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Thermochromatography study of volatile polonium species in various gas atmospheres

Emilio Andrea Maugeri [a], Jörg Neuhausen [a,*], Robert Eichler [a,b], David Piguet [a], Tania Melo Mendonça [c], Thierry Stora [c], Dorothea Schumann [a]

[a] Laboratory for Radio- and Environmental Chemistry, Paul Scherrer Institut, Villigen PSI, CH-5232 Villigen, Switzerland
[b] Department for Chemistry and Biochemistry, University of Berne, CH-3012 Bern, Switzerland
[c] CERN, ISOLDE, CH-1211 Geneva, Switzerland

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ABSTRACT

Phenomena related to the volatilization of polonium and its compounds are critical issues for the safety assessment of the innovative lead–bismuth cooled type of nuclear reactor or accelerator driven systems. The formation and volatilization of different species of polonium and their interaction with fused silica was studied by thermochromatography using carrier gases with varied redox potential. The obtained results show that under inert and reducing conditions in the absence of moisture, elemental polonium is formed. Polonium compounds more volatile than elemental polonium can be formed if traces of moisture are present in both inert and reducing carrier gas. The use of dried oxygen as carrier gas leads to the formation of polonium oxides, which are less volatile than elemental polonium. It was also found that the volatility of polonium oxides increases with increasing oxidation state. In the presence of moisture in an oxidizing carrier gas, species are formed that are more volatile than the oxides and less volatile than the elemental polonium. Considering the redox potential of the carrier gas those species are likely oxyhydroxides.

1. Introduction

According to [1] about 427,000 m^3 of high level waste (HLW) have been produced by the civil nuclear industry during the last five decades, only 4000 m^3 of which have been already disposed. This reflects the difficulty to dispose such type of waste, due to its high and long-lasting (from 100,000 to millions of years [2,3]) radiotoxicity. A few centuries after disposal, the total radioactivity of the HLW is mainly due to the long-lived minor actinides, plutonium and its decay products [4]. In order to reduce the long-term radiotoxicity of the HLW, it was proposed to separate the long lived minor actinides (half-lives of many thousands of years) from the HLW and to transmute them into nuclides with a shorter half-life (less than 30 years [4]). There are several nuclear reactor concepts that can be used to perform this process, e.g. fast nuclear reactors and accelerator-driven systems (ADS). The first research ADS, called MYRRHA, is planned to be built in Belgium in order to demonstrate the effectiveness of this process [5]. MYRRHA is an ADS using the liquid metal lead–bismuth-eutectic (LBE) as a reactor coolant and as spallation target material. One of the most problematic issues related to the use of LBE is the production of polonium by (p, xn) and (n, γ) reactions with bismuth in the target and in the coolant, respectively. Polonium is a very dangerous element because of its high radiotoxicity and relatively high volatility. Only few reliable data are available in literature for this element and its compounds, partly caused by both the instability of its isotopes and the intrinsic difficulty of performing experimental investigations.

One of the main problems for experimental studies of polonium volatility was pointed out by Eichler [6]. He argued that the discrepancy between the value of the vapor pressure of pure Po that he extrapolated from the thermodynamic properties of its lighter homologues in the chalcogens group, and the ones earlier derived from experimental works [7–10], was due to the effects of the radioactive decay of ^{210}Po used for the experiments that caused an overestimation of the value determined experimentally at low temperatures.

Another issue that must be considered when studying the volatility of polonium is related to the reactions of polonium with reactive species present in the atmosphere leading to the formation of compounds more volatile than elemental polonium. According to [11] polonium may react with water forming PoH_2. The boiling point of this compound was estimated to be about 310 K. Thus, it would increase considerably the amount of polonium released to the gas phase, representing a critical safety issue for LBE-based reactors.

* Corresponding author. Address: Laboratory for Radio- and Environmental Chemistry, Paul Scherrer Institut, OFLB/101, CH-5232 Villigen PSI, Switzerland. Tel.: +41 56 310 4463; fax: +41 56 310 4435.
E-mail address: joerg.neuhausen@psi.ch (J. Neuhausen).

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One of the techniques that can be used for studying polonium in sub-microgram quantities, avoiding problems related with the α-decay, and that allows studying the formation of different compounds in different reactive and inert atmospheres, is thermochromatography.

The thermochromatography method is based on the adsorption interaction between a volatile species and a stationary phase as a function of the temperature [12]. The experimental result of a thermochromatography experiment consists in a thermochromatogram in which the surface concentration of the adsorbed species is plotted as a function of either the column length or the temperature. The results of such thermochromatography experiments will allow for proving the existence of different gas phase species of polonium under various conditions, and for their identification and characterisation of their chemical nature as well as determination of their thermodynamic properties, e.g. enthalpies of adsorption. In this work we study the volatilization and deposition of polonium under different gas atmospheres using thermochromatography in fused silica columns. The results of these studies provide fundamental insights in the volatilization of polonium itself under various chemical conditions. Thus, they will serve as a foundation for assessing possible volatilization processes of polonium in ADS and other nuclear systems. The volatilization of polonium from diluted solution in liquid metals proposed to be used as target and coolant material in ADS – such as LBE – is the topic of a separate study.

2. Materials and methods

2.1. Production of ^{206}Po

^{210}Po, with a half life of 138 days, is the most widely available isotope, but the heat generated by its α-decay (140 W/g) complicates studying it in macroscopic amounts. The decay energy deposited in the samples prevents exact direct calorimetric measurements of chemical reactions or changes in its physical state. On the other hand, the α-decay would also facilitate the decomposition of any compounds. The more stable isotope, ^{209}Po, with a half-life of 102 years, is available in small amounts at very high cost.

For these reasons, ^{206}Po was chosen as isotope for this study, since it is a γ-emitter facilitating its off-line detection in thermochromatography experiments. ^{206}Po can be obtained in carrier-free amounts in the chemical form of its solid solution in metals using the following two different procedures:

(1) Implantation of the precursor ^{210}Fr in molybdenum and gold samples at the CERN–ISOLDE facility: 98% of the ^{210}Fr decays via $EC/\beta^+ \rightarrow {}^{210}\text{Rn} \rightarrow \alpha \rightarrow {}^{206}\text{Po}$, while 2% of the ^{210}Fr decays via $\alpha \rightarrow {}^{206}\text{At} \rightarrow EC/\beta^+ \rightarrow {}^{206}\text{Po}$. The ^{210}Fr beams were obtained by 1.4 GeV proton-induced spallation of a 50 g cm^{-2} ^{238}UC target connected to a tungsten surface cavity ionizer. Both target and ion source were kept above 2273 K. The beam intensity of ^{210}Fr was about 6×10^7 ions per second, allowing implanting 3 kBq per minute. In the molybdenum and gold samples, up to 7×10^{10} and 9×10^{10} ^{210}Fr atoms were implanted, respectively. The advantage of this method consists in obtaining a pure carrier free sample.

(2) Irradiation of bismuth metal with a 40 MeV proton beam with up to 3 μA of intensity, according the nuclear reaction $^{209}\text{Bi}(p,4n)\,{}^{206}\text{Po}$.

The samples obtained via production path 1 were directly used for thermochromatography experiments. The polonium produced via production path 2 was separated from the bismuth matrix by evaporation at 1223 K under He flow and deposited at lower temperatures on Au foils. This pre-separation step was necessary to avoid that large amounts of bismuth are transported into the column during the thermochromatography experiment, complicating the interpretation of the obtained thermochromatogram. Even after performing this separation procedure, it is still not possible to state if polonium evaporated from the bismuth and deposited on Au as elemental Po or as BiPo.

2.2. Thermochromatography

The thermochromatography method is based on the adsorption interaction between a volatile species (atoms or molecules) and a stationary phase as a function of the temperature [12]. In particular, a radioactive species is desorbed from a starting phase and carried by a gas into a column placed in a negative temperature gradient. The transport of the species in the column depends on the temperature gradient and other experimental parameters such as gas flow, experiment time, free surface of the stationary phase, molecular weight and interaction of the desorbed species with the stationary surface. Depending on these parameters, the volatile species will be adsorbed in a specific range of the column that translates to a specific deposition temperature. Two transport scenarios are possible. Either, a chemical species is formed at the starting conditions and is preserved throughout the experiment. This leads, depending on the gas flow and temperature gradient, to rather sharp deposition peaks in the thermochromatograms. Or, in a second scenario, the tracer changes its chemical speciation in a superimposed chemical reaction equilibrium. This so-called transport reaction leads, depending on the reaction kinetics, to broader deposition patterns in the thermochromatograms. In this case, the deposition temperatures become dependent on partial pressures of the reactive gas involved in the chemical equilibrium reaction.

From the deposition pattern it is possible to calculate the adsorption enthalpy of the deposited species, using a Monte Carlo simulation method for gas chromatography [12]. Thus, sequences in adsorption interaction of different species obtained using different carrier gases (in the case of using reactive gases) are assessable. From the adsorption enthalpy, it is possible to calculate other thermodynamic parameters, such as the sublimation enthalpy, allowing for the identification of the deposited species [13]. In particular the sublimation enthalpy of the deposited species can be calculated with empirical correlations proposed e.g. in [14] between adsorption and sublimation enthalpy.

3. Experimental

The obtained samples were studied using a thermochromatography setup consisting of a fused silica tube, 5 mm inner diameter, (1 in Fig. 1) hermetically encapsulated in an Inconel® tube placed in a negative temperature gradient (in the direction of the carrier

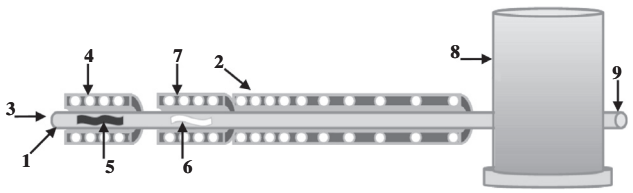

Fig. 1. Thermochromatography set-up: 1 – fused silica tube; 2 – negative gradient furnace; 3 – carrier gas inlet (He, H_2, O_2); 4 – getter furnace (1273 K); 5 – tantalum getter; 6 – sample; 7 – maximum furnace temperature (1220 or 1320 K); 8 – liquid nitrogen cryostat (77 K); 9 – carrier gas outlet.