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**Addendum to proposal P261 to the  
ISOLDE and Neutron Time-of-Flight Experiments Committee**

**Radiotracer diffusion in semiconductors and metallic  
compounds using short-lived isotopes**

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**Abstract**

A new diffusion chamber, which has been installed at ISOLDE and is ready to use since the beginning of the beam period 2011, enables the use of isotopes for radiotracer diffusion studies with half-lives down to several minutes. In 2011, however, most of the intended experiments using the new setup could not be performed due to several technical problems and only few exploratory experiments could be made in 2011. Thus, the present addendum to experiment IS489 will allow accomplishing the work of the running project, especially for experiments using the new diffusion chamber. In addition, new results on the diffusion of impurities in CdTe give rise for extending the corresponding investigations. In  $RIn_3$  compounds ( $R$  = rare earth element) diffusion processes can be investigated by perturbed  $\gamma\gamma$  angular correlation (PAC) on an atomic scale. Here, the motion of the atom of interest becomes visible directly via characteristic changes in the measured PAC spectra. Experiments using  $^{117}\text{Cd}/^{117}\text{In}$  in 2011 have established procedures for implanting and successfully annealing samples that are small enough to avoid significant source self-absorption. The goal for the next PAC experiments is to record spectra at elevated temperature to observe the atomic motion of the  $^{117}\text{In}$  atoms.

**Requested shifts:** 6 shifts, (split into 3-4 runs in 2012)



## 1. Introduction

Diffusion processes are of essential importance for metallurgy and doping of semiconductors as well. The first application of radioactive isotopes for diffusion experiments dates back to 1920, when radioactive Pb atoms were used for ‘tracer diffusion’ by G. v. Hevesey to study self diffusion in lead [1]. Nowadays, the wealth of short-lived isotopes delivered by ISOLDE extends substantially the possibilities of tracer-diffusion for investigating diffusion processes in solids. Diffusion experiments can also be performed on atomic scale if the motion of the respective species of atoms is detected locally. Such investigations are accessible with help of hyperfine techniques like the perturbed  $\gamma$ - $\gamma$  angular correlation (PAC) spectroscopy. In semiconductors the understanding and the control of diffusion profiles of intrinsic and extrinsic defects is of central importance for developing electronic and optoelectronic devices with reduced structural sizes. At temperatures required for crystal growth and device processing, intrinsic point defects, like vacancies and self-interstitials, are highly mobile and can interact with extrinsic point defects, like dopant atoms. Common to most diffusion profiles in semiconductors reported so far is the monotonously decreasing concentration depth profile if the source of the diffusing species is located at the surface of the crystal and the diffusion length is small compared to the thickness of the crystal. However, in compound semiconductors large concentrations of intrinsic point defects can be achieved by inducing deviations from stoichiometry in the respective material. By exposing a compound semiconductor to the vapor pressures of one of its constituents, variations of the deviation from stoichiometry of the compound crystal as a function of depth and time can result in concentration gradients of intrinsic point defects, which can drastically influence the diffusion of dopants, leading to anomalous diffusion profiles [2]. The uphill diffusion profiles observed can be well described by the interaction of the dopant atoms with intrinsic defects considering in addition the charge states of all participating defects [3].

Tri-indides formed with rare earth elements like La or Ru have a  $L1_2$  or  $Cu_3Au$  structure. The crystal structure has a face centered cubic arrangement with the rare earth atoms at corners and In atoms at face centers of the unit cell. These intermetallic compounds are “line compounds”, that is, intermediate phases appear as vertical lines in binary phase diagrams [4]. All PAC measurements performed on the indides  $RIn_3$  ( $R$  = rare earth element) until 2011 have used the probe atom  $^{111}In/^{111}Cd$  [5,6]. That means, the diffusion on the In-sublattice, which is observed locally by detecting the hyperfine interaction at the  $^{111}Cd$  daughter is not the diffusion of In but of Cd. An impurity Cd atom on the In-sublattice causes a local lattice distortion which might lead to an attractive or repulsive interaction with neighboring In-vacancies. This could influence thermodynamic properties such as the jump-frequency itself. While the phase  $In_3La$  appears as a line compound in the phase diagram, its phase field must have finite width, however small. PAC measurements were performed using  $^{111}In/^{111}Cd$  on samples purposely prepared to have the two, opposing phase boundary compositions. Even though the compositions differ by only about 0.1 at%, jump frequencies were observed to be 10-100 times greater at the more In-rich phase boundary than at the less In-rich boundary [6]. We proposed to use the PAC probe  $^{117}Cd/^{117}In$  to perform jump-frequency measurements in tri-indides formed with La, Ce, Pr, Nd, Gd, Er and Y. With this probe, it is the diffusion jumps of the daughter  $^{117}In$  atoms that are observed. Such a measurement is analogous to a “self-diffusion” study in which the intrinsic behavior of the pure compound is measured.

## 2. Present results

In the period 2009 – 2011 tracer diffusion experiments have been performed in CdTe using radioactive isotopes of the elements Ag, Cu, Au, Pt, Co, Ni, and Pd. For all these experiments the CdTe crystals have been sectioned by mechanical polishing since the investigated diffusions profiles extended over distances of more than 20  $\mu\text{m}$ . In case of Ni diffusion in CdTe a new unexpected result has been obtained (see Fig. 1). Based on an earlier investigation of Ni and Co diffusion in CdZnTe a box-shaped profile has been expected also for Ni in CdTe [7]. In contrast, for Ni an uphill diffusion profile was observed, similar to diffusion profiles exclusively known up to now for group I elements. In case of Ag diffusion in CdTe new results regarding the influence of evaporated metal layers have been obtained. For the case of an evaporated Cu layer conditions have been found causing an extremely strong push effect on the previously implanted  $^{111}\text{Ag}$  dopant (Fig. 2) that results in a shift of the whole Ag concentration profile by 400  $\mu\text{m}$  away from the implanted surface.

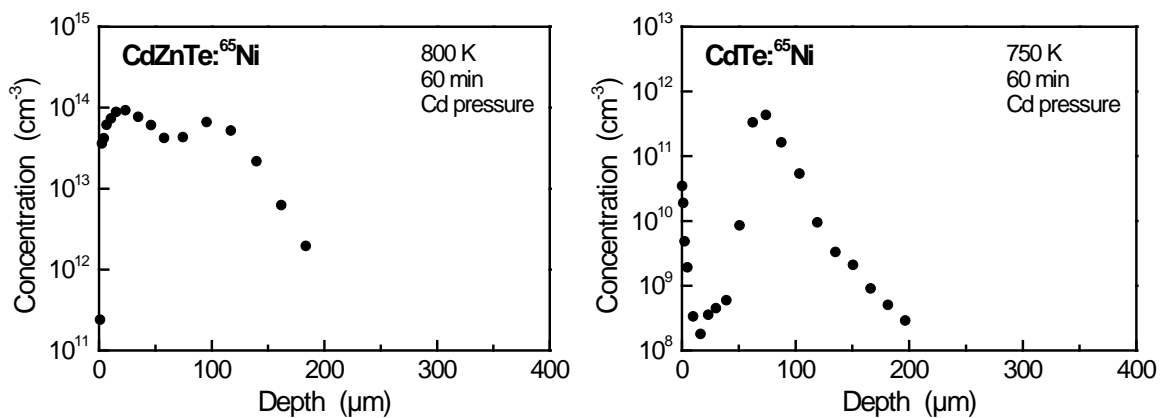


Fig. 1: Diffusion profiles of  $^{65}\text{Ni}$  in CdZnTe and CdTe. While in CdZnTe a box-shaped profile is observed the diffusion profile in CdTe shows uphill diffusion.

The new diffusion chamber is available at ISOLDE since the beginning of the beam period 2011. However, no real “on-line” diffusion experiments could be made for different reasons. Firstly, some technical problems required small modifications of the setup, which could not be made “on site” during actual beam times. Secondly, it turned out that a parallel use of the central beam line together with long-time experiments at the HRS separator is not suitable for using the diffusion chamber in on-line operation. Nevertheless, a few experiments were made in “off-line” operation, i.e. the

implantation of the radiotracer was performed externally in conventional way, but thermal treatment, sectioning of the sample and measuring the  $\gamma$ -irradiation of the sputtered layers have been performed in the diffusion chamber. In the framework of these experiments the capabilities of the new setup was demonstrated. In addition, it could be estimated that the appli-

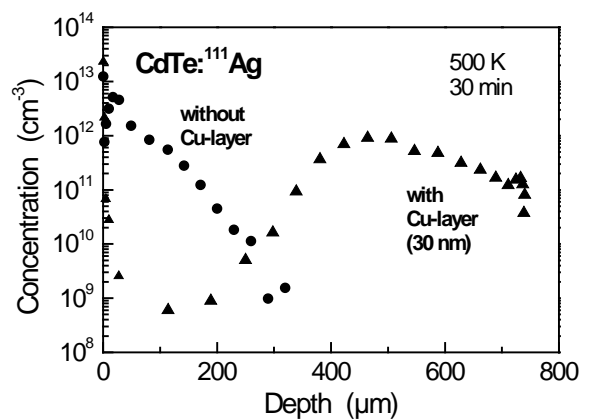


Fig. 2: Diffusion of  $^{111}\text{Ag}$  in CdTe under the influence of an evaporated Cu-layer (triangles) compared to the diffusion without Cu-layer (circles).

cation of isotopes with half-lives down to 20 min should not be a problem and even the use of the isotope  $^{29}\text{Al}$  with a half-life of only 6.6 min seems to be realistic.

The goal of PAC experiments using the  $^{117}\text{Cd}/^{117}\text{In}$  probe in  $\text{RIn}_3$  compounds (R = rare earth element) is to make measurements between 425 and 1200 K, at which temperatures damping of the hyperfine interaction due to diffusion of the PAC probe  $^{117}\text{In}$  is expected to be observed. This would provide the most direct observation of atomic jumps associated with self diffusion mediated by a vacancy diffusion process to date. Good progress toward reaching this goal was made in 2011 using the  $^{117}\text{Ag}$  beam. First PAC measurements of the quadrupole hyperfine interaction detected by  $^{117}\text{In}$  in  $\text{LaIn}_3$  and in  $\text{LuIn}_3$  were recorded. The quadrupole coupling constants of  $^{117}\text{In}$  were found to be  $\nu_Q = 166.4(2)$  MHz in  $\text{LaIn}_3$  and  $\nu_Q = 163.35(9)$  MHz in  $\text{LuIn}_3$ . These values are consistent with predictions made subsequently using density functional theory. Example spectra are shown in Fig. 3.

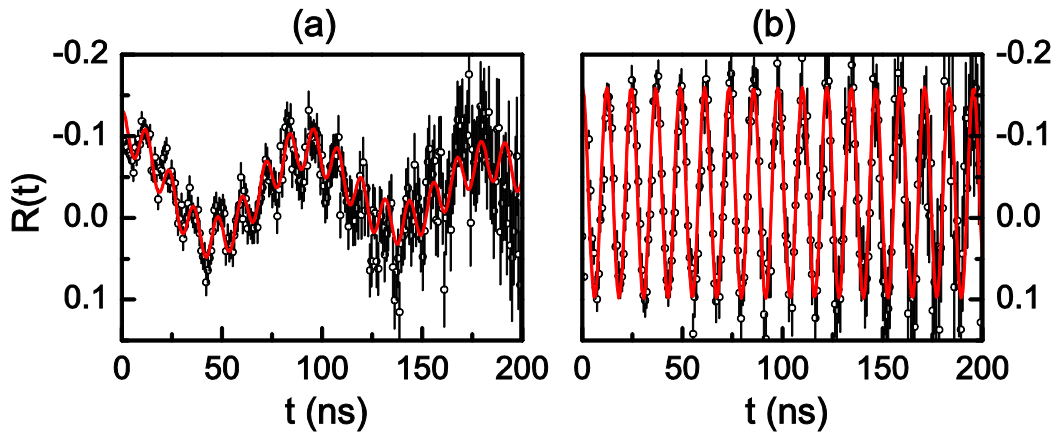


Fig. 3: PAC spectra using  $^{117}\text{In}$  obtained from two different samples: (a) two-phase mixture of pure In and  $\text{In}_3\text{La}$  and (b)  $\text{In}_3\text{Lu}$ .

Publications resulting from experiment IS489 are listed in the reference section of this addendum

### 3. Proposed experiments

#### 3.1 Impurity diffusion in CdTe on short length scales

Uphill diffusion should not be restricted to diffusion profiles extending over length scales of several 100  $\mu\text{m}$  as it is the case in most experiments performed up to now. With help of the new diffusion chamber the investigations of the phenomenon of uphill diffusion in CdTe will be investigated on much shorter length scales of only a few  $\mu\text{m}$ . This enables the investigation of uphill diffusion also for slow diffusing elements like Mn, Fe, and K, which diffuse in CdTe a few  $\mu\text{m}$  at suitable temperatures, i.e. below 800 K. In addition, in CdTe the uphill diffusion or other unusual diffusion effects of donor elements like In or Cl will be investigated. Because of the expected short diffusion lengths of these donor dopants such investigations are only possible by using the sputter technique for sectioning installed in the new diffusion chamber. It should be noted that the diffusion experiments applying the technique of mechanical polishing are restricted to diffusion profiles on length scales of more than 20  $\mu\text{m}$ .

### 3.2 Influence of metal layers on impurity diffusion in CdTe

The most prominent effect of uphill diffusion in CdTe induced by evaporated metal layers up to now is found for the combination Ag dopant and Cu layer (Fig. 2). The effect, however, is not restricted to evaporated Cu-layers but is also observed for Au, Ni, and Al, up to now. Since the most interesting case seems to be the effect of an evaporated Cu-layer on the Ag diffusion, this case will be investigated in more detail as a function of diffusion temperature and the stoichiometric initial condition of the CdTe crystal used. For the dopants Cu and Au up to now only weak effects of metal layers on their diffusion has been observed. Since there is no obvious reason for the absence of a similar effect as observed in case of Ag, it might be related to improper conditions of diffusion temperature and diffusion time in the present experiments. The investigations of the influence of evaporated metal layers on the diffusion of Cu and Au will be continued for different conditions, like diffusion temperature and diffusion time.

### 3.3 Self diffusion of Al atoms in Al and in Al compounds

The proposed investigation of the self diffusion in Al and Al compounds could not be performed up to now due to the technical and organizational problems by using the new diffusion chamber mentioned above. From the experiences gathered during the experiments performed in the off-line operation in 2011 it can be estimated that it is realistic to make diffusion experiments with the  $^{29}\text{Al}$  isotope having a half-life of only 6.6 min. It is intended, therefore, to start experiments on the investigation of self diffusion in Al. For these experiments the on-line operation of the diffusion chamber is indispensable.

### 3.4 Indium diffusion in tri-indides with (A<sub>3</sub>B) structure

The significance of the results achieved in 2011 is that a procedure for implanting and successfully annealing samples that are small enough to avoid significant source self-absorption due to the low  $\gamma$ -energy of  $^{117}\text{In}$  was established. The goal of the next experiments using the  $^{117}\text{Cd}/^{117}\text{In}$  probe is to perform PAC measurements using  $^{117}\text{Cd}/^{117}\text{In}$  on  $\text{In}_3\text{La}$  and  $\text{In}_3\text{Ru}$  at elevated temperature to observe damping due to atomic motion. This will allow the direct observation of atomic jumps associated with self diffusion in these compounds.

#### Summary of requested shifts

Target	RILIS	Isotope(s)	Diffusion experiment
UC <sub>x</sub>	LIS (Mn)	$^{56}\text{Mn}$ , $^{59}\text{Fe}$ , $^{61}\text{Co}$	DC, MP
UC <sub>x</sub>		$^{24}\text{Na}$ , $^{43}\text{K}$ , $^{29}\text{Al}$	DC, MP
TaNb		$^{38}\text{Cl}$	DC
ZrO UC <sub>x</sub>	LIS (Cu)	$^{61}\text{Cu}$ $^{64}\text{Cu}$ , $^{67}\text{Cu}$	MP
Pb		$^{192}\text{Hg}/^{192}\text{Au}$	MP
UC <sub>x</sub>	LIS (Ag)	$^{111}\text{Ag}$ , $^{117}\text{Ag}/^{117}\text{Cd}$	DC, MP, PAC

The great advantage of many of the beams required for this proposal is that they can be “shared” with other experiments. Typical collections for diffusion experiments in most cases need less than 1 hour after which the beam can be given to other users for gaps of often 1 shift or more. The total number of shifts requested is estimated to 6 and is distributed over the different isotopes as shown in the table. The experiments use either the new diffusion chamber (DC), the setup for mechanical polishing (MP), or the PAC spectrometer. It would be appreciated if the accelerating voltage could be 60 kV.

## References

- [1] J. Groh and G. v. Hevesey, *Ann. d. Phys.* **65**, 218 (1920).
- [2] H. Wolf, F. Wagner, Th. Wichert, and ISOLDE Collaboration, *Phys. Rev. Lett.* **94**, 25901 (2005).
- [3] H. Wolf, J. Kronenberg, F. Wagner, Th. Wichert, and Isolde Collaboration, *Phys. Status Solidi B* **247**, 1405 (2010).
- [4] T.B. Massalski (ed.), *Binary alloy phase diagrams* (ASM International, Materials Park, OH, 1990).
- [5] M.O. Zacate, A. Favrot, and G.S. Collins, *Phys. Rev. Lett.* **92**, 225901 (2004); and *Erratum*, *Phys. Rev. Lett.* **93**, 49903 (2004).
- [6] G.S. Collins, A. Favrot, L. Kang, D. Solodovnikov, and M.O. Zacate, *Defect Diff. Forum* **237–240**, 195 (2005).
- [7] H. Wolf, F. Wagner, J. Kronenberg, Th. Wichert, and ISOLDE Collaboration, *Defect and Diffusion Forum* **289-292**, 587 (2009).

## Publications related to IS489

H. Wolf, J. Kronenberg, F. Wagner, Th. Wichert, and Isolde Collaboration, *Pre-requisites for the formation of unusual diffusion profiles in II-VI semiconductors*, *Phys. Status Solidi B* **247**, 1405 (2010).

H. Wolf, F. Wagner, J. Kronenberg, Th. Wichert, and ISOLDE Collaboration, *On the formation of the unusual diffusion profiles in  $Cd_xZn_{1-x}Te$  crystals after implantation of different elements*, *Defect and Diffusion Forum* **289-292**, 587 (2009).

H. Wolf, J. Kronenberg, F. Wagner, M. Deicher, Th. Wichert, and ISOLDE Collaboration, *Shift of Ag diffusion profiles in CdTe by metal/semiconductor interfaces*, *Appl. Phys. Lett.*, submitted.

## Appendix

### DESCRIPTION OF THE PROPOSED EXPERIMENT

The experimental setup comprises: *(name the fixed-ISOLDE installations, as well as flexible elements of the experiment)*

Part of the Choose an item.	Availability	Design and manufacturing
SSP-GLM	<input checked="" type="checkbox"/> Existing	<input checked="" type="checkbox"/> To be used without any modification
On-line diffusion chamber in the ISOLDE hall	<input checked="" type="checkbox"/> Existing	<input checked="" type="checkbox"/> To be used without any modification <input type="checkbox"/> To be modified
Annealing furnaces in building 115	<input checked="" type="checkbox"/> Existing	<input checked="" type="checkbox"/> To be used without any modification <input type="checkbox"/> To be modified
Ge detector and polishing setup in building 115	<input checked="" type="checkbox"/> Existing	<input checked="" type="checkbox"/> To be used without any modification <input type="checkbox"/> To be modified
PAC setups in building 115	<input checked="" type="checkbox"/> Existing	<input checked="" type="checkbox"/> To be used without any modification <input type="checkbox"/> To be modified

### HAZARDS GENERATED BY THE EXPERIMENT

*(if using fixed installation)* Hazards named in the document relevant for the fixed **SSP-GLM chamber, on-line diffusion chamber and building 115 installations.**

Additional hazards:

Hazards			
	SSP-GLM	On-line diffusion chamber	Building 115
<b>Thermodynamic and fluidic</b>			
Pressure	[pressure][Bar], [volume][l]		
Vacuum	10 <sup>-6</sup> mbar at SSP chamber during collections	<10 <sup>-6</sup> mbar at diffusion chamber collections and measurements	
Temperature	Room temperature	400-1200 K during annealing	400-1200 K during annealing, up to 1200 K during PAC measurements.
Heat transfer			
Thermal properties of materials			
Cryogenic fluid			Liquid nitrogen, 1 bar, few litres used during the PAC measurements in appropriate glass dewar.
<b>Electrical and electromagnetic</b>			
Electricity	[voltage] [V], [current][A]		
Static electricity			
Magnetic field	[magnetic field] [T]		
Batteries	<input type="checkbox"/>		
Capacitors	<input type="checkbox"/>		
<b>Ionizing radiation</b>			
Target material	[material]		
Beam particle type (e, p, ions, etc)			
Beam intensity			
Beam energy	60kV (desired)	60kV (desired)	
Cooling liquids	[liquid]		

Gases	[gas]		O <sub>2</sub> , H <sub>2</sub> , Ar
Calibration sources:	<input type="checkbox"/>		
• Open source	<input checked="" type="checkbox"/>	All sources (see isotope list) are produced at ISOLDE and measured at different locations: <i>ODC: on-line diffusion chamber</i> <i>B115: Building 115</i> <i>Home: shipped to home institute</i>	
• Sealed source	<input checked="" type="checkbox"/>		22Na sources provided by RP services at CERN, used at building 115
• Isotope			
• Activity			
Use of activated material:			
• Description	Removal from chamber, transported to building 115 in standard Pb castle shielding.	Implanted, annealed and measured in situ in online diffusion chamber.	Annealed for 10-30 min at temperatures up to 1200 K in the furnaces in building 115. Measured either by PAC or the diffusion set-up in building 115.
• Dose rate on contact and in 10 cm distance	[dose][mSV]		
• Isotope	24Na (15 h)	measured at:	ODC, B115
	29Al (7 m)		ODC
	38Cl (37 m)		ODC
	43K (22.3 h)		B115
	56Mn (2.6 h)		ODC, B115
	59Fe (44.5 d)		B115, Home
	61Co (1.7 h)		ODC
	61Cu (3.3 h)		ODC, B115
	64Cu (12.7 h)		B115
	67Cu (61.8 h)		Home
	111Ag (7.5 d)		Home
	117Cd (2.5 h)		B115
	192Hg(4.9 h)		B115
• Activity	Activity per sample: 24Na (15 h) < 1 MBq 29Al (7 m) < 100 MBq 38Cl (37 m) < 10 MBq 43K (22.3 h) < 1 MBq 56Mn (2.6 h) < 1 MBq 59Fe (44.5 d) < 0.1 MBq 61Co (1.7 h) < 1 MBq 61Cu (3.3 h) < 1 MBq 64Cu (12.7 h) < 1 MBq 67Cu (61.8 h) < 1 MBq 111Ag (7.5 d) < 1 MBq 117Cd (2.5 h) < 10 MBq 192Hg(4.9 h) < 1 MBq		
<b>Non-ionizing radiation</b>			
Laser			
UV light			
Microwaves (300MHz-30 GHz)			
Radiofrequency (1-300MHz)			
<b>Chemical</b>			
Toxic	[chemical agent], [quantity]		



Harmful	[chemical agent], [quantity]		Acetone (ICSC: 0087), ethanol (ICSC: 0044) and methanol (ICSC: 0057). Less than few centilitres per chemical, used on cleaning samples on ventilated fume hood on building 115. The respective ICSC forms have been printed and will be handled during preparation and experiments.
CMR (carcinogens, mutagens and substances toxic to reproduction)	[chemical agent], [quantity]		
Corrosive	[chemical agent], [quantity]		
Irritant	[chemical agent], [quantity]		
Flammable	[chemical agent], [quantity]		
Oxidizing	[chemical agent], [quantity]		
Explosiveness	[chemical agent], [quantity]		
Asphyxiant	[chemical agent], [quantity]		
Dangerous for the environment	[chemical agent], [quantity]		
<b>Mechanical</b>			
Physical impact or mechanical energy (moving parts)	[location]		
Mechanical properties (Sharp, rough, slippery)	[location]		
Vibration	[location]		
Vehicles and Means of Transport	[location]		
<b>Noise</b>			
Frequency	Ambient noise at the ISOLDE Hall building 170	Ambient noise at the ISOLDE Hall building 170	
Intensity	Ambient noise at the ISOLDE Hall building 170	Ambient noise at the ISOLDE Hall building 170	
<b>Physical</b>			
Confined spaces	[location]		
High workplaces	[location]		
Access to high workplaces	[location]		
Obstructions in passageways	[location]		
Manual handling	All samples and sample holders are manually handled either by long tweezers to insert and extract the sample holder into and out of the SSP implantation chamber at GLM, or when manipulating the samples and sample holders inside glove boxes or fume houses in building 115 R-007.	All samples and sample holders are manually handled either by long tweezers to insert and extract the sample holder into and out of the on-line diffusion chamber, or when manipulating the samples and sample holders inside glove boxes or fume houses in building 115 R-007.	
Poor ergonomics	[location]		

### 3.1 Hazard identification

3.2 Average electrical power requirements (excluding fixed ISOLDE-installation mentioned above): *(make a rough estimate of the total power consumption of the additional equipment used in the experiment).*

There is no additional equipment with relevant power consumption on these small-scale experiments