International Journal of Mass Spectrometry 216 (2002) 203–208

www.elsevier.com/locate/ijms

Modelling isotope fractionation in thermal ionisation mass spectrometry filaments having diffusion controlled emission

H. Ramebäck*, M. Berglund, R. Kessel, R. Wellum

Institute for Reference Materials and Measurements, Commission of the European Communities-JRC, B-2440 Geel, Belgium

Received 5 February 2002; accepted 21 February 2002

Abstract

An isotope mass fractionation model for thermal ionisation mass spectrometry (TIMS) based on transport modelling of uranium in platinum was applied to filaments with diffusion controlled emission. The diffusivity of uranium in platinum at different temperatures was determined by fitting signal data from uranium measurements to the diffusion model. By combining these data, an activation energy and a frequency factor for the diffusion of uranium in platinum was obtained. These data were then used to predict the fractionation of uranium as a function of time, $K(t)$. The results from the model were compared with experimental fractionation data. A small and constant difference between the predicted and the experimental fractionation was observed. This residual K-factor (K_{res}) that the model did not account for was found to be 1.0055. (Int J Mass Spectrom 216 (2002) 203–208) © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Mass spectrometry; Uranium; Diffusion; Isotope fractionation; Modelling

1. Introduction

Isotope fractionation in mass spectrometry is a process that is not fully understood. However, to achieve both a high accuracy and a low uncertainty in mass spectrometric analysis, the magnitude of the fractionation must be well known. Usually the magnitude of the fractionation is obtained by measuring the ratio of two isotopes for a material with a certified isotopic ratio. This will give the magnitude of the fractionation, but it will provide no information on the processes taking place within the measurement system.

Basically, isotope fractionation in mass spectrometry is controlled either via an evaporation or a diffusion process. Gonfiantini et al. [1,2] modelled the gas inlet system in a gas mass spectrometer. They could predict the fractionation quantitatively for about 15 h of measurement. A fractionation model for an evaporation controlled process in thermal ionisation mass spectrometry was presented by Habfast [3]. Fractionation of methane in forest soil due to a diffusion process was described by Reeburgh et al. [4].

In this work, the diffusivity of uranium in platinum within a filament with a diffusion-controlled evaporation process was measured. Knowing the diffusion coefficient for the uranium isotopes in the system, the fractionation as a function of time can be calculated. The result of the fractionation from the model is compared with experimental data obtained by measuring the fractionation of uranium deposited on rhenium filaments covered with a platinum layer.

---

* Corresponding author. E-mail: henrik.ramebeck@irmm.jrc.be

PII S1387-3806(02)00591-2

2. Theory

A diffusion process can be described by Fick's second law of diffusion [5]. This diffusion equation can for the one-dimensional system be written as

$$\frac{\partial C_x}{\partial t} = D\frac{\partial^2 C_x}{\partial x^2} \tag{1}$$

where C_x is the concentration of the diffusing substance at distance x and D (m^2/s) is the diffusion coefficient of the diffusing substance. Here, D is assumed to be time-independent. For the geometry used in this work, the solution to Eq. (1) was given by Rec et al. [6]. The flux J at the surface L for the geometry valid in this work is

$$J(x = L, t) = \frac{2DS\pi}{L^2}\sum_{n=0}^{\infty}(n+1)(-1)^n \sin\frac{(n+1)\pi b}{L}\,\mathrm{e}^{-D(n+1)^2\pi^2 t/L^2} \tag{2}$$

where S the source term (number of atoms), L the total thickness of the source and b is the distance to the source from $x = 0$, see Fig. 1.

The K-factor for correction of mass fractionation in mass spectrometry is defined as

$$K = \frac{R}{r} \tag{3}$$

where R is the calibrated isotope amount ratio and r is the observed uncorrected ratio. Furthermore, the observed ratio is $r = I_1/I_2$ where I_1 is the intensity from isotope 1 and I_2 is the intensity from isotope 2. We now assume that there is no fractionation between the source (the filament) and the detector, i.e., $I_1 = J_1$ and $I_2 = J_2$. For uranium this gives

$$K_{\mathrm{source}}(t) = \frac{J_{238}(t)}{J_{235}(t)}R_{235/238} \tag{4}$$

In this equation, $K_{\mathrm{source}}(t)$ is the fractionation in the filament due to the diffusion process and $J_{238}(t)$ and $J_{235}(t)$ the fluxes of ^{238}U and ^{235}U atoms at the filament surface given by Eq. (2). The diffusivity of the diffusing species is one parameter in Eq. (2). In this work, the diffusivity of ^{238}U was obtained by fitting the model, Eq. (2), to experimental signal data. D_{235} was then calculated from [7]

$$D_{235} = D_{238}\sqrt{\frac{m_{238}}{m_{235}}} \tag{5}$$

The temperature dependence of the diffusion can be described with an Arrhenius expression

$$D(T) = D_0\,\mathrm{e}^{-E_a/RT} \tag{6}$$

where D_0 is the frequency factor, E_a the activation energy for the diffusion process and R is the universal gas constant.

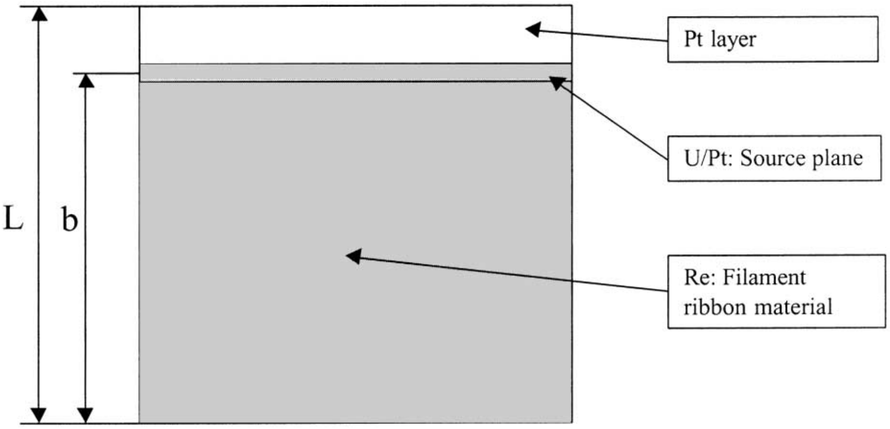

Fig. 1. Schematic picture showing the geometry of the modelled system.

3. Experimental

All TIMS measurements were performed with a modified version of a mass spectrometer originally developed at the National Bureau of Standards (NBS) [8], now National Institute of Standards and Technology (NIST). This TIMS instrument, known for its stability, has an analyser curvature of 30.5 cm and a deflection angle of 90°. Filaments with a diffusion-controlled emission were prepared by electrodeposition according to Perrin et al. [9]. Depending on signal strength, measurements were carried out in peak-jumping mode using either a Faraday detector or using a pulse counting system with an electron multiplier. The signal curves used for fitting the diffusivity of ^{238}U were obtained by measuring electroplated filaments loaded with the certified isotopic reference material (CRM) IRMM-184, whereas the *K*-factor measurements was done using the CRM IRMM-072/6. This material has a ^{235}U/^{238}U ratio close to 1 to rule out any major problem on the detector side when the pulse counting system was used although this system has been well characterised [10]. The geometry of the electroplated uranium/platinum was not optimised to the solution to the diffusion equation, Eq. (2). In the loading procedure used [9], uranium is first co-plated with platinum, and then a thicker layer of platinum is plated on top of the first layer. The thickness of the second layer of platinum is theoretically 2650 Å, whereas the thickness of the first uranium/platinum layer is about 1000 Å. In the calculations, the thickness of the source was assumed to be 3150 Å, i.e., half of the thickness of the first layer was added to the over-plated layer in the calculations.

4. Results and discussion

4.1. Diffusion modelling

The diffusivity of ^{238}U was determined at four different temperatures in the interval 1620–1710 °C. Experimental signal data at 1650 °C fitted to Eq. (2) are shown in Fig. 2 The diffusivity evaluated from this measurement was 1.17×10^{-17} m^2/s. The fit at 1710 °C is shown in Fig. 3. The Faraday detector was used in this measurement as well as in the experiment at 1680 °C. Pulse counting was used at lower temperatures. From this measurement a diffusivity of 5.55×10^{-17} m^2/s was evaluated. From data evaluated at different temperatures the activation energy for the diffusion of ^{238}U in platinum was found to be

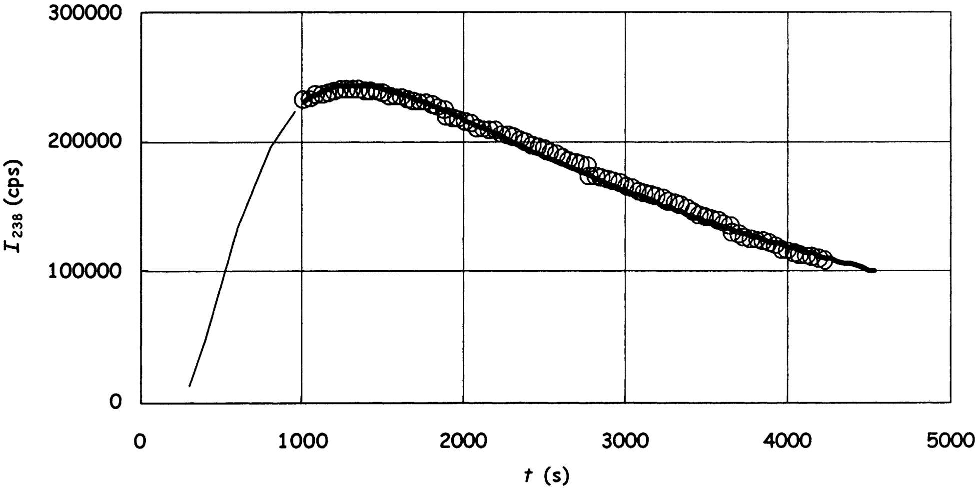

Fig. 2. Experimental and modelled data for the ^{238}U signal at $T = 1650\,^{\circ}$C.

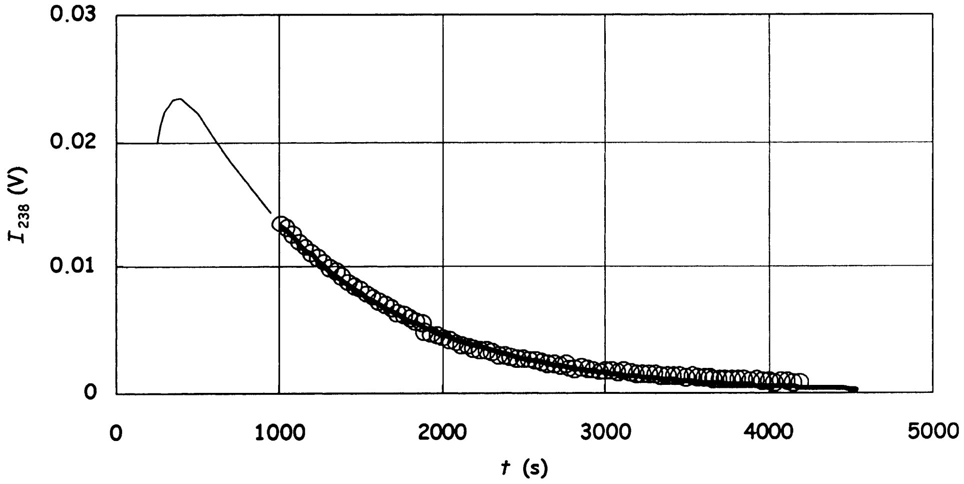

Fig. 3. Experimental and modelled data for the ^{238}U signal at $T = 1710\,^{\circ}$C.

827 ± 90 kJ/mol using Eq. (7). The Arrhenius plot is shown in Fig. 4. The evaluated Arrhenius expression for ^{238}U diffusion in platinum is then

$$D(T) = 3.33 \times 10^{5} \times e^{-827\times10^{3}/RT} \quad (7)$$

When extrapolating to $1/T = 0$ a frequency factor $D_0 = 3.33 \times 10^{5}$ m^2/s is obtained. However, the uncertainty will in this case be very high. To resolve this problem, the calculation of D at 1625 °C (the temperature for the experimental K-factor determination) was therefore instead done using

$$D(T) = 4.14 \times 10^{-17} \times e^{-827\times10^{3}/R(T-T_{\mathrm{ref}})} \quad (8)$$

where T_{ref} was set to 1700 °C. The uncertainty in the activation energy is the same, since it is characterised by the slope of the regression line shown in Fig. 4. The

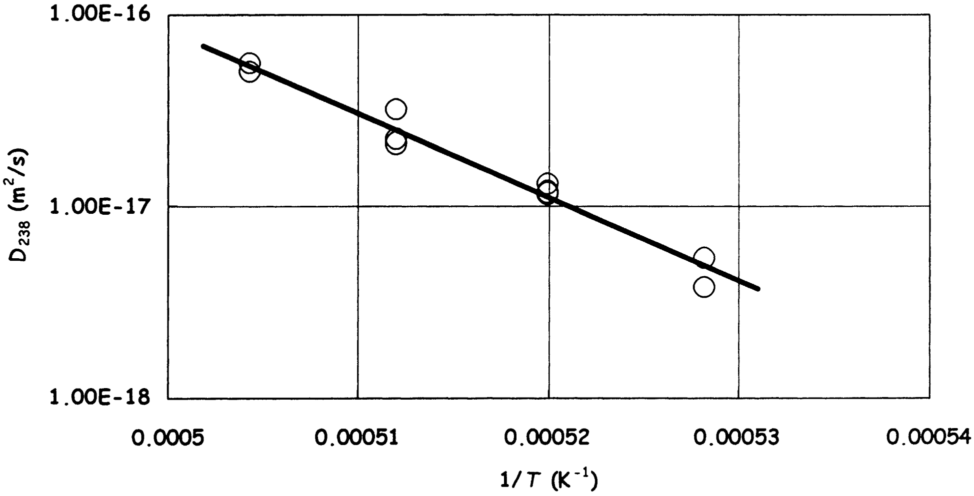

Fig. 4. Arrhenius plot for the diffusion of ^{238}U in platinum in the temperature interval studied. An activation energy of 827 ± 90 kJ/mol was evaluated from the slope.

value for the frequency factor in Eq. (8) is obtained by extrapolating to $1/(T - T_{\text{ref}})$. With this approach the uncertainty in the frequency factor for the diffusion process using Eq. (8) is much lower and about 15%.

4.2. Fractionation

The fractionation as a function of time, Eq. (4), was compared with experimental data obtained by measuring the amount ratio of the uranium isotope reference material IRMM-072/6 [11]. These measurements were performed at a temperature of 1625 °C. The experimental data are the average of four different measurements. Fig. 5 shows the experimental data together with the fractionation predicted by the model. A constant discrepancy of a factor of 1.0055 between the model and experimental data over 2 h of measurement could be observed (Fig. 6), i.e., if the total correction factor for fractionation during measurement as a function of time is written as

$$K_{\text{tot}}(t) = K_{\text{source}}(t)K_{\text{res}}(t) \tag{9}$$

where $K_{\text{res}}(t)$ is the residual fractionation, $K_{\text{res}}(t)$ is constant over the 2 h of measurement and equal to 1.0055. This residual correction factor is per mass unit in the same range as for silicon using a gas mass spectrometer [12]. The origin for this residual fractionation is not known. Fractionation from static (time independent) processes in TIMS is normally much smaller than fractionation from dynamic ones [3]. Examples of static processes within a mass spectrometer system are the ionisation on the surface of the filament and transmission in the ion optics. Fractionation due to different ionisation probabilities should be the same for different isotopes of the same element on a 10^{-5} level [13].

Sources which could cause in the residual deviation, apart from unknown fractionation processes, between model and experimental data are for example the correctness of the model, e.g., violation of boundary conditions, and the calculation of the diffusivity of ^{235}U using Eq. (5). Since this equation only is an approximation [7] it may contribute significantly to the observed deviation. Furthermore, the filament ribbon material is from rhenium, which means that the diffusion back into the filament ribbon is slightly different from that into the forward direction. However, no time-dependent deviation between experimental and

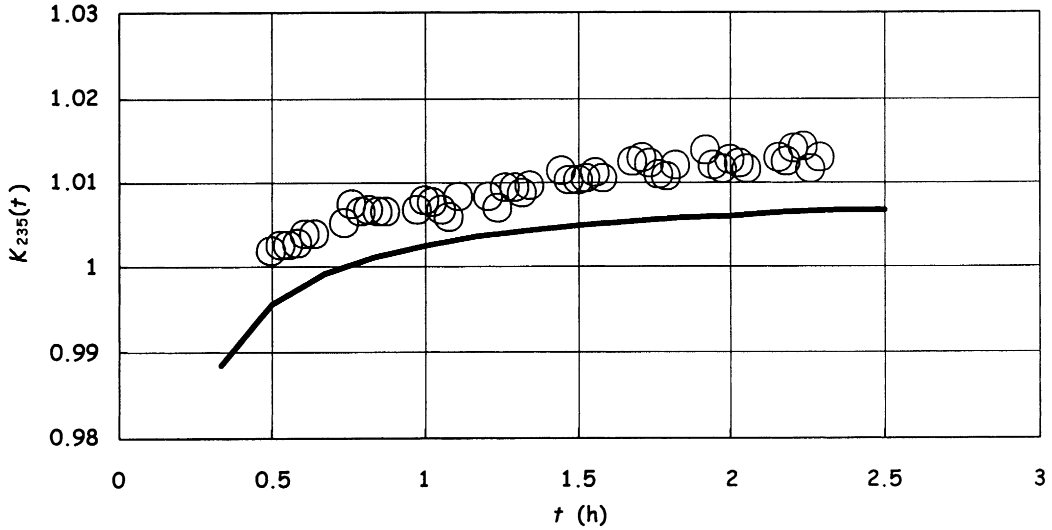

Fig. 5. Modelled and experimental K-factors vs. time for electro-deposited uranium filaments. The solid lines is the model (with upper and lower limits). The experimental data (circles) are the average of four different filaments with a standard uncertainty which is covered by the size of the circles. The experimental K-factor determinations were done at 1625 °C.

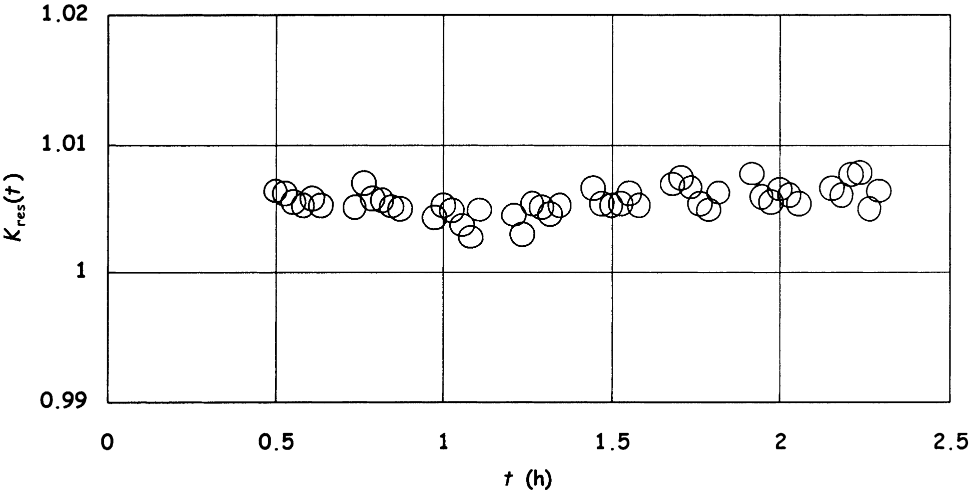

Fig. 6. Discrepancy between experimental data and the model.

modelled data could be seen, which indicates that the model can be used to predict the behaviour of the fractionation.

5. Conclusions

A model predicting fractionation in filaments with diffusion controlled emission for TIMS measurements was used successfully to predict the fractionation behaviour of uranium sources deposited on rhenium filaments and covered with a layer of platinum. A constant, but residual fractionation of about 1.0055 was observed. This residual fractionation could come from a combination of static discrimination processes within the mass spectrometer system.

Acknowledgements

The authors wish to thank Dr. Henrik Widestrand, Geosigma AB Kungälv Sweden, for valuable discussions on transport modelling.

References

[1] R. Gonfiantini, S. Valkiers, P.D.P. Taylor, P. de Bièvre, Int. J. Mass Spectrom. Ion Proc. 171 (1997) 231.
[2] R. Gonfiantini, S. Valkiers, P.D.P. Taylor, P. de Bièvre, Int. J. Mass Spectrom. Ion Proc. 163 (1997) 207.
[3] K. Habfast, Int. J. Mass Spectrom. 176 (1998) 133.
[4] W.S. Reeburgh, A.I. Hirsch, F.J. Sansone, B.N. Popp, T.M. Rust, Geochim. Cosmochim. Acta 61 (1997) 4761.
[5] J. Crank, The Mathematics of Diffusion, 2nd Edition, Oxford University Press, Oxford, 1975.
[6] J.R. Rec, W.G. Myers, F.A. White, Anal. Chem. 46 (1974) 1243.
[7] E.A. Mason, T.R. Marrero, The diffusion of atoms and molecules, in: D.R. Bates, I. Estermann (Eds.), Advances in Atomic and Molecular Physics, Academic Press, New York, 1970.
[8] W.R. Shields (Ed.), National Bureau of Standards (USA), Tech. Note no. 426, 1967.
[9] R.E. Perrin, G.W. Knobeloch, V.M. Armijo, D.W. Efurd, Int. J. Mass Spectrom. Ion Proc. 64 (1985) 17.
[10] H. Ramebäck, M. Berglund, D. Vendelbo, R. Wellum, P.D.P. Taylor, J. Anal. Atom Spectrom. 16 (2001) 1271.
[11] K.J.R. Rosman, W. Lycke, R. Damen, R. Werz, F. Hendrickx, L. Traas, P. De Bièvre, Int. J. Mass Spectrom. Ion Proc. 79 (1987) 61.
[12] P. de Bièvre, S. Valkiers, Metrologia 31 (1994) 245.
[13] P. de Bièvre, S. Valkiers, P.D.P. Taylor, Fresenius J. Anal. Chem. 361 (1998) 227.