂ Cl ₂	448 (Helas et al. 1978), 570 (Belov et al. 1972), 423 (Chuburkov et al. 1996), 423 (Yakushev et al. 1993)
WO ₃	>1,300 (Bayar et al. 1975)
H ₂ WO ₄	830 (Bayar et al. 1975), 650 (Vahle et al. 1999)

The adsorption temperatures of Tc and Re chlorides in the columns filled with KCl or CsCl increase to 813 or 873 K and to 613 or 643 K, respectively (Tsalas and Bächmann 1978). When Mg and Ca oxides were used as adsorbents (Zhuikov 1982a), this leads to a considerable increase in the adsorption temperatures. These solid phases very likely might be considered as effective filters in preparative radiochemistry.

■ **Table 53.4**

Volatile compounds of elements of group 7 of the periodic table

Probable compound	Adsorption temperature on quartz, K
MnCl ₂	773 (Novgorodov et al. 1986a), 733 (Kim et al. 1987b)
TcCl ₄	320 (Hickmann et al. 1993)
TcCl ₅	408 (B. Eichler and Domanov 1974)
TcBr _x	430 (Hickmann et al. 1993)
ReCl ₅	283 (Merinis and Bouissieres 1969), 313 (B. Eichler and Domanov 1974)
ReO	1,300 (Adilbish et al. 1977)
TcO ₂	~1,000 (Steffen and Bächmann 1978a) , ~1,000 (Steffen and Bächmann 1978b)
TcO ₃	470 (Steffen and Bächmann 1978b), 610–730 (B. Eichler and Domanov 1975), ~750 (Häfeli et al. 2000)
ReO ₂	950 (Bayar et al. 1973), 900 (Adilbish et al. 1977)
ReO ₃	670 (Merinis and Bouissieres 1961), 813 (Steffen and Bächmann 1978b), 823 (R. Eichler et al. 1999), 660 (Bayar et al. 1974), 593 (Bayar et al. 1973), 653 (Bayar et al. 1974), 423, 673, 783 (Bayar et al. 1978b), 780, 870 (B. Eichler and Domanov 1975), 663 (Domanov et al. 1981)
HTcO ₄	483 (Bächmann et al. 1976), 588 (Steffen and Bächmann 1978b), ~350 (Häfeli et al. 2000)
HReO ₄	373 (Bayar et al. 1978b), 503 (Bächmann et al. 1976), 390 (Zvara et al. 1982), 346 (R. Eichler et al. 1999), 620 (Steffen and Bächmann 1978b), 443 (Bayar et al. 1975), 353 (Bayar et al. 1978b), 353 (Domanov et al. 1981), 243 (B. Eichler and Domanov 1975), 375 (B. Eichler et al. 1999)

Group 8: Interest in this group of elements arises first of all from the existence of very volatile osmium tetroxide, with osmium being an analogue of element 108 (Hs). ▶ [Table 53.5](#) presents absorption temperatures for various volatile compounds of group 8 elements. The T_a value of Ru and Os chlorides on KCl or CsCl surfaces is 873 K (Tsalas and Bächmann 1978). Osmium tetroxide adsorbs on a CaO surface at 733 K (Zhuikov 1982a).

Table 53.5

Volatile compounds of elements of group 8 of the periodic table

Probable compound	Adsorption temperature on quartz, K
FeCl ₂	677 (Novgorodov et al. 1986a)
FeCl ₃	433 (Merinis and Bouissieres 1969), 433 (B. Eichler and Domanov 1974)
RuCl ₄	583 (B. Eichler and Domanov 1974), 708 (Davydov 1973)
OsCl ₄	333 (Merinis and Bouissieres 1969), 333 (Merinis and Bouissieres 1961), 393 (B. Eichler and Domanov 1974)
OsO	1,250 (Adilbish et al. 1977)
RuO ₂	1,430 (B. Eichler et al. 1992), 1,270 (Adilbish et al. 1979)
RuO ₃	600, 690, 730 (B. Eichler and Domanov 1975), 563 (Steffen and Bächmann 1978b), 625 (B. Eichler et al. 1992), 833 (Adilbish et al. 1979), 398 (Domanov and Zvara 1983), 580 (Düllmann et al. 1999)
OsO ₃	373 (Adilbish et al. 1977)
RuO ₄	453 (Steffen and Bächmann 1978b), 241 (B. Eichler et al. 1992)
OsO ₄	173 (Domanov and Zvara 1983), <298 (Steffen and Bächmann 1978b), <293 (Bayar et al. 1974), <191 (Düllmann et al. 2002)
RuO _x Cl _y	438 (Bayar et al. 1978e)

Group 9: The behavior of chlorides, oxides, and hydroxides of the elements from this group has been studied in thermochemical experiments (► Table 53.6). It is, however, very difficult to interpret the composition of these compounds, as is evident, for example, from T_a values for IrO₃ and H₂IrO₄.

Group 10: Elements of this group form relatively volatile dichlorides, the adsorption temperatures of which on quartz are 763, 863, and 803 K for NiCl₂, PdCl₂, and PtCl₂, respectively (B. Eichler and Domanov 1974). For the latter compound values of 543 and 663 K are (Merinis and Bouissieres 1969; Merinis and Bouissieres 1961), which is probably due to the presence of macro amounts of more volatile gold chloride. Compounds with oxygen are known only for platinum (Domanov et al. 1982; Domanov and Zvara 1983). The adsorption temperatures on quartz for PtO₂, PtO₃, and “platinum acid” PtO_x(OH)_y are estimated to be 573, 373, and 293 K, respectively. According to a later work (Zude et al. 1993), the adsorption temperatures of Pt on quartz in a flow of dry and humid air are 535 and 550 K, respectively.

■ Table 53.6

Volatile compounds of elements of group 9 of the periodic table

Probable compound	Adsorption temperature on quartz, K
CoCl ₂	771 (Novgorodov et al. 1986a), 658 (B. Eichler et al. 1976), 653 (Rudstam and Grapengiesser 1973)
RhCl ₃	883 (B. Eichler et al. 1976)
IrCl ₄	848 (Merinis and Bouissieres 1961), 823 (Merinis and Bouissieres 1969), 1,008 (B. Eichler and Domanov 1974)
IrO ₂	673 (Steffen and Bächmann 1978b)
RhO ₃	373 (Domanov and Zvara 1983)
IrO ₃	530 (B. Eichler and Domanov 1975), 523 (Domanov et al. 1982), 353 (Domanov and Zvara 1983), 493 (Steffen and Bächmann 1978b), 520 (B. Eichler et al. 1993)
H ₂ IrO ₄	433 (Domanov et al. 1982), 288 (Domanov and Zvara 1983), 580 (B. Eichler et al. 1993)

The high volatility of “platinum acid” arouses special interest and calls for further investigations. In addition, Pt forms thermochemically promising volatile carbonyl halogenides (Herrmann and Denschlag 1969).

Group 11: In this group of elements it is difficult to identify a single type of compound, which could be used in systematic investigations. The most stable valence states for Cu, Ag, and Au are +2, +1, and +3. The most volatile compound is gold trichloride with the adsorption temperature on quartz of approximately 463 K (Merinis and Bouissieres 1961). Silver chloride is reported with $T_a = 893$ K (B. Eichler and Domanov 1974) or 823 K (Rudstam and Grapengiesser 1973). Behavior of elemental Ag and Au was investigated and their adsorption temperatures were found to be very high, 1,133 and 1,403 K (B. Eichler 1976), respectively. Volatile sulfides show more promise in this group – the adsorption temperatures of ¹⁹⁵Au and ¹¹¹Ag sulfides in a sulfur vapor flow were found to be 770 and 650 K, respectively (Korotkin et al. 1988).

Group 12: Elements of this group are among the most intensively ones studied. T_a of quartz for Zn, Cd, and Hg are approximately 660, 600, and 300 K, respectively (B. Eichler 1976). The adsorption temperatures for their chlorides are also relatively low: 580, 630, and 350 K, respectively (B. Eichler 1976). Sulfide adsorption temperatures are slightly higher, namely 830 and 880 K for ZnS and CdS (Korotkin et al. 1988). Mercury sulfide, like mercury oxide, is unstable at high temperature and shows the behavior of the element. With copper or nickel used as adsorbents, T_a sharply increases (approximately 1,000 K) only for zinc (B. Eichler 1976). The adsorption temperatures of Zn, Cd, and Hg on quartz surface in vacuum are about 1.5 lower than in a hydrogen atmosphere: 460, 350, and 200 K, respectively (B. Eichler 1976). Adsorption of Hg on different surfaces (Cu, Ag, Au, Ni, Pd, Pt) has been studied by Niklaus et al. (2003).

Group 13: Adsorption temperatures for elements of this group on quartz surface in a hydrogen atmosphere are quite low: 830, 580, and 610 K for Ga, In, and Tl, respectively (B. Eichler 1976). Strong absorption on copper and nickel surfaces is observed only for Ga (B. Eichler 1976), as in the case of Zn (see above). In vacuum, T_a on quartz is slightly lower: 455 K for In and 420 K for Tl. For chlorides, T_a on quartz is 610 K for In and 440 K for Tl (B. Eichler 1976). At low (0.7–7.0 Pa) pressures of HCl and H₂O gas mixtures, absorption peaks are found which correspond to InOCl, InCl, and InCl₃ with $T_a = 655, 475,$ and 385 K, respectively (Novgorodov et al. 1986b). For InCl₃, a value of $T_a = 313$ K was found (Rudstam and Grapengiesser 1973). Thallium reveals increased volatility in the oxygen atmosphere; the adsorption temperature is approximately 500 K (Bayar et al. 1978c). An interesting observation is the volatility of thallium micro amounts in sulfur vapor; the adsorption temperature is 450 K (Kim et al. 1988). An even more unexpected result was obtained in thermochemical experiments at a reduced HF vapor pressure. The adsorption temperatures of Ga, In, and Tl monofluorides or oxyfluorides were 460, 350, and 340 K, respectively (Novgorodov et al. 1987a, b, 1988).

Group 14: The best-studied compounds among the group 14 elements are Ge, Sn, and Pb dichlorides. Their absorption temperatures on quartz are 840, 590 (Rudstam and Grapengiesser 1973), and 588 K (B. Eichler and Domanov 1974). For the highly volatile GeCl₄ and SnCl₄, T_a is estimated to be approximately 300 K (B. Eichler and Domanov 1974). The metals show low volatility, their adsorption temperatures on quartz in a hydrogen flow are 1,050, 1,060, and 780 K for Ge, Sn, and Pb, respectively (B. Eichler 1978). The effect of the carrier gas on Pb adsorption is shown: its adsorption temperature is 950 K in an argon gas flow compared to 730 K in a hydrogen gas flow (Fan and Gaggeler 1982). Adsorption of these elements in metallic TCC (Ni, Mo, Au) is also strong, and T_a varies from 900 to 1,200 K (B. Eichler 1978). Tetravalent lead may form highly volatile tetraalkyl (methyl-, ethyl-) compounds, which might be considered in thermochemistry.

Group 15: As, Sb, and Bi trichlorides are adsorbed on quartz at 300, 330, and 420 K, respectively (B. Eichler and Domanov 1974). A similar adsorption temperature (300 K) was found for SbCl₃ (Hickmann et al. 1993). The adsorption temperature of antimony pentachloride was only mentioned (Rudstam and Grapengiesser 1973), and T_a for SbCl₃ and SbCl₅ were found to be 840 and 590 K, respectively. The T_a for BiOCl was found to be 580 K (R. Eichler et al. 2000). TC of the elements in the form of metals yields similar values of $T_a \approx 830$ K on quartz surfaces for all three elements (B. Eichler 1976). If copper or nickel is used as an adsorbent instead of quartz, the As- and Bi-adsorption temperatures increase to approximately 1,100 K (B. Eichler 1976). Ultramicro amounts of Bi show interesting behavior in sulfur vapor: T_a on quartz is 590 K (Korotkin et al. 1988). For BiO(OH) hydroxide a $T_a \approx 770$ K was observed (R. Eichler et al. 1999).

Group 16: The data on the thermochemical behavior of the elements from this group are difficult to systematize. Tellurium and polonium in the elemental state are adsorbed on quartz in hydrogen flow at $T_a \approx 730$ and 520 K, respectively; and in vacuum at 575 and 370 (B. Eichler 1976). With copper and nickel used as adsorbents, T_a significantly increases, reaching 1,088 K for Se(Ni), 823 K for Po(Cu), and 943 K for Po(Ni) (B. Eichler 1976). Polonium adsorption on various surfaces under isothermal conditions is considered (Gaggeler et al. 1985), where it was found to be very strongly adsorbed on the palladium surface ($T_a > 1,300$ K). Volatile Te and Po tetrachlorides are adsorbed on quartz at $T_a = 448$ and 563 K (B. Eichler and Domanov 1974); a value of T_a for PoCl₄ was reported to be 450 K (Gärtner et al. 1999). A similar value for TeCl₄ ($T_a = 450$ K) was obtained (Hickmann et al. 1993),

where T_a for tellurium tetrabromide and tetraiodide are also given, which are 560 and 480 K. With KCl and CsCl used as adsorbents, tellurium tetrachloride adsorbs at $T_a = 473$ and 713 K, respectively (Tsalas and Bächmann 1978). For PoOCl_2 , the T_a value was determined to be 320 K (R. Eichler et al. 2000) or 530 K (Gärtner et al. 1999). Adsorption of TeO_2 on quartz at approximately 900 K was also mentioned (B. Eichler 1976).

Group 17: All halogens and interhalogens are highly volatile. Their temperatures of adsorption on quartz lie within the range from 241 to 473 K (Merinis et al. 1972). Interestingly, monatomic iodine is adsorbed at 473 K, while molecular iodine is adsorbed at 268 K. Compounds of Br, I, and At with oxygen in air flow have $T_a = 273$, 263, and 280 K (B. Eichler and Domanov 1975). For compounds of iodine with oxygen (IO_x) a value of $T_a = 573$ K is given (Rudstam and Grapengiesser 1973). The adsorption temperatures of iodine and astatine on quartz in vacuum (B. Eichler 1977) are 275 and 230 K. With various metals used as adsorbents, T_a substantially increases because of formation of more stable chemical compounds. For example, the adsorption temperatures of iodine and astatine on silver are very different, 1,200 and 663 K, respectively. Bromine and iodine adsorb on the platinum adsorbent at 873 and 798 K (Rudstam and Grapengiesser 1973). The adsorption temperature of astatine on the Pd surface is 515 K (B. Eichler and Chun 1985).

Group 18: There is no study on the adsorption of noble gases in open thermochemical quartz columns available because of the difficult set-up for adequate experiments. It is safe to suggest that the Xe adsorption temperature should be below 100 K (B. Eichler et al. 1995). With palladium as an adsorbent, Rn was adsorbed at 168 K (B. Eichler and Chun 1985). This indicates that elements of this group must be purified of all other elements to a very high degree.

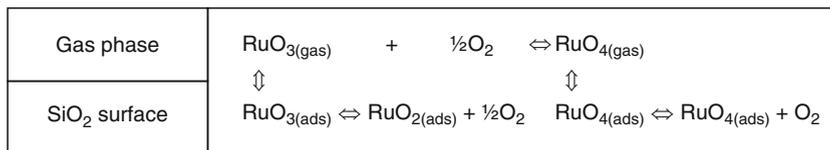
The brief review of volatile compounds of the elements of the periodic table used in thermochemical experiments in some cases reveals discordance of adsorption temperatures. This inconsistency, sometimes quite substantial, is probably due to incorrect experimental condition and interpretation which results first of all from the following:

- Insufficient purification of the carrier (reactant) gas
- Inadequate purification of the adsorbent
- Variation in the chemical form of substances injected in the starting zone of thermochemical columns for formation of volatile compounds
- Limited information on the kinetics of formation and dissociation of volatile compounds
- Variation in the sample injection profile (“online” or “off-line” experiments)
- Some above-mentioned variation in the period of experiments

Naturally, most investigators studied or took into account the effect of these factors on the adsorption temperature, though not fully and accurately, perhaps. Most important for the accurate characterization of volatile compounds and their T_a are, in the authors' opinion, experiments with various pure reactant gases or their mixtures (Domanov and Kim 1988; Domanov et al. 1988; Nguen et al. 1984a), with significantly different periods of duration of the TC experiments (Fan and Gäggeler 1982), and with different initial starting compounds (Chuburkov et al. 1996; Steffen and Bächmann 1978b). These approaches will be adequate, when compounds, transferred through the TCC, are chemically stable both in the gas phase and on the surface of the adsorbent. The picture considerably complicates if the transfer of the substance under study is accompanied by chemical reactions resulting in decomposition and formation of the initial and secondary volatile compounds on the surface of the adsorbent. This is most conspicuous in the case of polyvalent elements of groups 6–9. For example, the

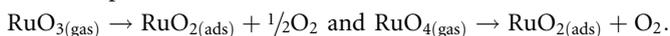
Fig. 53.5

Dissociative character of ruthenium oxide adsorption on the SiO₂ surface



scheme on Fig. 53.5 is accepted for transfer of ruthenium compounds with oxygen (Steffen and Bächmann 1978a).

Developing this assumption, B. Eichler et al. (1992) determined the enthalpy and entropy of the dissociative adsorption for the reactions



Thorough investigation of noncarrier-added amounts of ^{183,184}Re in dry and humid oxygen allowed (R. Eichler et al. 1999) to conclude that there was no volatile ReO₂ in the temperature range considered (up to 1,400 K) and that the peaks previously ascribed by other authors to ReO₂, ReO₃, and HReO₄ actually corresponded only to the latter two compounds formed in different ways.

Far more complications arise when volatile Mo and W oxychlorides are dealt with. Even in pure chlorinating reactant gases, tetra-, penta-, and hexavalent states of Mo and W may exist in the form of not only chlorides but also oxychlorides due to chemical reactions involving the adsorbent (SiO₂). In these complicated cases useful information can be probably gained in thermochemical experiments at reduced reactant gas pressures (about 0.1 Pa) (Adilbish et al. 1977), i.e., when the stepped nature of formation of volatile oxidation products is particularly conspicuous. It should be mentioned that the volatility of monomeric molecules, such as MoO₃, PdCl₂, FeCl₃, RhCl₃, is very small. Experimental values of *T_a* for these compounds most probably correspond to their polymer species such as (MoO₃)₃, (PdCl₂)₅, (FeCl₃)₂, etc.

53.5 Preparative Radiochemistry

The rapid development of thermochemistry in the 1960–1970s was stimulated first of all by the desire of researchers to discover new short-lived radionuclides and to investigate their nuclear-physical and chemical properties. Various methods for fast chemical separation in both liquid and gaseous phases were described in a review (Herrmann and Denschlag 1969), allowing investigation of radionuclides with half-lives of about 1 s. New radionuclides produced at reactors (neutron-rich radionuclides) and at medium-energy particle accelerators (neutron-deficient radionuclides) have been discovered and investigated. For gas chemistry, chemically stable substances were utilized as targets, from which the produced radionuclides were transferred under controllable conditions into known volatile compounds for their subsequent thermochemical separation. The most comprehensively studied targets were UF₄ (Weber et al. 1971), U₃O₈ (Röder and Herrmann 1966; Wolf 1973), AgCl (Novgorodov 1982), Au (Adilbish et al. 1977; Bayar et al. 1974), and others. The most widely used source of neutron-rich radionuclides was ²⁵²Cf (Bögl and Bächmann 1975).

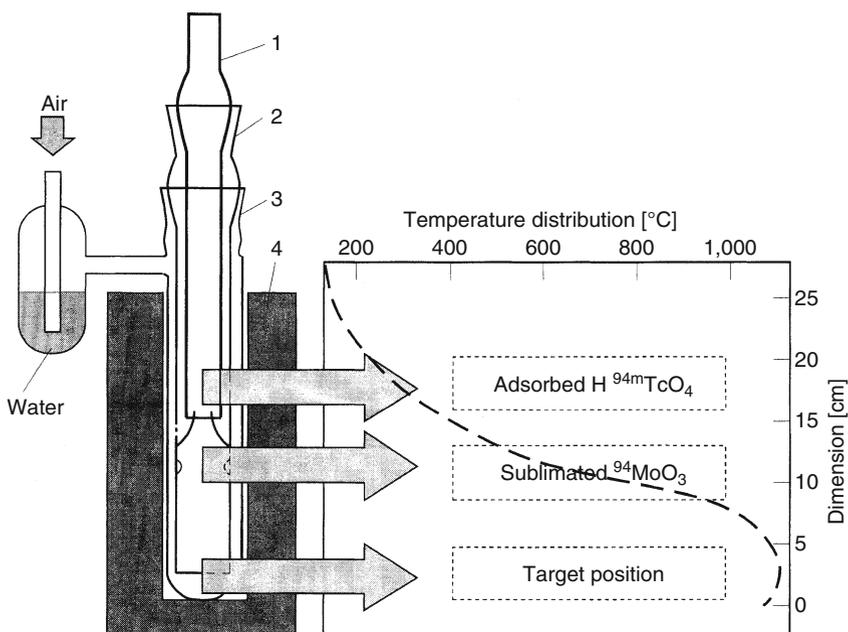
TC remained advantageous for these investigations until the advent of ISOL (isotope separator online) facilities operating online with reactors or medium-energy accelerators (Talbert 1970). Radioisotopes of known elements with half-lives well below 1 s (^{11}Li , ^{35}Na , ^{74}Rb , ^{150}Lu , Hg isotopes, and others) were discovered and investigated at these facilities with targets composed of metal melts or finely dispersed powder (Beyer et al. 1989). The tubular connection of the target to the ion source may in principle be regarded as a TCC.

Consideration was also given to potentialities of TC for separation and concentration of relatively large amounts of radionuclides used in science and technology (Khalkin et al. 1979). The data given in ▶ Sect. 53.4 of this review described conditions of thermochemical separations to be selected for virtually any target-product pair. This may be distillation of macro amounts of the target elements, e.g., Zn (Novgorodov et al. 1990), Cd, and Hg (B. Eichler and Domanov 1974) in vacuum or Au via chlorination (Merinis and Bouissieres 1961). Of interest is scenario in which the irradiated target is burnt in the reactant gas (O_2 , Cl_2 , and others) with the formation of a nonvolatile residue, while the nuclear reaction product is transferred by the gas flow further to the TCC (Bayar et al. 1978b; Vakhtel et al. 1976). These separations were usually carried out in a horizontal apparatus similar to that displayed in ▶ Fig. 53.1, but recently the vertical arrangement of the TCC is believed to be more rational (Rösch et al. 1994) (▶ Fig. 53.6).

This arrangement greatly decreases the carry-away of gaseous products against the direction of incoming reactant gas flow and allows the process to be easily automated. The target is

■ Fig. 53.6

Apparatus for routine separation of $^{94\text{m}}\text{Tc}$ from irradiated ^{94}Mo targets: (1) – TCC-inner quartz tube for adsorption of $^{94\text{m}}\text{Tc}$; (2) – middle quartz tube for condensation of $^{94}\text{MoO}_3$; (3) – outer quartz tube; (4) – electric resistance oven (Rösch et al. 1994)



loaded in bottom of the open apparatus, the apparatus is closed using inserted smaller quartz tubes, the reactant gas is passed through it, and then the assembly is placed in the vertical oven with the required temperature distribution. After the termination of the separation process the assembly is taken out of the oven, cooled, and from it the inner TCC is removed with the adsorbed product, which can be washed off with a minimum volume of an appropriate solution. This apparatus, first developed to separate the positron emitter ^{94m}Tc from the irradiated molybdenum oxide in 25 min (Röscher et al. 1994), was subsequently used more universally for separations of the systems $^{110}\text{Sn}/^{111}\text{In}$ (Röscher et al. 1997), $^{186}\text{W}/^{186}\text{Re}$, $^{188}\text{W}/^{188}\text{Re}$ (Novgorodov et al. 2000), and $^{72}\text{Se}/^{72}\text{As}$ (Novgorodov et al. 2001).

Multiple use of the target material, when separation of nuclear reaction products does not entail changes in its chemical composition, holds the greatest promise for production of some radionuclides. ▶ [Table 53.7](#) presents examples of using such targets for producing radionuclides relevant for nuclear medicine. The ^{67}Ga , ^{111}In , and ^{201}Tl separation procedure consists in merely heating massive targets at controllable pressure of the reactant gas. The target material loss does not exceed 0.1% in one cycle of radiochemical separation, but it is easily restored after 20–30 target irradiation-radionuclide separation cycles. In addition, multiple use of the target material gradually leads to a high specific activity of the produced radioactive samples due to periodic separation of impurities. Moreover, the use of gaseous reactants at lowered pressure (1–10 Pa) allowed the application of the thermochemical columns for ISOL setups (*Isotope Online Separations*) as a chemical transport between target and mass separators, cf. ▶ [Table 53.7](#) and Adilbish et al. (1977, 1979).

It should be noted that thermochemistry might be used for construction of generator systems (B. Eichler 1976). By now the parent–daughter radionuclide pairs $^{188}\text{W}/^{188}\text{Re}$ (Novgorodov et al. 2000) and $^{72}\text{Se}/^{72}\text{As}$ (Novgorodov et al. 2001) have been comprehensively studied.

53.6 Investigation of New Transactinide Elements

Thermochemistry entered into wide use for the identification of new elements due to the assumption that transactinide elements ($Z = 104–118$) belong to groups 4–18 of the periodic table, where lighter homologues are known to form volatile compounds. The crucial

■ [Table 53.7](#)

Separation of medical radionuclides from massive targets

Radionuclide	Target	Reaction	Separation conditions	References
^{67}Ga	^{70}Ge	(p,xpyn)	1,375 K, (HF+H ₂ O 1:1), 1.5 Pa	(Novgorodov et al. 1988)
^{111}In	Ag	(α ,2n)	1,150 K, (HCl+H ₂ O 10:1), 7 Pa	(Schomächer et al. 1988) (Novgorodov et al. 1986b)
^{111}In	^{112}Sn	(γ ,n)EC	1,225 K, (HF+H ₂ O 1:1), 0.4 Pa	(Novgorodov et al. 1987a)
^{201}Tl	$^{204,206,208}\text{Pb}$	(p,xn)EC, EC	825 K, (HF+H ₂ O 1:1), 0.4 Pa	(Novgorodov et al. 1987b)

feature of the method was its “high speed,” i.e., the time needed to transfer accelerator-produced atoms of the elements under study from the target to the detectors, which was a few tenths of a second, according to various estimates (Belov et al. 1974). Chemical studies of new elements is an extreme challenge, because the lifetime – even of comparatively long-lived ones of their isotopes – is of the order of a few seconds or tens of seconds only and the rate of their production at modern accelerators is very low (an atom per a few hours or even days). Other problems are laborious measurements of decay events and incomplete knowledge of the decay properties (half-lives, ratios of spontaneous fission, alpha decay, and electron capture), though chemical identification is normally preceded by elaborate physics experiments on determining the yield of the desired isotope of the new element, its decay mode, and half-life. The experiments are carried out with varying combinations of target nuclei and accelerated ions, the energies of which also vary. To achieve a high yield of the desired isotope of the new element, neutron-rich isotopes of both the target and the accelerated ion are used, e.g., ^{238}U , ^{244}Pu , ^{248}Cm and ^{18}O , ^{22}Ne , ^{26}Mg , ^{48}Ca , respectively. Using accelerated ions of neutron-rich radionuclides like ^{90}Kr , ^{132}Sn , or ^{140}Xe has been suggested, but not reported for the production of the heaviest elements so far.

During the experimental studies of chemical properties of transactinides early approaches exploited the possibility to detect spontaneous fission in thermochemical columns by mica or quartz track detectors at temperatures below 400°C, while more modern setups employ Si detectors to register α decay or spontaneous fission at room temperature and below (liquid nitrogen). Then, the technique, however, is limited to the study of highly volatile atoms or compounds.

The history of discovery of the first transactinide elements is closely associated with the rivalry for priority of their discovery and identification and with mutual criticism of the researchers (Flerov and Zvara 1971; Hyde et al. 1987; Flerov and Ter-Akopian 1987). Now these matters are no longer acute owing to establishment and joint work of international collaborations.

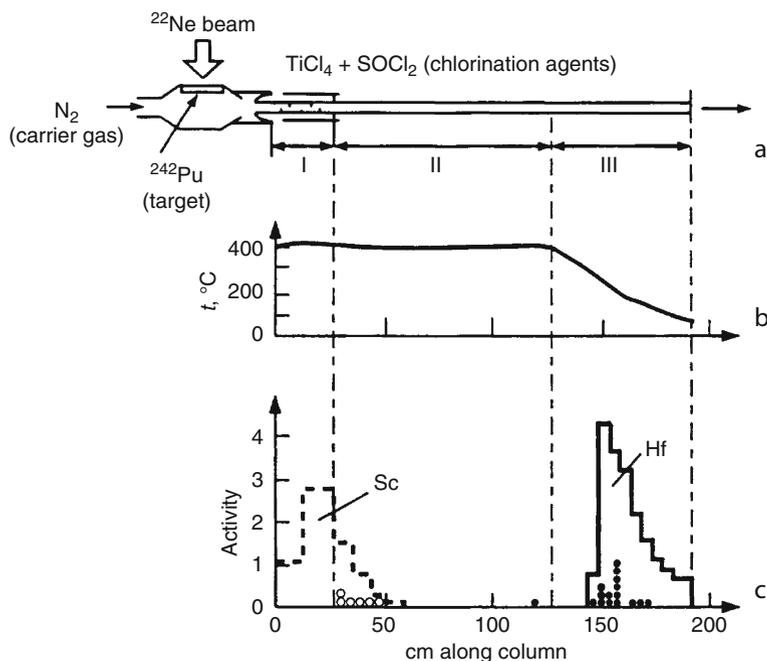
On the assumption of analogy between transactinide elements and group 4–18 elements halides, oxyhalides, and oxides of the first transactinide elements were expected to have increased volatility, which might allow good selectivity of their separation and concentration by gas chemistry methods (IC and TC). The first identifications of Rf (element 104) were carried out by isothermal chromatography of its most volatile compound, the chloride (Zvara et al. 1969a, b; Chuburkov et al. 1969). It was shown that the behavior of Rf chloride was analogous to the behavior of Hf tetrachloride. Thermochemistry was first used in investigations of transactinide elements in 1971 (Zvara et al. 1971). ▶ [Figure 53.7](#) shows a schematic diagram of the apparatus used and the results obtained, i.e., the distribution of spontaneous fission events.

The measured distribution of decay events over the thermochemical column is a basis for evaluating the adsorption enthalpy ΔH_a^0 . Evaluation of ΔH_a^0 for a single decay event is performed by the method proposed by Zvara (1985), who developed a microscopic model of TC. On its basis the migratory process of individual atoms in the column is simulated by the Monte Carlo method with allowance made for their radioactive decay.

Similar setups were used to study chemical properties of volatile compounds of elements 105–108 (Db, Sg, Bh, Hs) at different laboratories. Recently, a monograph (Zvara 2008) in detail covered theoretical considerations related to the thermochemical behavior of single atoms of transactinide elements. A remarkable contribution (Türler 1999) most

Fig. 53.7

(a) Schematic of the experimental apparatus to investigate the volatility of ^{259}Rf and $^{170,171}\text{Hf}$ chlorides; (b) temperature profile in the column; (c) distribution of spontaneous fission tracks (circles) and distribution of γ -activity $^{44\text{m}}\text{Sc}$, $^{170,171}\text{Hf}$ (lines) (reproduced with permission from Dissertation B., Türler 1999)



comprehensively describes gas chemistry of halides of the first two transactinides, Rf and Db, and oxychlorides of the third one, Sg. Sg was shown to form volatile oxychlorides (Schädel et al. 1998; Türler et al. 1999) as well as oxyhydroxides (Hübener et al. 2001). Considering the high volatility of rhenium hydroxide HReO_4 , many researchers (Belov et al. 1972; B. Eichler 1976) planned to use and used (Zvara et al. 1984) an analogous compound for the identification of element 107 (Bh). However, HReO_4 turned out to partially decompose in the TCC at a temperature of about 600 K (R. Eichler et al. 1999) with formation of ReO_3 . Evidently, this is why Bh was chemical identified with its oxychloride BhO_3Cl (R. Eichler et al. 2000b), though under isothermal conditions. High volatility of HsO_4 , expected in analogy to OsO_4 , has motivated the development of thermochemistry setups where the TCC consists of detectors suitable for the registration of α -particles and fission fragments emitted by species adsorbed within the TCC (Kirbach et al. 2002). This technique has first been used to compare adsorption of OsO_4 and HsO_4 (Düllmann et al. 2002). It appears that the volatility of HsO_4 , though high, is somewhat lower than that of OsO_4 . This highly efficient radiochemical separation technique has since found application in studies of nuclear aspects related to the production of Hs isotopes (Dvorak et al. 2006, 2008).

The lack of isotopes with half-lives long enough for their chemical investigation of elements 109–111 (Mt, Ds, Rg) prevented chemistry experiments with these elements to date. However,

the closed-shell element 112 – for which the name *copernicium* (Cn) has recently been approved – has been the focus of a series of experiments. Following initial experiments (Yakushev et al. 2001, 2002), recent studies suggest (R. Eichler et al. 2007) that the trend in sublimation enthalpies established in group 12 by the lighter homologues is fully preserved (R. Eichler et al. 2008).

It should be noted that all experiments on the study of properties of transactinide elements aim at finding first of all the distinctions between the properties of the analogue elements under study. As for elements with high Z electrons close to the nucleus have relativistic velocities, “relativistic effects,” which are proportional to Z^2 , strongly affect their chemical properties. These effects are expected to be most pronounced in transactinide elements and their compounds. Theoretical investigations in this area (Pershina 1996) showed, for example, that elements with larger Z are more noble and more volatile (B. Eichler et al. 1995). Analogy of Rf (as a p-element) and Pb was predicted (Glebov et al. 1988), but experiments disproved the prediction (Zhuikov et al. 1989). At present the series of relative volatilities of some analogue elements or compounds have been established in ascending order:

$\text{HfCl}_4 < \text{RfCl}_4 \approx \text{ZrCl}_4$
$\text{HfBr}_4 < \text{RfBr}_4 \approx \text{ZrBr}_4$
$\text{DbOCl}_3 < \text{NbOCl}_3$
$\text{DbBr}_5 < \text{TaBr}_5 \approx \text{NbBr}_5$
$\text{SgO}_2\text{Cl}_2 \approx \text{WO}_2\text{Cl}_2 < \text{MoO}_2\text{Cl}_2$
$\text{BhO}_3\text{Cl} < \text{ReO}_3\text{Cl} < \text{TcO}_3\text{Cl}$
$\text{HsO}_4 < \text{OsO}_4$
$\text{Hg} < \text{element 112 (Cn)}$

Scarce experimental data on chemical behavior of transactinides gained for many years emphasize enormous difficulties of the investigations, on the one hand, and their scientific importance for further study of the periodical table and structure of matter, on the other hand.

53.7 Conclusion

The relatively short time of development of thermochemistry and the value of the results obtained with it allow the lines of its further development to be outlined as follows:

- Theory and experimental investigations of the gas–solid interaction of a variety of adsorbent–adsorbate systems.
- Study of physicochemical properties of transactinides to find distinctions between their behavior and the behavior of the analogue lighter elements. Obviously, thermochemistry compares favorably with isothermal gas chromatography in the study of extremely rare events of formation and decay of isotopes of new elements.
- Use of thermochemistry in production of radionuclides for science and technology (first of all for nuclear medicine). It should be noted that this method holds promise too for development of generator systems.

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References

- Adams J, Eichler B, Türler A, Gäggeler HW, Peterson J (1998) Annual report 1997 PSI, Labor für Radio- und Umweltchemie, 16
- Adilbish M, Zaitseva NG, Kovacs Z, Novgorodov AF, Sergeev YuYa, Tikhonov VI (1977) Preprint JINR, P12-10584
- Adilbish M, Zaitseva NG, Kowalev A, Kovacs Z, Novgorodov AF, Fominykh MI (1979) Preprint JINR, P6-12746
- Bächmann K, Matschoß V, Rudolph J, Steffen A, Tsalas S (1976) Nucl Instr Meth 139:343
- Bayar B, Novgorodov AF, Zaitseva NG (1973) Radiochem Radioa Let 15:231
- Bayar B, Novgorodov AF, Vocilka I, Zaitseva NG (1974) Radiochem Radioa Let 19:43
- Bayar B, Novgorodov AF, Vocilka I, Zaitseva NG (1975) Radiochem Radioa Let 22:53
- Bayar B, Vocilka I, Zaitseva NG, Novgorodov AF (1978a) Radiochem Radioa Let 34:63
- Bayar B, Vocilka I, Zaitseva NG, Novgorodov AF (1978b) Radiochem Radioa Let 34:75
- Bayar B, Zaitseva NG, Novgorodov AF (1978c) Radiochem Radioa Let 34:89
- Bayar B, Novgorodov AF, Vocilka I, Zaitseva NG (1978d) Radiochem Radioa Let 35:109
- Bayar B, Vocilka I, Zaitseva NG, Novgorodov AF (1978e) J Inorg Nucl Chem 40:1461
- Belov VZ, Zvara I, Korotkin YuS, Shalavsky MR, Shchegolev VA, Domanov VP (1972) Preprint JINR, P6-6685
- Belov VZ, Zvara I, Shalavsky MR (1974) Preprint JINR, P12-8216
- Beyer GJ, Novgorodov AF (1976) Zfk-305, Dresden
- Beyer GJ, Novgorodov AF, Rösch F, Ravn HL (1989) Isotopenpraxis 25:2
- Bögl W, Bächmann K (1975) J Inorg Nucl Chem 37:1115
- Bretshneider S (1966) Svoystva gasov i zhidkostei. Moskow-Leningrad
- Chuburkov YuT, Zvara I, Shilov BV (1969) Radiokhimija 11:174
- Chuburkov YuT, Nam HS, Alpert LK, Zvara I (1993) Preprint JINR, P6-93-289
- Chuburkov YuT, Kim SC, Timokhin SN, Belov AG, Alpert LK (1996) Preprint JINR, P12-96-425
- Curie P, Curie M (1898) C R Acad Sci Paris 127:1215
- Davydov AV (1973) J Radioanal Chem 14:285
- Domanov VP, Kim UJ (1988) Preprint JINR, P6-88-56
- Domanov VP, Zvara I (1983) Preprint JINR, P6-83-245
- Domanov VP, Hübener S, Shalagavsky MR, Timokhin SN, Petrov DV, Zvara I (1981) Preprint JINR, P6-81-768
- Domanov VP, Eichler B, Zvara I (1982) Preprint JINR, P6-82-859
- Domanov VP, Kim UJ, Berdonosov SS, Kopylova IA, Lebedev VJa (1988) Preprint JINR, P6-88-633
- Domanov VP, Buklanov GV, Lobanov YuV (2002) Abstracts 14th Radiochem Conf Marianske Lazne 188
- Düllmann ChE, Eichler B, Gäggeler HW, Türler A (1999) Annual report 1998 PSI, Labor für Radio- und Umweltchemie, 4
- Düllmann ChE, Bruchle W, Dressler R, Eberhardt K, Eichler B, Eichler R, Gäggeler HW, Ginter TN, Claus F, Gregorich KE, Hoffman DC, Jäger E, Jost DT, Kirbach UW, Lee DM, Nitsche H, Patin JB, Pershing V, Piguet D, Qin Z, Schädel M, Schausten B, Schimpf E, Schött H-J, Soverna S, Sudowe R, Thörle P, Timokhin SN, Trautmann N, Türler A, Vahle A, Wirth G, Yakushev AB, Zielinski PM (2002) Nature 418:859
- Dvorak J, Bruchle W, Chelnokov M, Dressler R, Düllmann ChE, Eberhardt K, Gorshkov V, Jäger E, Krücken R, Kuznetsov A, Nagame Y, Nebel F, Novackova Z, Qin Q, Schädel M, Schausten B, Schimpf E, Semchenkov A, Thörle P, Türler A, Wegrzecki M, Wierczinski B, Yakushev A, Yerebin A (2006) Phys Rev Lett 97:242501
- Dvorak J, Bruchle W, Chelnokov M, Düllmann ChE, Dvorakova Z, Eberhardt K, Jäger E, Krücken R, Kuznetsov A, Nagame Y, Nebel F, Nishio K, Perego R, Qin Z, Schädel M, Schausten B, Schimpf E, Schuber R, Semchenkov A, Thörle P, Türler A, Wegrzecki M, Wierczinski B, Yakushev A, Yerebin A (2008) Phys Rev Lett 100:132503
- Eichler B (1976) Dissertation B, Technische Universität Dresden

- Eichler B (1977) ZfK-346, Dresden
- Eichler B (1978) ZfK-374, Dresden
- Eichler B, Chun KS (1985) *Isotopenpraxis* 21:180
- Eichler B, Domanov VP (1974) Preprint JINR, P12-7775
- Eichler B, Domanov VP (1975) *J Radioanal Chem* 28:143
- Eichler B, Malzeva NS (1976) Preprint JINR, P12-9959
- Eichler B, Zvara I (1975) Preprint JINR, P12-8943
- Eichler B, Zvara I (1982) *Radiochim Acta* 30:233
- Eichler B, Domanov VP, Zvara I (1976) Preprint JINR, P12-9454
- Eichler B, Hübener S, Roßbach H (1985a) ZfK-560, Dresden
- Eichler B, Hübener S, Roßbach H (1985b) ZfK-561, Dresden
- Eichler B, Zude F, Fan W, Trautmann N, Herrmann G (1992) *Radiochim Acta* 56:133
- Eichler B, Zude F, Fan W, Trautmann N, Herrmann G (1993) *Radiochim Acta* 61:81
- Eichler B, Baltensperger U, Ammann M, Jost DT, Gäggeler HW, Türlér A (1995) *Radiochim Acta* 68:41
- Eichler B, Adams J, Eichler R, Gäggeler HW, Peterson J (2002) *Radiochim Acta* 90:895
- Eichler R, Eichler B, Gäggeler HW, Jost DT, Dressler R, Türlér A (1999a) *Radiochim Acta* 87:151
- Eichler R, Gäggeler HW, Eichler B, Türlér A (1999) Annual report 1998 PSI, Labor für Radio- und Umweltchemie, 5
- Eichler R, Eichler B, Gäggeler HW, Jost DT, Pignet D, Türlér A (2000a) *Radiochim Acta* 88:87
- Eichler R, Brüchle W, Dressler R, Düllmann ChE, Eichler B, Gäggeler HW, Gregorich KE, Hoffman DC, Hübener S, Jost DT, Kirbach UW, Laue CA, Lavanchy VM, Nitsche H, Patin JB, Piguet D, Schädler M, Shaughnessy DA, Strellis DA, Taut S, Tobbler L, Tsyganov YS, Türlér A, Vahle A, Wilk PA, Yakushev AB (2000b) *Nature* 407:63
- Eichler R, Aksenov NV, Belozherov AV, Bozhikov GA, Chepigin VI, Dmitriev SN, Dressler R, Gäggeler HW, Gorshkov VA, Haenssler F, Itkis MG, Laube A, Lebedev VYa, Malyshev ON, Oganessian YuTs, Petrushkin OV, Piguet D, Rasmussen P, Shishkin SV, Shutov AV, Svirikhin AI, Tereshatov EE, Vostokin GK, Wegrzecki M, Yeregin AV (2007) *Nature* 447:72
- Eichler R, Aksenov NV, Belozherov AV, Bozhikov GA, Chepigin VI, Dmitriev SN, Dressler R, Gäggeler HW, Gorshkov AV, Itkis MG, Haenssler F, Laube A, Lebedev VYa, Malyshev ON, Oganessian YuTs, Petrushkin OV, Piguet D, Popeko AG, Rasmussen P, Shishkin SV, Serov AA, Shutov AV, Svirikhin AI, Tereshatov EE, Vostokin GK, Wegrzecki M, Yeregin AV (2008) *Angew Chem Int Ed* 47:3262
- Fan W, Gäggeler H (1982) *Radiochim Acta* 31:95
- Frenkel J (1924) *Z Phys* 26:117
- Gäggeler H, Dornhöfer H, Schmidt-Ott WD, Grenlich N, Eichler B (1985) *Radiochim Acta* 38:103
- Gärtner M, Boettger M, Eichler B, Gäggeler HW, Grantz M, Hübener S, Jost DT, Pignet D, Dressler R, Türlér A, Yakushev AB (1997) *Radiochim Acta* 78:59
- Gärtner M, Dressler R, Eichler B, Türlér A, Gäggeler HW (2000) Annual report 1999 PSI, Labor für Radio- und Umweltchemie, 18
- Giddings JC, Seager SL (1960) *J Chem Phys* 33:1579
- Glebov VA, Kasztura L, Nefedov VS, Zhuikov BL (1988) Preprint JINR, P6-88-201
- Glebov VA, Kasztura L, Nefedov VS, Zhuikov B (1989) *Radiochim Acta* 46:117
- Graf U, Eichler B, Türlér A, Gäggeler HW, Hairl RG (1999) Annual report 1998 PSI, Labor für Radio- und Umweltchemie, 12
- Häfelí T, Gäggeler HW, Eichler B, Düllmann ChE (2000) Annual report 1999 PSI, Labor für Radio- und Umweltchemie, 11
- Helas G, Hoffmann P, Bächmann K (1978) *J Radioanal Chem* 47:159
- Herrmann G, Denschlag HO (1969) *Ann Rev Nucl Sci* 19:1
- Hickmann U, Greulich N, Trautmann N, Gäggeler H (1980) GSI 80-3, Darmstadt, S.154
- Hickmann U, Grenlich N, Trautmann N, Herrmann G (1993) *Radiochim Acta* 60:127
- Hübener S, Zvara I (1979) Preprint JINR, E12-12753
- Hübener S, Zvara I (1982) Preprint JINR, E12-82-103
- Hübener S, Taut ST, Vahle A, Faughänel TH (2001) GDCh-Jahrestagung Chemie 2001, Universität Würzburg, S.15
- Khalkin VA, Novgorodov AF, Kolaczowski A (1979) Report IFJ N-1073/c, Krakow
- Kim UJ, Timokhin SN, Domanov VP, Chuburkov YuT (1987a) Preprint JINR, P6-87-158
- Kim UJ, Timokhin SN, Zvara I (1987b) Preprint JINR, P6-87-159
- Kim UJ, Timokhin SN, Domanov VP, Korotkin JuS (1988) Preprint JINR, P6-88-635
- Kirbach U, Folden CM III, Ginter T, Gregorich KE, Lee DM, Ninov V, Omtvedt JB, Patin JB, Seward NK, Strellis DA, Sudowe R, Türlér A, Wilk PA, Zielinski PM, Hoffman DC, Nitsche H (2002) *Nucl Instrum Meth A* 484:587
- Korotkin YuS, Kim UJ, Timokhin SN, Orelobitch OL, Altynov VA (1988) Preprint JINR, P6-88-595
- Merinis J, Bouissieres G (1961) *Anal Chim Acta* 25:498
- Merinis J, Bouissieres G (1969) *Radiochim Acta* 12:140
- Merinis J, Legoux Y, Bouissieres G (1970) *Radiochem Radioa Let* 3:255
- Merinis J, Legoux Y, Bouissieres G (1972) *Radiochem Radioa Let* 11:59
- Nguen CT, Novgorodov AF, Kaskevitch M, Kolatchkowski A, Chalkin VA (1984a) *Radiokhimija* 26:60

- Nguyen CT, Kolatchkowski A, Novgorodov AF (1984b) Preprint JINR, 6-84-849
- Niklaus J-P, Eichler R, Soverna S, Gäggeler HW, Tobler L (2003) Scientific report 2002 PSI, VI, 70
- Nogare SD, Juvert RS (1962) Gas-liquid chromatography. Wiley Interscience, New York/London
- Novgorodov AF, Kolatchkowski A (1979) Preprint JINR, P6-12457
- Novgorodov AF (1982) Dissertation, Preprint JINR 6-82-839
- Novgorodov AF, Kolatchkowski A, Nguyen CT, Zelinski A, Kaskevitch M (1986a) Radiokhimija 28:380
- Novgorodov AF, Buklanov GV, Zielinski A, Kolachkovski A, Rösch F, Schomäcker K (1986b) Appl Radiat Isot 37:445
- Novgorodov AF, Belov AG, Zelinski A, Kolatchkowski A (1987a) Radiokhimija 29:254
- Novgorodov AF, Belov AG, Zelinski A, Kolatchkowski A, Ageev VA, Kljutchnikov AA, Mikecs P, Mikulski JA, Misiak R, Sazhenjuk AD, Sobezka M (1987b) Radiokhimija 29:549
- Novgorodov AF, Zelinski A, Kolatchkowski A, Misiak R, Sobezka M, Ageev VA, Belov AG, Kaskevitch M, Kljutchnikov AA, Odinzov AA, Mikulski JA (1988) Radiokhimija 30:672
- Novgorodov AF, Rösch F, Zielinski A, Misiak P, Kolaczkowski A, Beyer GJ, Schomäcker K (1990) Isotopenpraxis 26:118
- Novgorodov AF, Bruchertseifer F, Brockmann J, Lebedev NA, Rösch F (2000) Radiochim Acta 88:163
- Novgorodov AF, Schmidt A, Brockmann J, Qaim SM, Rösch F (2001) J Labelled Compd Rad 44:778
- Ohline RW, DeFord DD (1963) Anal Chem 35:227
- Pershina VG (1996) Chem Rev 96:9177
- Röder E, Herrmann G (1966) Z Anal Chem 219:93
- Rösch F, Novgorodov AF, Qaim SM (1994) Radiochim Acta 64:113
- Rösch F, Qaim SM, Novgorodov AF, Tsai Y-M (1997) Appl Radiat Isot 48:19
- Roßbach H, Eichler B (1984) ZfK-527, Dresden
- Rudstam G, Grapengiesser B (1973) Radiochim Acta 20:97
- Schädel M, Brüchle W, Dressler R, Eichler B, Gäggeler HW, Günther R, Gregorich KE, Hoffman DC, Hübener S, Jost DT, Kratz JV, Paulus W, Schumann D, Timokhin S, Trautmann N, Türler A, Wirth G, Yakushev A (1997) Nature 388:55
- Schomäcker K, Schwarzbach R, Beyer G-J, Novgorodov AF (1988) Appl Radiat Isot 39:483
- Steffen A, Bächmann K (1978a) Talanta 25:551
- Steffen A, Bächmann K (1978b) Talanta 25:677
- Talbert WL Jr (1970) CERN 70-30, 1:109
- Taut S, Hübener S, Eichler B, Türler A, Gäggeler HW, Timokhin SN, Zvara I (1998) J Alloy Comp 271-273:316
- Taut S, Vahle A, Hübener S, Eichler B, Jost D, Türler A (2000) Annual report 1999 PSI, Labor für Radio- und Umweltchemie, 17
- Taut S, Hübener S, Eichler B (2001) GDCh-Jahrestagung Chemie 2001, Universität Würzburg, S.60
- Tsalas S, Bächmann K (1978) Anal Chim Acta 98:17
- Türler A (1999) Dissertation B: gas phase chemistry of the transactinide elements Rf, Db and Sg, Universität Bern
- Türler A, Eichler B, Jost DT, Dressler R, Piguet D, Gäggeler HW, Hübener S, Boettger M, Grantz M (1996) Annual report 1995 PSI, Labor für Radio- und Umweltchemie, 28
- Türler A, Brüchle W, Dressler W, Eichler B, Eichler R, Gäggeler HW, Gärtner M, Glatz J-P, Gregorich KE, Hübener S, Jost DT, Lebedev V Ya, Pershina VG, Schädel M, Taut S, Timokhin SN, Trautmann N, Vahle A, Yakushev AB (1999) Angew Chem Int Ed 38:2212
- Vahle A, Hübener S, Eichler B (1995) Radiochim Acta 69:233
- Vahle A, Hübener S, Dressler R, Eichler B, Türler A (1997) Radiochim Acta 78:53
- Vahle A, Hübener S, Funke H, Eichler B, Jost DT, Türler A, Brüchle W, Jäger E (1999) Radiochim Acta 84:43
- Vakhtel VM, Vinel GV, Vylov Z, Gromova II, Novgorodov AF, Norseev JuV, Khalkin VA, Chumin VG (1976) Isotopenpraxis 12:441
- Weber M, Trautmann N, Herrmann G (1971) Radiochem Radioa Let 6:73
- Wolf GK (1973) GSI 73-7
- Yakushev AB, Timokhin SN, Xu H, Zvara I (1993) Scientific Report FLNR 1991-2, E7-93-57, 169
- Yakushev AB, Buklanov GV, Chelnokov ML, Chepigin VI, Dmitriev SN, Gorshkov VA, Hübener S, Lebedev VYa, Malyshev ON, Oganessian YuTs, Popeko AG, Sokol EA, Timokhin SN, Türler A, Vasko VM, Yeremin AV, Zvara I (2001) Radiochim Acta 89:743
- Yakushev AB, Zvara I, Belozorov AV, Dmitriev SN, Eichler B, Hübener S, Sokol EA, Türler A, Yeremin AV, Buklanov GV, Chelnokov ML, Chepigin VI, Gorshkov VA, Gulyaev AV, Lebedev VYa, Malyshev ON, Popeko AG, Soverna S, Szegłowski Z, Timokhin SN, Tretyakova SP, Vasko VM, Itkis MG (2002) Preprint JINR, E12-2002-297
- Yakushev AB, Eichler B, Türler A, Gäggeler HW, Peterson J (2003) Radiochim Acta 91:123
- Zhuikov BL (1982a) Preprint JINR, P12-82-63
- Zhuikov BL (1982b) Preprint JINR, 12-82-736
- Zhuikov BL, Chuburkov YuT, Timokhin SN, Kim UJ, Zvara I, (1988) Preprint JINR, P6-88-109
- Zude F, Fan W, Trautmann N, Herrmann G, Eichler B (1993) Radiochim Acta 62:61
- Zvara I (1985) Radiochim Acta 38:95

- Zvara I (2008) The inorganic radiochemistry of heavy elements. Methods for studying gaseous compounds. Springer, ISBN: 978-1-4020-6601-6
- Zvara I, Chuburkov YuT, Zvarova TS, Tsaletka R (1969a) Radiokhimija 11:154
- Zvara I, Chuburkov YuT, Tsaletka R, Shalaevsky MR (1969b) Radiokhimija 11:163
- Zvara I, Belov VZ, Chelnokov LP, Domanov VP, Hussonois M, Korotkin YuS, Schegolev VA, Shalaevsky MR (1971) Inorg Nucl Chem Lett 7:1109
- Zvara I, Belov VZ, Domanov VP, Shalaevsky MR (1975) Preprint JINR, P12-8740
- Zvara I, Domanov VP, Hübener S, Shalaevsky MR, Timokhin SN, Zhuikov BL, Eichler B, Buklanov GV (1982) Preprint JINR, P6-82-616
- Zvara I, Domanov VP, Hübener S, Shalaevsky MR, Timokhin SN, Zhuikov BL, Eichler B, Buklanov GV (1984) Radiokhimija 26:76
- Zvara I, Yakushev AB, Timokhin SN, Xu H, Perelygin VP, Chuburkov YuT (1998) Radiochim Acta 81:179