Gas chemical methods for the separation of elements in radioisotope production and activation analysis

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An analytical system is suggested to separate a number of elements of the Periodic Table in a hydrogen or oxygen stream at temperatures up to 1400 °C. High temperature chemical filters are used to separate volatile products. The approach has demonstrated its efficiency in a number of examples of carrier-free isotope production from targets irradiated at an accelerator: ^{109}Cd from In; ^{22}Na from Al; ^{72}Se from GaAs; ^{188}Pt, ^{183}Re, ^{185}Os and ^{201}Tl from Pb or Bi; separation of Po from Pb and Bi, etc. Another application of high temperature chemical sublimation of elements and oxides was realized in activation analysis of noble metals in various ores and samples.

Introduction

Gas chemical separation methods are widely used for recovery of carrier-free isotopes from irradiated accelerator targets and for chemical processing in order to increase the sensitivity of activation analysis. Another important application of the gas chemical methods is in the new element research. Different gas carriers and correspondingly different volatile compounds have been used in many cases (elements, oxides, chlorides, fluorides, volatile organic substances) for particular purposes.

Here we demonstrate examples of the application of an universal analytical system developed for the separation of a great number of elements of the Periodic Table.[1,2] The principle of the approach is a combination of the followings.

(1) Sublimation of various elements from irradiated targets or natural samples in hydrogen or oxygen (air) stream.

(2) The addition of non-volatile reagents to the samples consisting of various metals, oxides or chlorides in order to destroy better the matrix of the sample and increase the sublimation yield, and/or transfer the desired elements into volatile or nonvolatile form.

(3) The sublimated volatile elements or oxides may be separated from each other not only via their different volatility in their original chemical form but also, more effectively, via chemical reactions at the surface.

The important general advantage of the gas chemical methods with solid reagents and chemical filters is that it is useful and predictable both for macro and micro-quantities of sublimated analyzed elements. In this paper a theoretical background is given for carrier-free amounts with surface chemical reactions as well as new experimental examples are demonstrated of successful application of this system in isotope production and activation analysis.

Experimental

A regular gas chemical technique is simple and in most cases no special reagents and complicated equipment are required for the processing. Thermochromatography, i.e., deposition on a negative (versus gas flow) temperature gradient, is mainly used for investigation of the process for the separation of volatile products. Simple isothermal furnaces are used in routine separations.

Radioactive isotopes were produced at the proton accelerator of the Institute for Nuclear Research (Troitsk) or the heavy ion accelerator of Joint Institute for Nuclear Research (Dubna). Various nuclear facilities have been used for neutron- and gamma-activation analysis: nuclear reactors and electron accelerators. Neutron fluence ranged up to 10^{18} cm^{-2}. Gamma-ray spectrometry with Ge and Ge(Li) detectors as well as X-ray fluorescence analysis with Si(Li)-detector have been used.

Theoretical

It is rather easy to determine the deposition temperature of a pure substance in the case of the condensation of macro-quantities even involving a chemical reaction at the surface. In the case of micro-quantities not sublimation and condensation are considered but desorption and adsorption. Thermodynamic parameters of the adsorption-desorption process are usually not known and are difficult to measure, calculate theoretically and interpret in each case.

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Nevertheless, it is possible to establish a correlative connection between sublimation and the desorption process. EICHLER and ZVARA[4] developed an approach for the calculation of deposition temperatures in thermochromatography. A reasonable approximation of this equation[5,6] is:

$$T_a = \Delta H_d^0 \ [\Delta S_d^0 + R \cdot \ln(0.11 \cdot t \cdot Q \cdot g/s)]^{-1} \qquad (1)$$

where ΔH_d^0 is the enthalpy of desorption, ΔS_d^0 is the entropy of desorption, T_a is the maximum of adsorption peak temperature, K; t is the period of separation, s, Q is the gas flow rate, cm^3/s; g is the temperature gradient, K/cm; s is the support surface per unit of column length, cm^2/cm.

We suggest an approximation[6] providing a good correlation with the experimental results. This is a semi-theoretical approach where the entropy of desorption is calculated from the thermodynamic data based on the assumption of partial similarity of adsorption and monolayer desublimation processes:

$$\Delta S_d^0 = \Delta S_{sub}^0 + R \cdot \ln[1.02 \cdot 10^6 \cdot M^{2/3} \cdot \rho^{-2/3} \cdot T^{-1}) \qquad (2)$$

where M is the molecular weight of the adsorbed form, g; ρ is the density of the adsorbed form in macro-quantity, g/cm^3; ΔS_{sub}^0 is the entropy of reaction of sublimation, calculated from thermodynamic data.

In this approximation a good correlation $\Delta H_d^0 \approx \Delta H_{sub}^0$ has been demonstrated for cases where the chemical form is obvious. Thus the adsorption temperature may be calculated with the Eqs (1) and (2). It is important in this approach, that there is a possibility to explain the processes involving chemical reactions on the surface, where the entropy of the reaction of adsorption may differ greatly from that of the simple adsorption. This happens very often especially in processes of oxide adsorption.

Results

In the followings several examples are presented to demonstrate the effectiveness of the given approach in different applications for various radioanalytical tasks.

Separation of Pb, Bi and Po:
Macro- and micro-quantities

Separation of polonium from lead and bismuth is a classical radiochemical problem. The experimental results on thermochromatography of Pb, Bi and Po with different amounts of carrier in a stream of hydrogen in open columns are shown in Fig. 1. One can easily calculate that under the given experimental conditions in the peak area a mono-layer amount will take about 0.3 μg of the substance. In the case of much smaller amount of atoms at the surface, they will not "feel" each

other if we do not assume the existence of specific activation centers which may cover a minimal part of the whole surface. And really, it is seen in Fig. 1a (no carrier added, less than ng) that polonium is well separated from Pb and Bi since it has a much higher volatility in the elemental state. The addition of about 1 μg Pb and Bi carrier (Fig. 1b) results in two peaks of Po: one for Po itself and one for its interaction with Pb and Bi with the formation of polonide. Milligram amounts of Pb and Bi (Fig. 1c) result in a sole polonium peak on the surface of Bi and Pb metal. A similar result is observed in thermochromatography in an air stream: the formation of binary oxides of Po and Pb is observed with carrier amounts of 1 μg. So, these experiments demonstrate clearly what "carrier-free" means for the given chemical system. Of course, there may be quite different regularities in various chemical systems. The equations in the theoretical part predict the deposition temperatures with a high accuracy in all known experiments of various authors (see, e.g., Reference 7).

Polonium may be easily separated from micro- or macro-amounts of Bi and Pb with the help of chemical filters. Po (as well as Bi) demonstrate an irreversible adsorption in a stream of air on a CaO-filter at 1100–1200 °C (formation of calcium polonite) (Fig. 2), while Pb passes through this filter. Thus Pb is "more volatile" than Po in a stream of air on CaO. On the contrary, with a different chemical filter SiO$_2$ in oxygen (under continuous sublimation-adsorption procedures, see below) Pb as well as Bi become non-volatile because of the formation of a stable silicate. Polonium does not form such stable silicate and is transported to lower temperature of about 500–600 °C.

It is important to note that in the case of CaO and SiO$_2$ chemical filters the separation of Po, Bi and Pb is efficient both for macro- and micro-quantities of Bi and Pb. This is because the stability of binary oxides of these elements with CaO and SiO$_2$ is higher than the stability of binary oxides of bismuth–polonium and lead–polonium at high temperature. Po, Pb, Bi absorbed by chemical filters of CaO and SiO$_2$ may be removed from CaO or SiO$_2$ by heating in hydrogen, but in case of SiO$_2$ this process is going very slowly.

Some of these regularities may be important from the viewpoint of the proposed technique of nuclear waste transmutation with the use of Pb–Bi targets.

Recovery of radionuclides produced in Pb and
Bi targets irradiated with protons and α-particles

A great number of various nuclides are generated in the irradiation of metallic lead by protons of intermediate energy of 160–600 MeV. These are in particular: ^{183}Re, ^{185}Os, ^{186,188,189}Ir, ^{188,191}Pt, ^{196,199}Au, ^{203}Hg, $^{200, 201,202}$Tl, ^{203}Pb, ^{205,205,207}Bi.

Though lead itself is volatile, most of these radioelements may be extracted from the lead target by gas chemical methods in a stream of air and separated with the help of high temperature chemical filters. In several experiments the pieces of irradiated Pb were mixed with quartz sand (weight ratio 1:3.5 or more) and heated slowly from 500 to 1100 °C. The heating was continued at this temperature for few hours in a stream of air. Thus lead and bismuth were transformed into nonvolatile silicate form. Re, Os, Ir, Pt, Hg and Tl radionuclides were sublimated. Re, Os, Ir and Pt were separated in a stream of oxygen with the help of chemical filters. Thus, metallic gold absorbs Pt at high temperatures (1000 °C or more) and Ir at about 300–500 °C.[8] Re and Os are more volatile in a stream of oxygen, these elements may be most effectively separated with the help of MgO or CaO filter absorbing Re at about 1100 °C.[8]
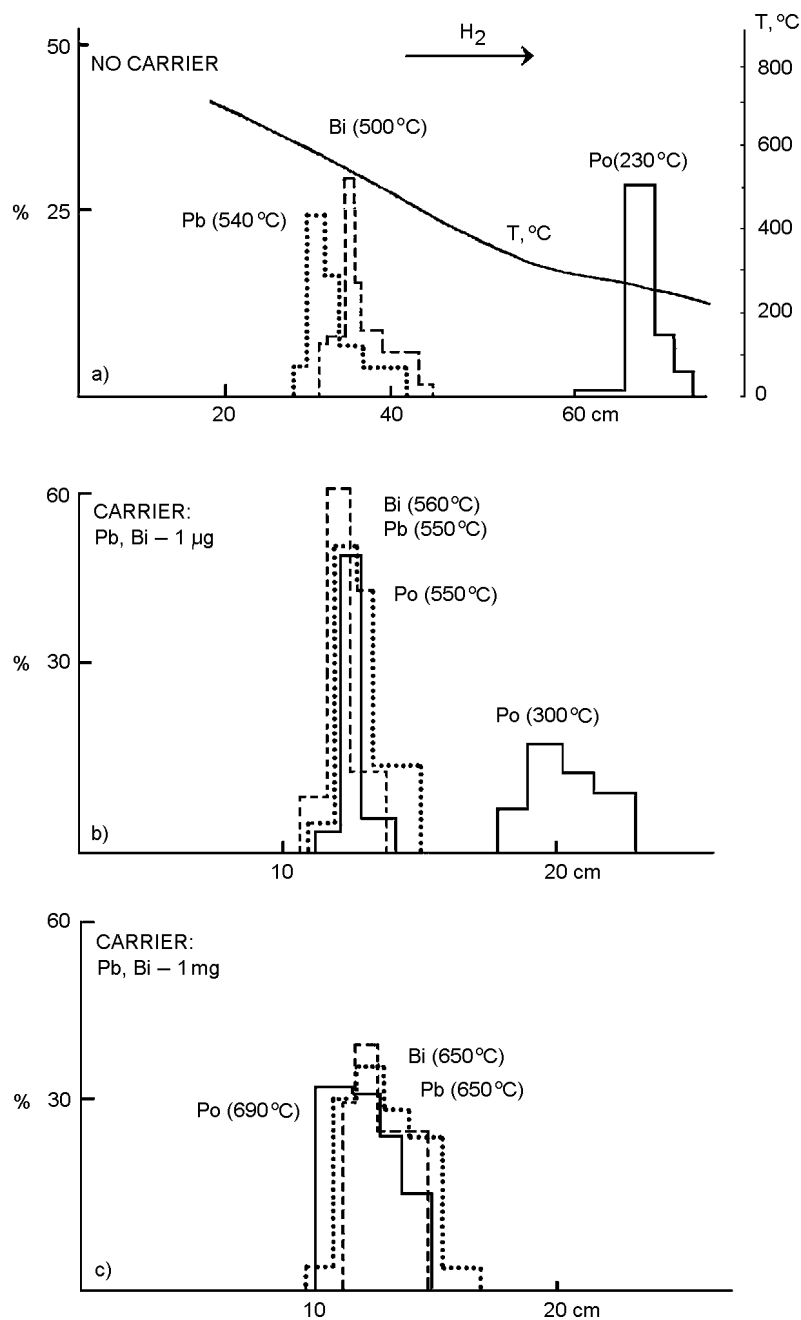

Fig. 1. Thermochromatography of Pb, Bi and Bi in hydrogen stream in stainless column with various amounts of carrier: (a) no carrier added; (b) Pb, Bi carrier 1 μg; (c) Pb, Bi carrier 1 mg, Po, no carrier
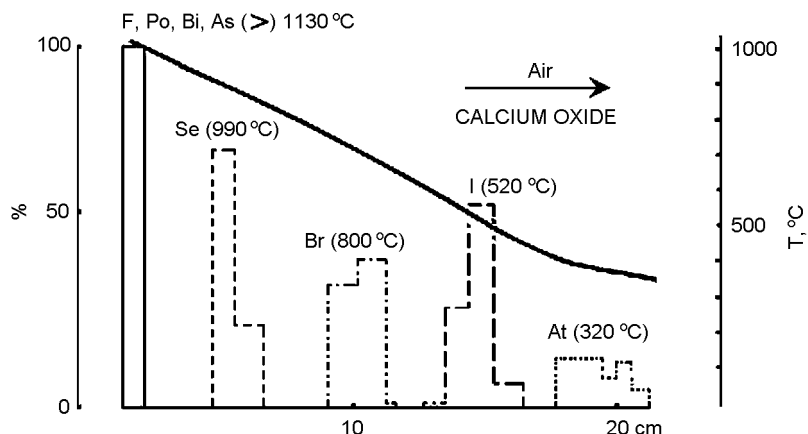
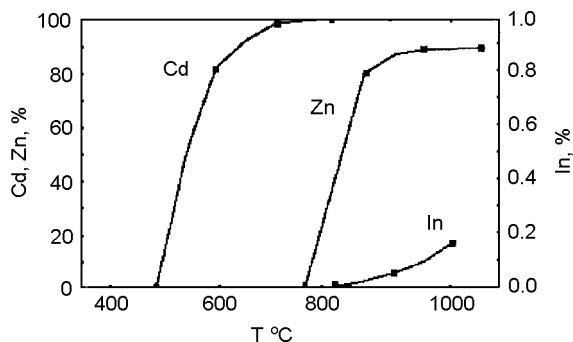*Fig. 2.* Thermochromatography of radioelements in no-carrier-added amounts at CaO-column in air stream

Fig. 3. Temperature dependence of evaporation rate of ^{109}Cd from metallic indium and ^{65}Zn from gallium

With a similar technique we have investigated the process of recovery of ^{206,210}Po from lead irradiated with accelerated α-particles, as well as ^{210,211}At and ^{210}Po from bismuth. The regularities of isolation of radionuclides from irradiated bismuth targets are similar to lead, but we found that bismuth is more actively absorbed by SiO$_2$, than lead. We also found that the recovery of At from Bi-targets is more efficient with the use of CaO: the traces of sublimated Bi and Po may be absorbed by a CaO-filter at about 1100 °C while the deposition temperature of At is much lower (Fig. 2).

Figure 2 demonstrates also an interesting example of separating of micro-quantities of halogen elements in a stream of air in a CaO-thermochromatography column. Though all halogens have similar volatility, in this case they form different compounds at the surface of CaO and are separated well. This phenomena has been used in a procedure to purify iodine isotopes from ^{17,18}F [9] and on-line recovery of Os-isotopes in search of its chemical analog element 108 – hassium in oxygen stream from products of the nuclear reactions with a heavy ion beam.[10]

Recovery of ^{109}Cd, ^{65}Zn and ^{22}Na from liquid metallic targets

Cadmium-109 may be efficiently produced in indium target irradiated with 100–800 MeV protons.[12] The recovery of ^{109}Cd from indium is another example a of successful application of the gas chemical method. We evaporated ^{109}Cd from molten indium (see temperature dependence in Fig. 3) in an inert gas (helium) stream with 5% hydrogen addition to stabilize the elementary form. At temperature of 700 °C, cadmium in carrier-free quantities is fully volatilized from molten indium while volatilization of ^{65}Zn impurities starts at 800 °C. The evaporation of indium itself begins in very small amount (less than 0.1%) only at temperature above 900 °C. We have observed similar temperature dependences for the evaporation of ^{65}Zn from metallic gallium.

The additional separation of ^{109}Cd from ^{65}Zn impurities is achieved with the help of chemical filters of metallic copper. Intermetallic interaction of Zn with copper provides much better separation of ^{109}Cd than a simple separation based on higher the volatility of Cd in inert (e.g., quartz) columns.[13]

Sodium-22 is a valuable isotope which may be produced at proton energies of 100–800 MeV from aluminum or magnesium targets. ^{22}Na may be volatilized from liquid metallic aluminum,[14] but the process has some important complications because of chemical reactions in the system. An oxide film is formed at the surface of metallic aluminum. This film prevents diffusion and evaporation of sodium from aluminum. Therefore, the process is performed in highly purified helium (Zr-getter). Metallic aluminum is placed on graphite powder that evidently reduces the oxide film. Sodium itself has a high volatility but because of chemical reactions its deposition temperature in carrier-free amount in helium (hydrogen) stream on quartz,

alumina ceramic or stainless steel surface is as high as 900–1100 °C, while it is much lower on platinum.

Production and recovery of ^{72}Se from gallium arsenide targets

Selenium-72 is a very prospective radionuclide for the preparation of a Se/As-72 generator to be used in positron emission tomography. The most prospective is to obtain ^{72}Se from nuclear reactions of intermediate protons on arsenic-containing targets.[15] GaAs has been suggested as a production target. It is not simple to recover ^{72}Se from this or other As-containing target with gas chemical methods since arsenic is sublimated as well as selenium (see experimental temperature dependence in Fig. 4a). The addition of metallic Fe to the target material[16] destroys the crystalline structure of GaAs. Iron reacts both with arsenic forming a stable arsenide and with gallium forming Ga–Fe alloy. As the result

^{72}Se is sublimed in purified inert gas at about 1350 °C without any As impurities (Fig. 4b). Moreover, a selective separation from ^{65}Zn impurities may be achieved in preliminary heating at 1100–1150 °C.

Recovery and determination of noble metals from natural samples

Another effective application of the described chemical separation system is pre-concentration to increase the sensitivity of activation analysis of natural samples.[2,3,17] The elements which usually constitute the matrix of natural samples (such as Fe, Ca, Mg, Si, Al, Cu, Ni, Ti) are not volatile in hydrogen and oxygen streams. Many of various micro-elements may be recovered from natural samples before or after neutron or γ-irradiation or with the help of different analytical instrumental methods. The most effective is the determination of noble metals: Pt, Ir, Au, Ru and Ag.
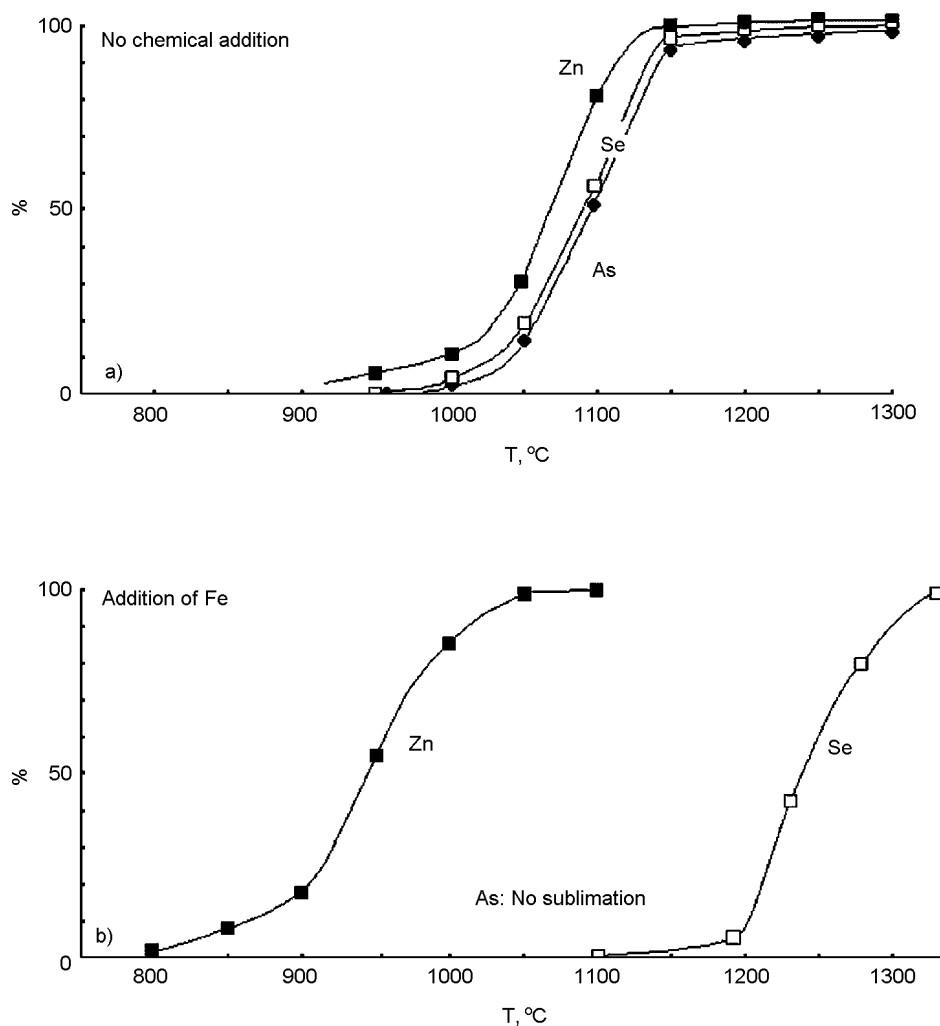

Fig. 4. Temperature dependence of ^{72}Se and ^{65}Zn sublimation from irradiated GaAs target in pure helium stream without addition (a) and with addition of iron reagent (b) (1 : 2 in weight)

The following sample types have been studied: chromites, ferruginous laterites, combustible shales, harzburgites, ultrabasic rocks, titanomagnetites, sulfide copper and nickel ores and concentrates, ocean concretions. The method has demonstrated its efficiency for all types of samples, but sometime a given sample type has specific features in processing.

The addition of non-volatile reagents to the samples, consisting of various metals, oxides or chlorides, allows to destroy better the matrix of the sample and increases the sublimation yield, and/or transfers the desired elements into volatile or nonvolatile forms. We have used Ti or Nb metals or oxides to destroy stable oxides in natural samples, and additions of $FeCl_2$ to transfer some noble elements into volatile chloride or oxy-chloride form in oxygen stream while the main matrix remained as non-volatile oxides.[2]

Chemical filters of CaO, MgO and Al_2O_3 at high temperature (1100–1200 °C) were used for purification from interfering volatile elements in air stream (As, Sb, Bi, Te, Cr, In, Mo, W). Nb_2O_5 is effective for purification from Pb, Bi and Zn. Chemical filters at lower temperature (MgO or Al_2O_3) were used as collectors of noble metals while some of the volatile elements (Br, Se, Cd) passed through this filter. These collectors were irradiated for neutron- and gamma-activation. Thin plastic films at cooled rod were used as noble element collectors in X-ray fluorescence analysis.

The absolute sensitivity of noble element determination in neutron activation method achieve 10 ng for Pt, 0.1 ng for Ir, 0.01 ng for Au, and 20 ng for Ag. X-ray fluorescence analysis provides sensitivity 200 ng for Pt, Ir and Au. The accuracy of the analysis determined by the uncertainty and reproducibility of the chemical yield is within 10–20% but much more stable for samples of one type.

Conclusions

The procedure for recovery and separation of various elements in hydrogen and oxygen stream demonstrates its efficiency in many cases. It may be considered as an universal approach to recover various isotopes from irradiated targets as well for pre-concentration in activation analysis of natural samples.

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