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DEPARTMENT OF PHYSICS

MASTER THESIS

Negative Ion Source Development and Photodetachment Studies at ISOLDE

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December 2017



Abstract

Astatine is one of the rarest elements on earth. The small amount of existing astatine is either created in decay chains of heavier elements or artificially. One of its longer lived isotopes, ^{211}At , is of interest for targeted alpha therapy, a method of treating cancer by using the alpha decay of radioactive elements directly at the location of a tumor. However, its chemical properties are yet to be determined due to the short life time of astatine.

A milestone towards the determination of the electronegativity of astatine was the measurement of its ionization potential (IP) at CERN-ISOLDE. However, its electron affinity (EA, the binding energy of the additional electron in a negative ion), is still to be measured.

In order to determine the EA of radioisotopes by laser photodetachment spectroscopy, the Gothenburg ANion Detector for Affinity measurements by Laser Photodetachment (GANDALPH) has been built in recent years. As a proof-of-principle, the EA of the ^{128}I negative ion, produced at the CERN-ISOLDE radioactive ion beam facility, was measured. This was the first ever photodetachment measurement of a radioactive isotope.

During those first campaigns, it was evident that the astatine experiment would not be successful under the current conditions. In this thesis, steps are taken to address the issues from two sides: Increase the ionization efficiency of elements with low electron affinity by finding new low work function materials and improving the GANDALPH beam-line.

For the negative ion source development, a dedicated ion source test stand was conceived and constructed. Candidates for new ion source materials were determined via x-ray diffraction. The electron emission of the samples were investigated and compared to the standard source material, LaB_6 , as a benchmark. Second, several upgrades to improve the beam tuning capabilities of the GANDALPH beam-line were implemented. A dedicated negative ion source was conceived and constructed which was used for off-line testing and fine-tuning of the neutral atom detector, as well as the electrostatic elements in the beam-line. These results will be presented and the feasibility to conduct an EA measurement of astatine will be discussed.

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1 Introduction

Astatine is the rarest naturally occurring element on earth with an estimated total abundance of 70 mg [1]. The element has no stable isotopes but decays to bismuth, polonium or radon [2]. The little amount of natural astatine on earth is due to its presence in some decay chains of heavier elements. One of its longer-lived isotopes, ^{211}At , which has a half life of about 7.2 hours is of interest for targeted alpha therapy (TAT) [2, 3, 4]. TAT is a method which is used to treat cancer by delivering radioactive isotopes precisely to the tumor cells which are then damaged by the alpha particles resulting from the decay of the isotope. This is done by binding a suitable radioactive isotope to a carrier targeting agent which specifically attaches to the cancer cells [4]. In that way even small tumors can be treated with a minimum amount of damage to the surrounding healthy tissue. ^{211}At is a promising candidate for this kind of treatment for multiple reasons: every decay of ^{211}At is associated with the emission of an alpha particle, either directly to ^{207}Bi or with an electron capture to ^{211}Po . Both ^{207}Bi and ^{211}Po decay to stable ^{207}Pb , ^{211}Po with a half life of 520 ms via alpha decay. Compared to other candidates for TAT, this decay chain minimizes the harm to the healthy tissue. As an example, the other long-lived astatine isotope, ^{210}At , decays into ^{210}Po , known for its use in killing the russian Alexander Litvinenko in 2006 [5]. Additionally, ^{211}At is expected to be compatible with a wide variety of potential cell-specific targeting agents using either its halogenic or metallic properties [2].

To be able to chemically bind astatine to a molecule, one has to gain insight in its chemical properties such as its electrophilicity, hardness and specifically its electronegativity, since this is what determines how it forms the chemical bonds [6]. This is difficult since only minute amounts of ^{211}At , obtained from artificial production, are available. In order to support chemists, these properties can be determined via quantum chemical calculations [7].

In order to verify these calculations, some basic properties of astatine have to be known, such as the electron affinity (EA) and the ionization potential (IP). The IP is the energy required to remove the valence electron, thereby creating a positive ion. The EA is the binding energy of the additional electron in a negative ion. Both values are linked to the redox potential of astatine in solution [7, 3] and enable the calculation of its electronegativity.

A first milestone towards the determination of the electronegativity of astatine was achieved with the measurement of its ionization potential, which was determined to be 9.31751(8) eV at CERN-ISOLDE [8].

The next step towards a determination of the electronegativity of astatine is to measure the electron affinity of astatine which is predicted to be 2.4 eV [9]. In order to investigate astatine experimentally it has to be produced artificially due to its rarity and investigated

rapidly within a short time after its creation because of its short half-life. ^{211}At can be produced as a spallation product of a heavy target irradiated with a beam of high-energetic alpha particles [2]. At ISOLDE negative At beams have been produced with ThO or UCx as target materials by proton induced spallation reactions [10].

The measurement of the electron affinity of a negative ion is typically performed via laser photodetachment spectroscopy [11]. Here, negative ions are neutralized by interacting with a laser beam of suitable photon energy, which is typically in the infra-red or visible of the electromagnetic spectrum. By tuning the laser frequency, the photodetachment threshold energy and thereby the electron affinity, can be determined.

Negative ions are generally very fragile systems. Due to the screening of the Coulomb potential, the binding of the additional electron is dominated by an induced dipole potential resulting from the additional electron. Hence, the electron correlation of the system is crucial for the stability of a negative ion. Thus, electron affinities are typically in the order of a few electron volt.

In order to create negative ions one needs a suitable ion source. Negative ions are difficult to create and sustain since they are easily destroyed through particle collisions [12, 13]. Usually negative ions are created using an electron donor material with a work function lower than the electron affinity of the desired negative ion in a hot environment. This can be achieved in multiple ways such as sputtering of the positively ionized low work function material onto a cathode of the desired negative ions or by surface ionization on a hot low work function surface. Since the difference between work function and electron affinity is one of the key factors which determines the ionization efficiency [14] at a given temperature, low work function materials are required. Other factors are the possibility of destruction through collisions and chemical or electrical trapping inside the source.

The Gothenburg ANion Detector for Affinity measurements by Laser PHotodetachment (GANDALPH) was built in previous years at Gothenburg and CERN [15] for the purpose of measuring the EA of radioactive isotopes. The first attempts to measure the electron affinity of astatine with GANDALPH were made in previous years [16], but it was evident that the astatine experiment would not be successful under the current conditions. The main problem being an insufficient astatine ion beam current, resulting in difficulties to tune the beam and perform measurements with GANDALPH. However, it was possible to measure the electron affinity of a radiogenic isotope, ^{128}I , for the first time [15].

In this thesis, the problem of the low ion beam currents for elements with low electron affinity such as astatine is addressed from two sides: developments towards increasing the production efficiency of such elements shall be initiated and the sensitivity of the GANDALPH detector setup is improved.

Further, a dedicated off-line negative ion source has been designed and coupled to the GANDALPH beamline. This enables testing and fine-tuning of the GANDALPH beam-line, preparing the setup for the upcoming on-line experiments at ISOLDE.

As a first step towards the improvement of the production efficiency of the negative surface ion source at ISOLDE, new low work function materials are investigated and compared to the currently used lanthanum hexaboride (LaB_6). The synthesis of a

promising candidate, strontium vanadate (SrVO_3) with a predicted work function of 1.73 eV [17, 18] was attempted and the produced sample phases identified and also tested against LaB_6 . For these tests, a dedicated test stand was conceived and constructed. The setup consists of a vacuum chamber able where a standard ISOLDE target unit can be coupled with the main features being an ion extraction system that allows monitoring the total beam current and a residual gas analyzer to monitor ion source degradation and outgassing. The test stand was used to investigate the electron emission benchmark of the work function of new materials against LaB_6 . This test-stand will also enable a program aiming for testing and long-term performance of ion sources, which will give valuable insight into operational limits and optimal conditions for on-line use.

Both, the updates of the GANDALPH beam line and the development of the negative surface ion source are leading towards the measurement of the EA of astatine planned to take place at CERN-ISOLDE.

2 Fundamentals

In this chapter, a brief discussion of the key concepts of negative ions and their production process as well as negative ion sources, will be given. A good overview of the field is given in [13] and [12].

2.1 Negative ions

Negative ions are atoms or molecules with an additional electron, so that their net charge is negative. In neutral atoms and positive ions, electrons are bound by attraction from the nucleus. For a negative ion though, the Coulomb force for the outermost electron at a large distance is screened. The binding therefore depends on a polarization effect: similar to Van-der-Waals binding in neutral atoms. The electric field of the incident electron can induce a polarization of the charge cloud in the atom, which creates a dipole potential which binds the additional electron. The binding energy of a negative ion is called electron affinity (EA) and is given by

$$EA(A) = E_{ground}(A) - E_{ground}(A^-), \quad (2.1)$$

where $E_{ground}(A; A^-)$ are the ground states of the neutral atom A and the negative ion A^- respectively. An energy scheme of an negative ion and its neutral atom is shown in figure 2.1.

The short-range dipole potential scales as r^{-4} (r being the distance between nucleus and electron) and is therefore much weaker than the Coulomb potential in atoms and positive ions which scales as r^{-1} . This makes negative ions a more fragile system than positive ions.

While the Coulomb potential supports an infinite number of bound states converging to the ionization potential, the more shallow induced dipole potential usually supports only a single bound state, as depicted in figure 2.1. However, some negative ions show a variety of quasi-bound excited states in the continuum above the detachment threshold which results from excitations of more than one electron. These states are usually short lived and decay via the autodetachment process. There are only three elements where there are bound excited states with a parity opposite to the ground state. These elements are Os, Ce and La [19, 20, 21, 22, 23].

2.1.1 Wigner law and photodetachment

One of the most precise ways to determine the electron affinity of an element is by the laser photodetachment threshold spectroscopy method [24]. Here, a tunable laser beam

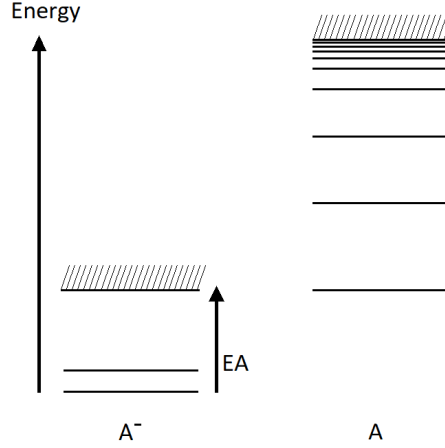


Figure 2.1: Energy diagram of the bound states of a negative ion and its neutral atom.

is superimposed on a beam of negative ions. If the photon energy $h\nu$ is equal or greater than the electron affinity of the negative ion A^- , the ion can be neutralized and either the neutral particle or the detached electron can be detected:



The cross-section σ of the detachment process in the threshold region is described by the Wigner threshold law

$$\sigma \propto k^{2l+1}, \quad (2.3)$$

where σ is the cross section, k the linear momentum and l the orbital angular momentum of the detached electron [25]. Written in terms of energy one can deduce

$$\sigma(E) \propto (E_{ph} - E_{thr})^{l+\frac{1}{2}}, \quad (2.4)$$

where $E_{ph} = \hbar\omega$ is the energy of the photon, E_{thr} the threshold energy necessary to detach the electron and l the orbital angular momentum quantum number of the emitted electron.

Due to the electric dipole transition rules, the angular momentum of the detached electron is given by $l = l_0 \pm 1$, where l_0 is the initial angular momentum of the bound electron. For $l > 0$, the electron has to tunnel through the potential barrier resulting from the centrifugal force. The derivative of the cross section of these p-wave electrons is zero at the threshold giving a shallow onset of the photodetachment process. The threshold in this case is therefore harder to determine, while the cross section of s-wave electrons with $l = 0$ shows a sharp, square root like behaviour which allows to determine the threshold energy with higher accuracy.

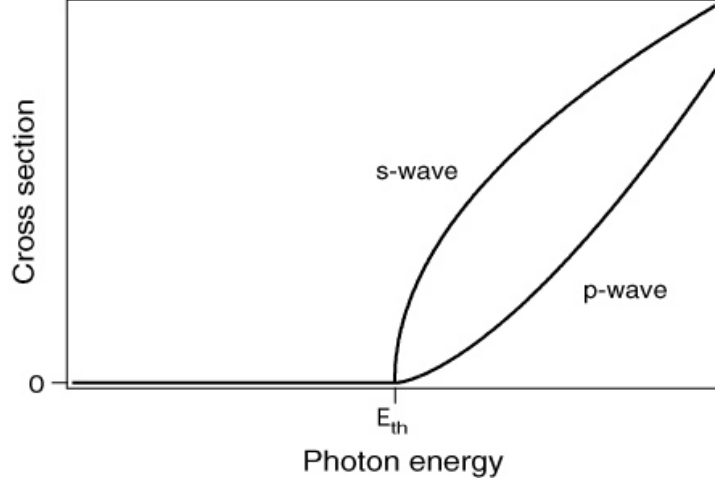


Figure 2.2: Threshold behavior of the cross section according to the Wigner law into s-wave corresponds to $E^{\frac{1}{2}}$, the p-wave to $E^{\frac{3}{2}}$ [12].

2.1.2 Doppler shift

In order to correctly determine the electron affinity via laser photodetachment, one has to consider the Doppler shift of the laser frequency ω in case of a collinear or an anti collinear geometry. This Doppler-shift can be written as

$$\omega' = \omega \cdot \frac{1 - \frac{v}{c_0} \cos(\theta)}{\sqrt{1 - \frac{v^2}{c_0^2}}}, \quad (2.5)$$

where ω' is the Doppler-corrected laser frequency, v the ion beam velocity, c_0 the speed of light in vacuum and θ the incident angle between ion and laser beam. In cases of non-relativistic ion beam velocities one can approximate $\frac{v^2}{c_0^2} \ll 1$ and calculate the Doppler-corrected energy $E_{p,a}$ using

$$E_{p,a} = E_0 \cdot \left(1 \pm \frac{v}{c_0}\right), \quad (2.6)$$

where $E_{p,a}$ is the energy measured in collinear or anti collinear configuration of the laser and E_0 the unshifted photon energy.¹ The linear alignment is often preferred instead of using crossed beams since it grants lower sensitivity against small changes in the angle between ions and laser (see eq. 2.5) and an increase in signal due to the larger interaction region as well as a compression of the Doppler spread due to the acceleration of the ions by the same potential in the ion source [26].

¹For an iodine ion beam with 20 keV, the correction factor $1 + \frac{v}{c_0}$ is about 1.00058

2.2 Negative ion sources

An ion source is a device used to ionize neutral atoms or molecules. It usually consists of an inlet for vapour of the desired element, an interaction region where the ions are produced and an exit aperture for extraction via a positive electric potential (in case of negative ion sources). In order to obtain and sustain the ions, ion sources are operated in a low pressure atmosphere. This reduces the probability of neutralization due to collisions with other atoms, which is especially important for negative ions due to their low electron binding energies. The attachment of an additional electron requires the release of the gained binding energy. This can happen for example via the radiative capture of free electrons (e.g. in a plasma) or charge transfer by collisions with an electron donor material [12, 27]. Due to their fragility, negative ions are easily destroyed making the construction of an efficient ion source challenging. In the following, some of the more common negative ion sources are described.

2.2.1 Surface ion sources

If a material is heated, the additional energy can lead to the emission of an electron from its surface. The current density j of the thermionic emission of electrons from a hot metal is described by the Richardson-Dushman equation [28].

$$j = A_0 \cdot \lambda_R \cdot T^2 \cdot e^{\left[\frac{-\phi}{k_B T}\right]}, \quad (2.7)$$

where T is the absolute temperature, ϕ the work function of the material, k_B the Boltzmann constant, λ_R a material specific correction factor and $A_0 = \frac{4\pi m_e k_B^2 e}{h^3} = 120.2 \frac{A}{cm^2 K^2}$ is the Richardson constant. Table 2.1 shows the work function, and corrected Richardson constants for materials that are typically used for the construction of ion sources.

Table 2.1: Work function and corrected Richardson constants for selected materials [28, 13].

Name	chemical symbol	work function [eV]	$A_0 \cdot \lambda_R \left[\frac{A}{cm^2 K^2}\right]$
Molybdenum	Mo	4.15	55
Tantalum	Ta	4.12	60
Rhenium	Re	4.7	100
Lanthanum hexaboride	LaB ₆	2.5-2.7	29
Gadolinium hexaboride	GdB ₆	1.5-2.7	7.6
Strontium vanadate	SrVO ₃	1.79 [18]	unknown

If a neutral atom comes in contact with such a heated material, it can be ionized, hence being transformed into a negative or positive ion. The likelihood of ionization depends on the work function and the electron affinity or the ionization potential of the interacting atom as well as the temperature of the system. For negative ion production, a material with a much work function lower (and therefore higher electron emission probability) than the electron affinity is desired. The ionization probability α for negative ions is described by the Saha-Langmuir equation [29]

$$\alpha = \frac{g_-}{g_0} e^{\left[\frac{EA - \phi}{k_b T}\right]}, \quad (2.8)$$

where ϕ is the work function of the surface, EA the electron affinity of the atom and g_0 and $g_- = 2 \sum_i s_i + 1$ are the quantum degeneracy from the charged and neutral states with s_i being the angular momentum of the electron [13]. (It is assumed that no temperature dependent reflection on the surface occurs.)

The ionization efficiency ϵ is then given by

$$\epsilon = \frac{1}{1 + \frac{1}{\alpha}}. \quad (2.9)$$

Experimental results with hollow tube ionizers showed discrepancies. Therefore, two correction factors were introduced. The emission of electrons and a small amount of positive ions, e.g. created by collisions, create a low density plasma within the source which can trap the ions. This is accounted for by ω . Additionally, the number of collisions of the atom with the hot surface is described by κ [14]. With these corrections, the ionization efficiency for hollow-tube ionizers can be written as

$$\epsilon = \frac{1}{1 + \frac{1}{\omega \kappa \alpha}}. \quad (2.10)$$

At CERN, H^- beams at the LINAC 4 are created with a cesiated surface ion source [30] and at ISOLDE a LaB6 pellet is used as the low work function material at the MK4 surface ion source [31]. This thesis focuses on surface ion sources, in particular the MK4 at ISOLDE.

2.2.2 Sputter-type ion sources

In a negative ion sputter source a low work function metal, usually cesium, is vaporized and ionized thermally. The positive cesium ions are then accelerated onto a cathode. To avoid heat or charge build up, the cathode consists of a metal cylinder in which the desired beam material is placed in [32, 13]. Besides sputtering the material, the cesium also forms a thin layer on the surface of the cathode, which increases the likelihood of negative ion creation of the sputtered cathode material. An illustration of this process called secondary negative ion emission is given in figure 2.3 [13].

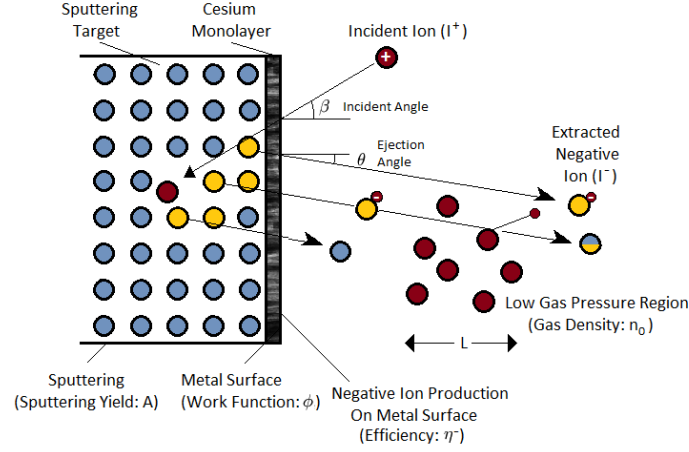


Figure 2.3: The process of secondary negative ion emission. An atom is sputtered or reflected and leaves the cathode with a velocity greater than the thermal velocity and gains an electron via passing through the cesium monolayer.

The ion current I^- of the secondary emission is given by

$$I^- = I^+ A \eta^- e^{(-n_0 L \sigma_0)}, \quad (2.11)$$

where I^+ is the positive ion current, A is the sputtering yield, η^- the efficiency of the negative ion production, σ_d the electron detachment cross section and n_0 the gas density in the ion beam path of length L [13]. A schematic picture of an negative ion sputter source is shown in figure 2.4.

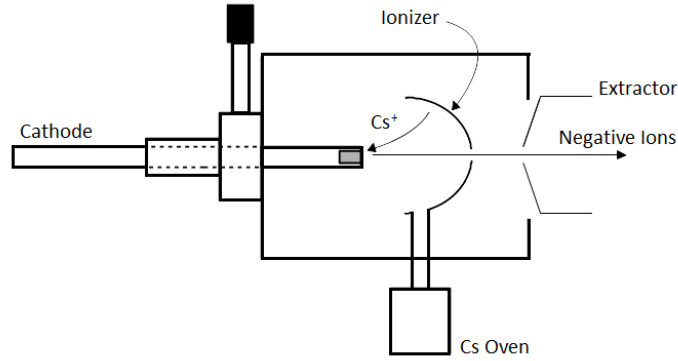


Figure 2.4: Schematic drawing of a cesium sputter source for the production of negative ions at Gothenburg University Negative Ion Laser Laboratory (GUNILLA) [33]. The cesium is evaporated, thermally ionized and accelerated towards the cathode.

2.2.3 Charge exchange ion sources

Negative charge exchange sources use a conventional positive ion source and a charge exchange cell to produce negative ions. The positive ions are extracted into a low pressure gas chamber, where the collision with the neutral gas particles can lead to the production of negative ions. Usually alkaline metals or alkaline earth metals are chosen as electron donor since they easily release their electrons. The ionization efficiency of charge transfer ion sources for negative ions is usually between 10 and 40 percent [34, 35]. In figure 2.5, the production efficiency F of positive and negative ions as well as neutralization of a positive 30 keV tellurium ion beam is shown depending on the target thickness μ . Here, the negative ion efficiency reaches its maximum at 60%.

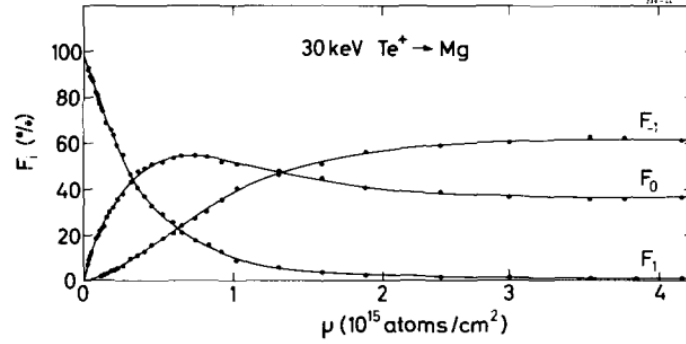


Figure 2.5: Positive and negative ionization as well as neutralization of a positive 30 keV tellurium in a charge transfer cell filled with magnesium [35].

2.2.4 Penning ion source

The penning source consists of a cylindrical anode with cathodes on both ends, which is depicted in figure 2.6. These cathodes emit electrons in the space between them, which is filled with a gas of the desired ion species. The gas pressure is kept in a range of 1 to 10^{-3} mbar to ensure a mean free path of electrons to be in the order of the source length. A magnetic field is applied parallel to the cylinder axis, which decreases the probability of emitted electrons to strike the other cathode. This leads to electrons oscillating between the cathodes due to the magnetic field and the repulsion of the cathodes. The collisions of the free electrons with the neutral gas creates a plasma. This plasma can be divided into a hot core and a cold surrounding, where the electron temperature is lower. From this region negative ions can be extracted through a slit.

An alternative to this process called volume production is the so called surface plasma penning source. Here, the surfaces of the cathode are coated with cesium which leads to the creation of negative ions when positive ions hit the walls and are reflected as discussed in the secondary emission part of the sputter source section.

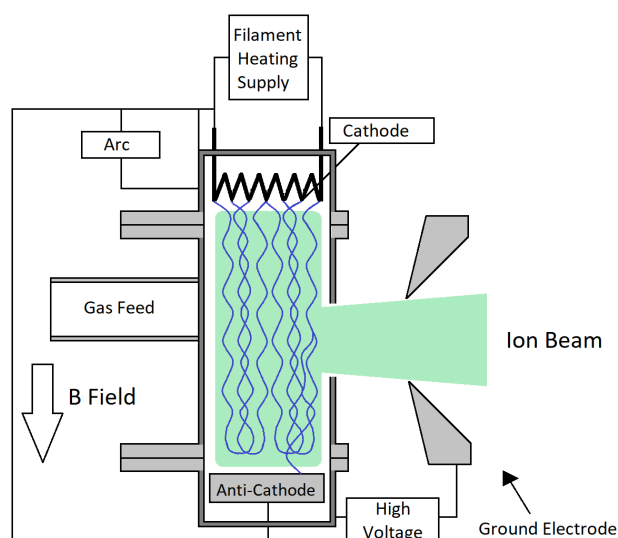


Figure 2.6: Schematic drawing of a penning ion source for the production of negative ions. Some exemplary electron paths are shown in blue.

2.2.5 Magnetron ion source

Similar to the penning source, the magnetron source uses electron discharge to create a plasma from which ions can be extracted. Here, the cathode is surrounded by the anode as depicted in figure 2.7. For negative ion production, additionally to the gas of the desired ion material, cesium vapor is introduced.

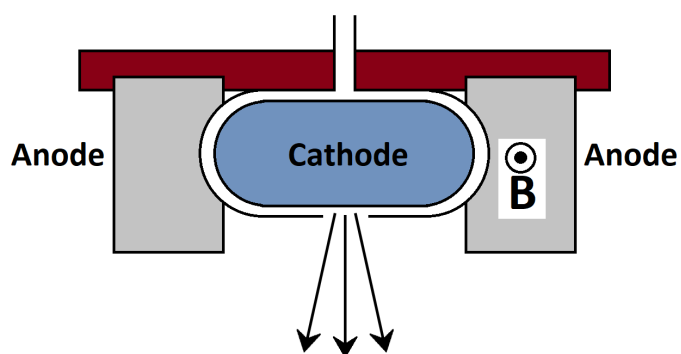


Figure 2.7: Schematic drawing of a magnetron ion source for the production of negative ions.

A magnetic field is applied normal to the electric field which results in a strong electron confinement and efficient plasma creation. Similar to the process in the penning and the sputter source, positive ions are accelerated from the plasma to the cathode where they are negatively ionized by the cesium covering the cathode surface. The negative ions can then be extracted through a slit.

A more detailed overview of magnetron and penning ion sources can be found in [36] and [13].

2.3 Material characterization techniques

2.3.1 x-ray diffraction

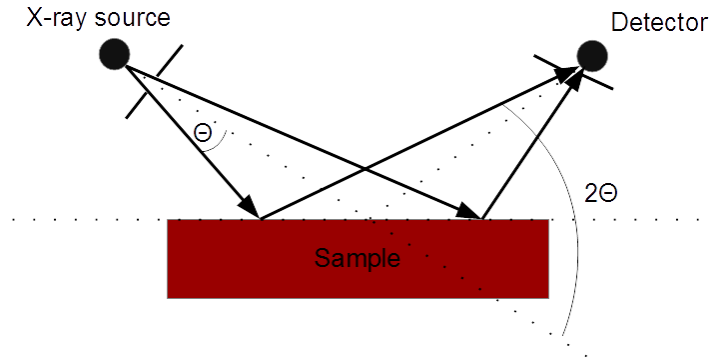


Figure 2.8: schematic view of a XRD setup.

X-ray diffraction (XRD) is a technique used to determine the phase composition of a crystalline material. Hereby, the sample is ground to a fine powder in order to exhibit all crystal orientations [37]. X-rays are used because their wavelength of a few angstrom is in the same order as inter-atomic distances. Therefore, the X-rays will constructively interfere depending on the lattice parameter, crystal structure and the incident angle. This is described by Bragg's law

$$n\lambda = 2d\sin(\theta), \quad (2.12)$$

where, λ is the wavelength of the x-ray photon, d the lattice parameter, n a positive integer and θ the incident angle of the beam. By scanning the incident angle of the x-ray and detecting the diffracted beam, a spectrum with diffraction maxima at a specific set of d -values is obtained. Since these result from the lattice parameters and crystal structure, unique to the phase, one can determine the phase in the sample by comparing the acquired diffractogram with existing databases. A typical XRD setup consists of a X-ray source, sample holder and a detector, as shown schematically in figure 2.8. The

X-rays are produced by bombarding a metal plate with an electron beam created by electrons accelerated from a hot filament. If the electrons have sufficient energies in the range of a few keV, the inner shell electrons of the metal can be excited, which leads to X-ray emission.

2.3.2 Scanning electron microscopy

In a scanning electron microscope (SEM), a beam of electrons with energies between a few and tens of keV is used to scan across the surface of a sample. The electrons of the beam collide inelastically with the electrons of the outer shell of the surface atoms of the sample. Electrons close to the surface of the sample can thereby gain enough energy to leave the surface and can be detected as secondary electrons. By scanning over the sample surface and detecting of the secondary electrons, a 3D-like image of the surface of the sample can be created and insight in chemical composition and phase composition contrast can be gained [38].

2.3.3 Energy dispersive X-ray spectroscopy

In energy dispersive X-ray spectroscopy the uniqueness of the atomic spectra is used to identify the elements in a sample. Similar to SEM, the sample is bombarded with a high energy beam of charged particles, typically electrons, exciting the electrons in the inner shell of the sample, thereby producing X-ray emission characteristic for the specific element. By detecting the emitted X-ray spectrum and comparing it to the known emission lines of elements, the chemical elements and their abundance in the sample can be approximated.

3 ISOLDE

3.1 The ISOLDE facility

The Isotope Separator On Line DEvice (ISOLDE) [39, 40] is a radioactive ion beam facility at the European Center for Nuclear Research (CERN), producing a large variety of radioactive ion beams. ISOLDE is one of the major ISOL-type facilities, where over 1000 radioactive isotopes from 74 chemical abundant elements are produced by irradiation of a thick target with a proton beam [39, 40]. The impinging protons with an energy of 1.4 GeV induce nuclear reactions such as fission, spallation and fragmentation in the target material. The reaction products then diffuse out of the thick target into an ion source where they are ionized. The produced ions are extracted as beam from the ion source and mass separated using dipole magnets.

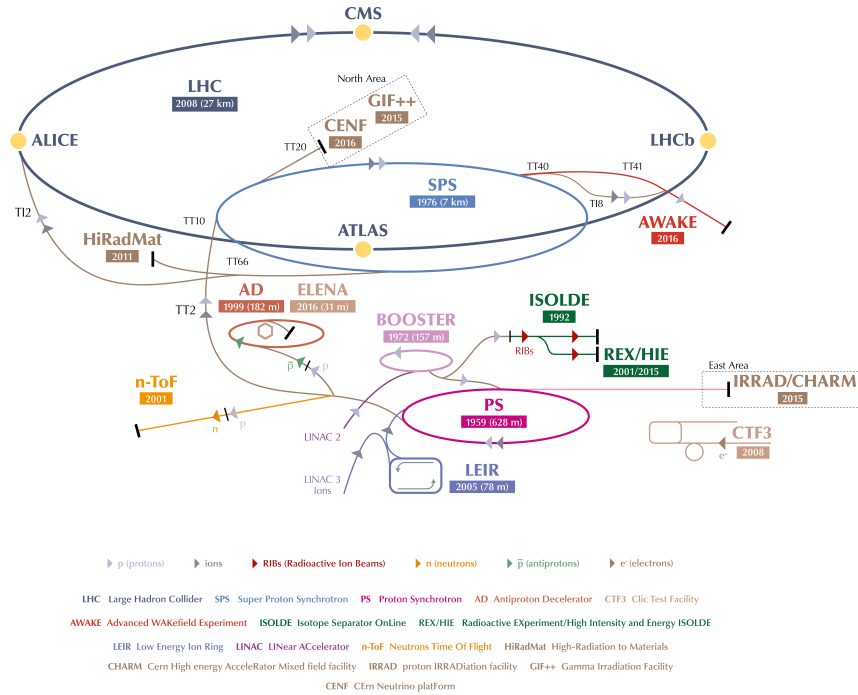


Figure 3.1: The accelerator complex of CERN [41].

ISOLDE is located after the Proton-Synchrotron Booster (PSB) of the CERN accelerator complex which is shown in figure 3.1. The PSB delivers proton beams with an energy of 1.4 GeV to ISOLDE.

The ISOLDE facility has two isotope separators connected to a common beamline but with independent front ends to which the target units are coupled. The two isotopes separators are the General Purpose Separator (GPS) and the High Resolution Separator HRS. In order to increase the mass resolution, HRS has a second mass separating magnet. As shown in figure 3.2 both GPS and HRS are feeding the central beamline, while GPS is also connected to the General Low Mass (GLM) and General High Mass (GHM) beamlines [42].

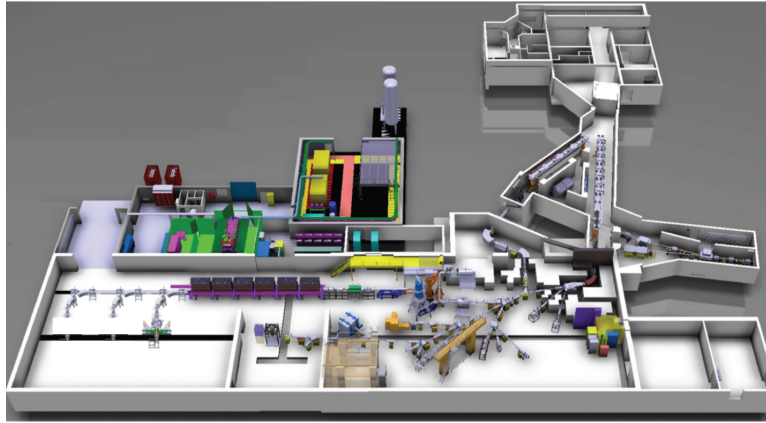


Figure 3.2: A schematic view of the ISOLDE hall with its beamlines [43].

In 2001 the REX-ISOLDE upgrade was operational, which enables beam energies with up to 3MeV/u through a post acceleration process of the 60keV beam coming from ISOLDE [44]. In 2015 the first stage of the HIE-ISOLDE upgrade enabled beam energies up to 5.5MeV/u for ions with a mass-to-charge ratio below 4.5.

3.2 ISOLDE targets and ion sources

In order to produce radioactive ion beams at ISOLDE, the desired radioactive isotopes has to be created, ionized and extracted. This is done in the so called target and ion source system (short: target unit or target) which is shown schematically in figure 3.3.

A target unit usually consists of the target container which is connected to the ion source via a heated transfer line.

3.2.1 Isotope production

The target container is filled with a material which is produces the desired radioisotopes via proton-induced nuclear reactions (spallation, fission or fragmentation) [31]. All three

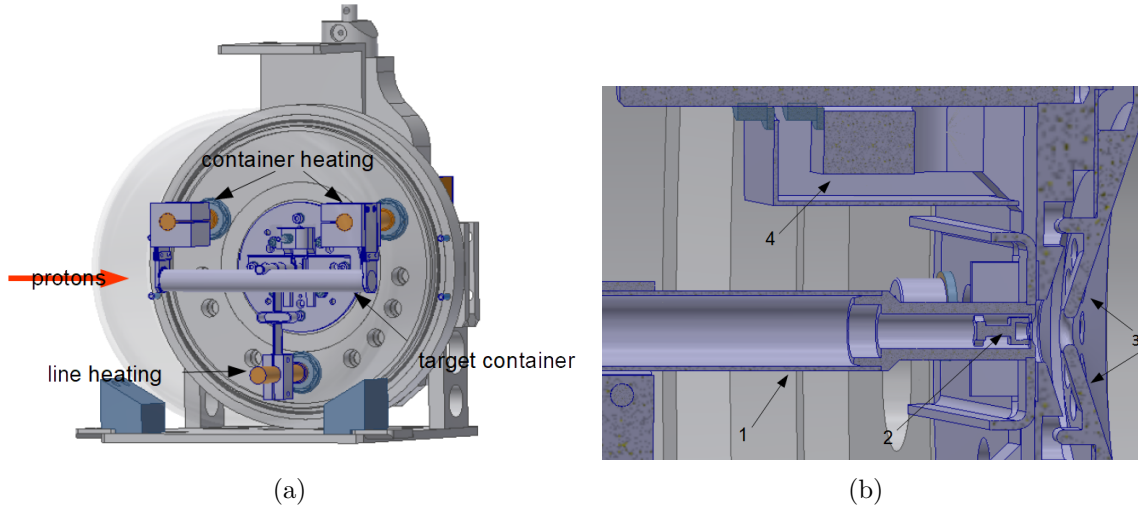


Figure 3.3: (a): A target unit for an negative ion source with the target container, the transfer line and connections for resistive heating. (b) Half section view of the target with transfer line (1), surface ion source (2), electron catcher (3) and magnet (4). The created electrons are deflected onto the electron catcher by its potential of 1 kV and the 0.04 T magnetic field from the bending magnet.

of these processes start with an excitation of some nucleons by the collision with the proton beam. These nucleons have enough energy to strike their neighbours thereby creating an intranuclear cascade which already leads to the emission of some nucleons from the core. The residual core is highly excited. In case of spallation the core decays by evaporating neutrons and protons. This process is dominant for projectile energies above 100 MeV and results mostly in nuclei 10 to 20 u lighter than the target nucleus. Fragmentation is defined as the nucleus decaying by emitting multiple lighter nuclei like ^4He and ^{12}C . In a heavy target, fission is the dominating process, where the nucleus undergoes a radioactive decay by splitting into two or more lighter nuclei. There is a wide variety of target materials: liquid targets are made of metals or salts with low melting points, solid targets can be used in the form of pressed pills, fibers, carbides or oxides [31] .

3.3 ISOLDE ion sources

After production of radioisotopes in the target container, they diffuse into the transfer line. The transfer line is heated, depending on the type of target and desired element to ensure fast and efficient transmission into the ion source. The temperature of the transfer line can also be used to achieve some physical selectivity of the ion beam due to differences in volatility.

The types of ion sources mostly used at ISOLDE are surface ion sources, Forced

Electron Beam Ionization Arc Discharge (FEBIAD) type sources, and the Resonance Ionization Laser Ion Source (RILIS) [45, 46].

3.3.1 Surface ion source

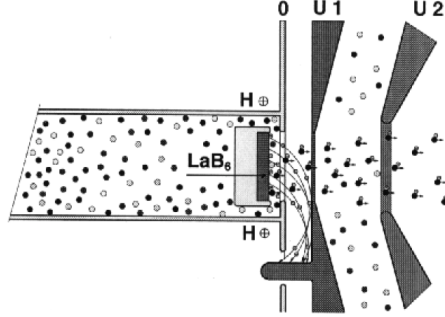


Figure 3.4: Neutral isotopes diffuse from left to right, where some interact with the LaB_6 and are negatively ionized. Emitted electrons are bent away by a 1kV potential at U1 and a small magnet at the target base, while the negative ions are extracted with the extraction electrode U2 [47].

These sources have to meet many requirements such as the robustness to withstand the dose coming from the radioactive isotopes, be able to provide maximal ionization efficiency, stable operation under varying gas loads and to be selective enough to produce sufficiently pure beams. The surface ion source is used for the production of positive as well as negative ion beams. Typical materials for positive surface ionization are tantalum, rhenium and tungsten, due to their high work function and their robustness. For negative surface ionization a LaB_6 pellet is used. The negative ion sources have an additional copper disk kept at a potential of 1kV which, in addition to a bending magnet at the target base, is used to capture electrons from being accelerated. Some selectivity is accomplished due to the difference in ionization potential/ electron affinity of different isotopes. An illustration of the negative surface ion source with a LaB_6 pellet can be seen in figure 3.4.

3.3.2 Laser ion source

The Resonance Ionisation Laser Ion Source (RILIS) is ISOLDE's laser ion source for production of positive ions. Here, different laser beams are specifically tuned to step-wise resonantly excite the atoms of the element of interest. The excited atoms are then ionized through non-resonant laser-ionization to the continuum or into auto-ionizing states. The laser beams are directed into the ion source cavity through a quartz window in the mass separator. Figure 3.5 shows examples of three-step laser ionization schemes and the setup of a RILIS laser beam into the ion source. RILIS can also be combined

with other sources such as the surface and VADIS to increase efficiency or selectivity of the source.

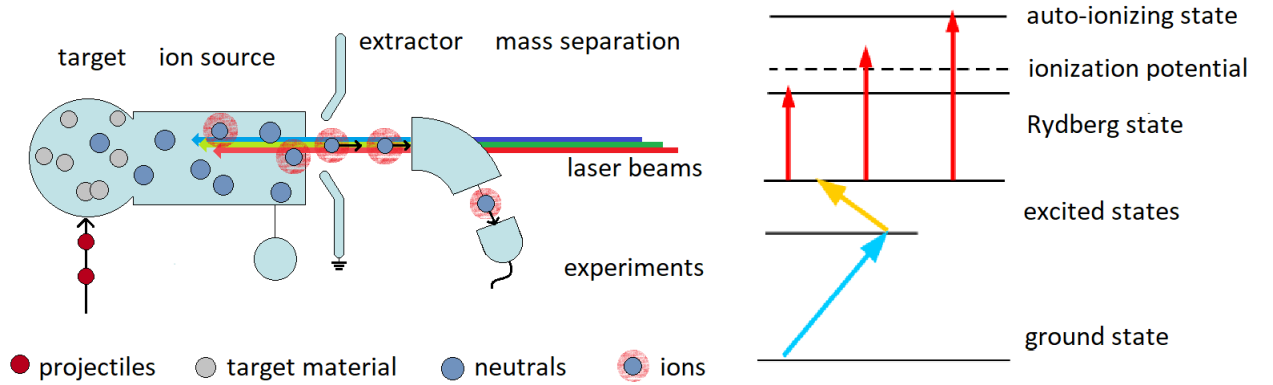


Figure 3.5: Schematic of the RILIS ion source at ISOLDE (left) and ionization exemplary scheme (right) .

3.3.3 VADIS

The Versatile Arc Discharge Ion Source (VADIS) [48] is a FEBIAD type ion source used at ISOLDE. Electrons are emitted by a heated cathode and accelerated by the cylindrical anode held at 100- 150 V with respect to the cathode. The cathode facing side of the

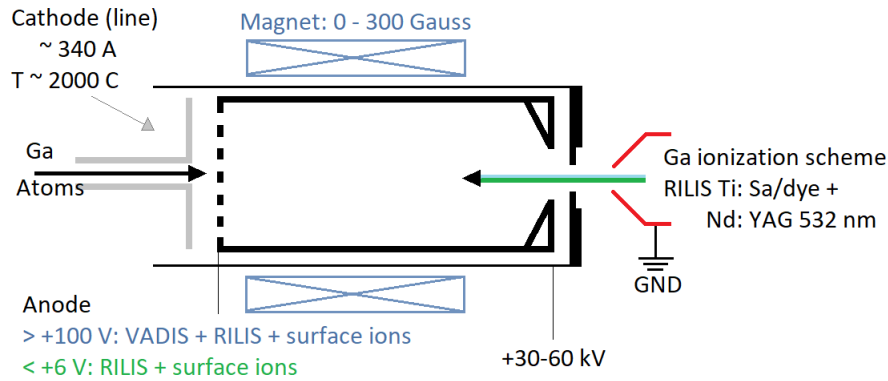


Figure 3.6: Schematic illustration of a VADLIS, a VADIS source combined with the RILIS laser ion source for Gallium atoms [49].

anode cylinder is a molybdenum grid, allowing the electrons to enter the anode volume. A magnetic field applied in the anode volume leads to an increased ionization efficiency due to collisions of atoms and electrons result in ionization. The created ions can then

be extracted at the other side of the anode. The VADIS source can be combined with a laser ion source to increase ionization efficiency and selectivity of the source. The anode voltage is then reduced to about 6 V. An illustration of a VADIS in combination with a laser ion source, then called VADLIS, is shown in figure 3.6 [49].

4 Negative ion source development

As illustrated in chapter 2, the production of negative ions can be quite challenging due to their fragile nature, which often results in lower efficiencies than desired. In order to meet the demand for negative ion beams of elements of the chalcogen or halogens groups or molecules, the efficiency and reliability of the negative ion source at ISOLDE has to be improved. It is especially challenging to produce negative ions of elements with low electron affinities such as astatine or polonium, with an expected EA of 2.4 eV and 1.9 eV, respectively [9].

4.1 Motivation

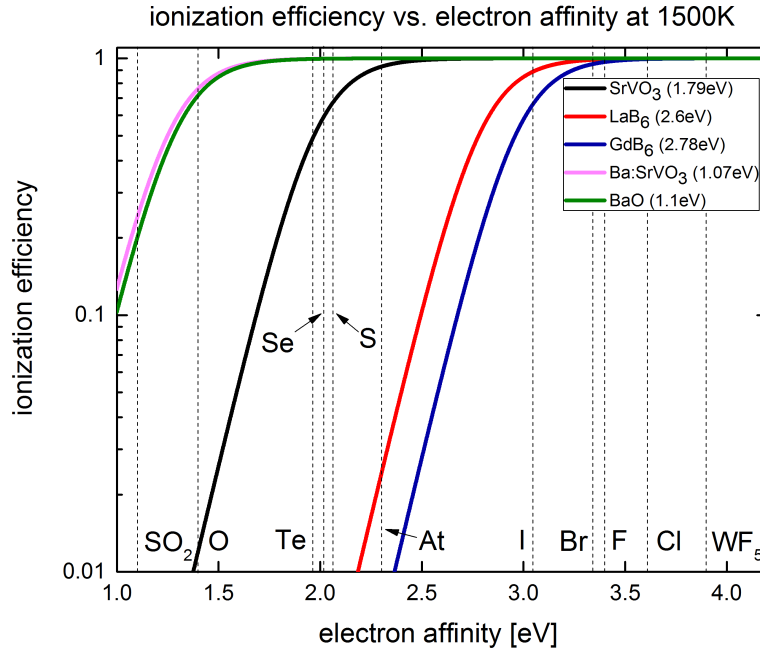


Figure 4.1: The ionization efficiency of different source materials is calculated and plotted against the electron affinity of different elements. The expected work functions of the source materials are given in brackets.

Figure 4.1 shows the theoretical surface ionization efficiency for different source materials for selected elements. The figure shows that the currently used source material, LaB_6 , with a work function of about 2.6 eV, displays very high theoretical efficiencies ($> 70\%$) for elements with an electron affinity greater than 3 eV. For elements with low electron affinities the efficiency decreases drastically.

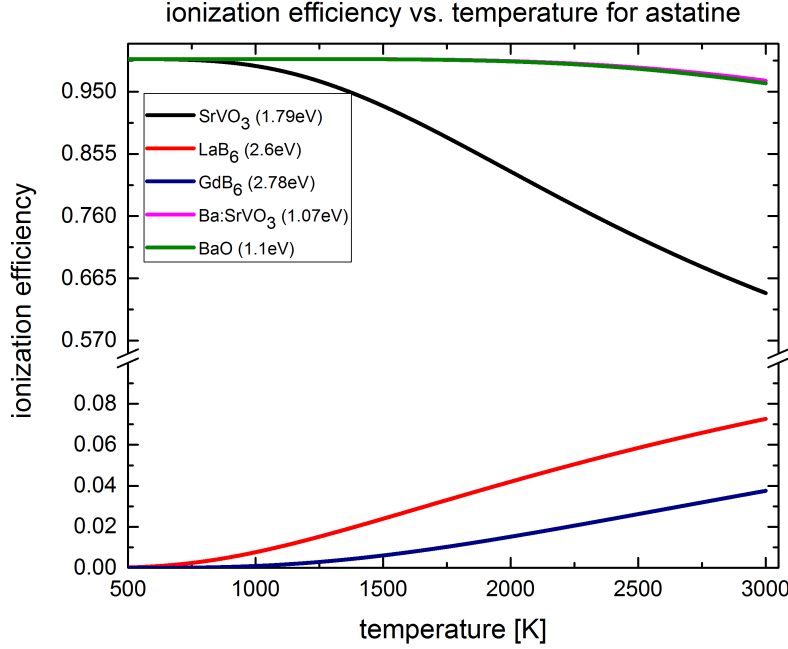


Figure 4.2: Expected ionization efficiency for astatine (with an EA of 2.4 eV) plotted against the temperature of the source. The ionization efficiencies were calculated according equation 2.9. The expected work functions of the source materials are given in brackets.

In order to improve the ionization efficiency one can investigate materials with lower work functions. Another way is to improve the geometry of the source, to increase the number of atoms or molecules which interact with the surface of the material. GdB_6 , SrVO_3 , BaO and Ba doped SrVO_3 are shown in fig 4.1 as alternatives to LaB_6 . These materials are all expected to exhibit work functions below 2 eV [28, 18]. This would increase the theoretical ionization efficiency for astatine by a factor of about 65 from about 0.015 to 1. We therefore decided to focus first on alternative low work function materials rather than the optimization of the geometry.

Low work function materials also have the advantage that they can be operated at lower temperatures, which is shown in figure 4.2 for the case of astatine. Here, the ionization efficiency is plotted against the temperature. The figure shows that LaB_6 and GdB_6 with a work function around the expected electron affinity of astatine (2.4 eV)

have to be at high temperatures to reach an ionization efficiency of 2-4 percent, while the lower work function materials actually decrease in efficiency with high temperatures. Hence, the maximum source temperature would not depend on the source material but mostly by sticking and diffusion parameters of the isotopes in the transfer line.

4.2 The ion source test stand

The ISOLDE pump stand, shown in figure 4.3, is used generally to test targets for their vacuum tightness and perform temperature calibrations, before they are further tested at an offline mass separator and ultimately connected to an ISOLDE front-end and irradiated. The original pump stand consists of a 5-way vacuum cross connected to an ISOLDE front-end flange where target units can be coupled. The coupling flange is equipped with multiple feedthroughs for electrical connections, water cooling and thermocouple readouts. In order to increase the capabilities for the development and characterization of ion sources, a second, upgraded pump stand (in the following called test stand) was conceived. This new infrastructure will also enable thorough studies of lifetime and degeneration of the ion source during heating cycles.

As a first addition, an ion extraction flange was designed and constructed. This allows testing the ion source performance, which was previously only possible when the target was coupled to the off-line separator. A second edition of the extraction flange could introduce mass separation via a quadrupole mass filter. Secondly, a residual gas analyzer was added which allows detection of possible chemical reactions and potential degradation of the source material during heating and cooling.

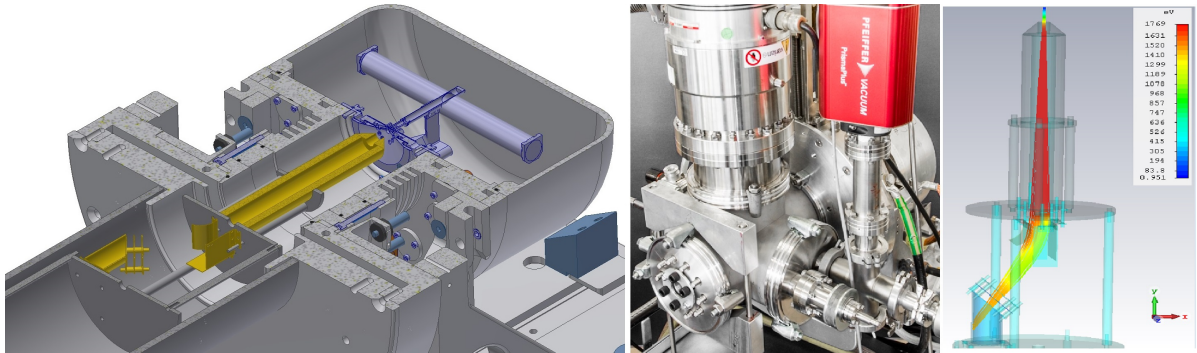


Figure 4.3: Left: Design of the test stand with extraction flange and coupled target. Center: Picture of the test stand with extraction flange and residual gas analyzer. Right: Simulation of the ion beam trajectory

As an initial step towards the improvement of the negative surface ion source, the new test stand was used to investigate new materials with LaB_6 as a benchmark. For these tests a suitable development target had to be manufactured.

4.2.1 Development target #316

The target unit #316, used in this thesis has a standard MK4 negative pellet source geometry. It was used previously for ion source development. The target was cleaned and modified for the electron emission tests. The target container was replaced with an electrical connection from the power feedthrough to the transfer line. This enabled samples to be inserted from the back of the ion source. A new magnet for electron deflection ($B=0.04\text{ T}$) was added and a sample holder was designed. The target #316 with its modifications is shown in figure 4.4. The wire isolated by white ceramic breads is a thermocouple, which is connected to the multi-pin feedthrough. It was problematic to find an appropriate position for the thermocouple, since it could be easily displaced due to small movements. Unfortunately, such motion is unavoidable when coupling the target to the test stand. Hence, proper placement could not be assured and temperature measurements turned out to be inaccurate. It was therefore not further used. The copper feedthrough at the bottom of the right part of figure 4.4 is used to connect the power supply for resistive heating of the transfer line, which is connected to the feedthrough by a tantalum plate.

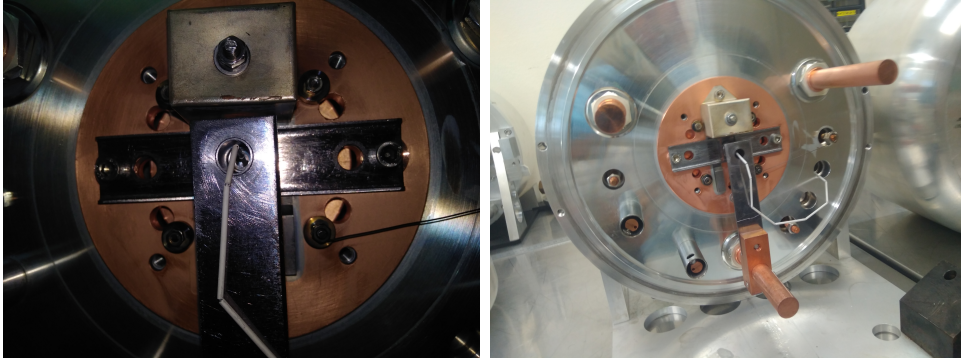


Figure 4.4: View of the inside of a target unit in the direction of the the transfer line (left). The wire with the white isolation is the thermocouple going into the transfer line, the box is the heat screen for the permanent magnet it contains. The line is held by the horizontal tantalum piece. The vertical tantalum plate is the heating connection. The small wire to the right is the voltage connection for the electron catcher. Right: Overview of the negative test-target.

After about a month of daily use for the electron emission measurements of the samples, the Ta plate was found deformed, resulting in displacement of the line and heating of the target base. To avoid this problem in the future, the design of the connection was improved. The new transfer line was shielded from the sample holder by a rhenium foil to prevent chemical reactions at the sample holder. This was previously achieved by wrapping the foil around the sample holder. The redesigned development target is shown in figure 4.5.

4.2.2 Sample holder

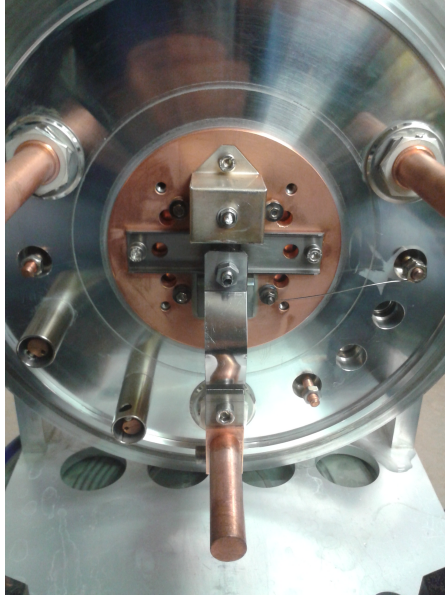


Figure 4.5: Repaired test-target with new transfer line heating connection and rhenium foil inside the transfer line.

The sample holder was designed to possess properties as similar as possible to the original pellet source without making it too difficult to machine. Therefore, cylinders with a 2 mm diameter and 2 mm cavity were machined, matching the dimensions of the original pellet source. Both the original source and the sample holder are depicted in figure 4.6.

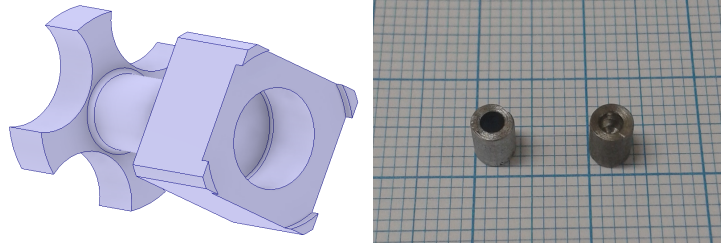


Figure 4.6: left: 3D view of the pellet holder of the MK4 negative ion source. right: picture of the sample holders.

The sample holders were made from tantalum or molybdenum in order to sustain the heating without reacting with the samples or stick to the tantalum transfer line. Both tantalum and molybdenum have a high work function of about 4.2 [28], which reduces possible background effects. The samples were prepared by pressing the powder of the

material under test into the sample holder until it was full and the powder compressed enough to not fall out. The sample was then inserted and pushed to the end of the transfer line using a tantalum pin. This ensured the same distance and position for all samples. For the initial electron emission measurements without extraction flange the electron catcher was set to 1 kV and the resulting current on the plate measured while heating the sample. The electrical circuit to perform the measurements is shown in figure 4.7.

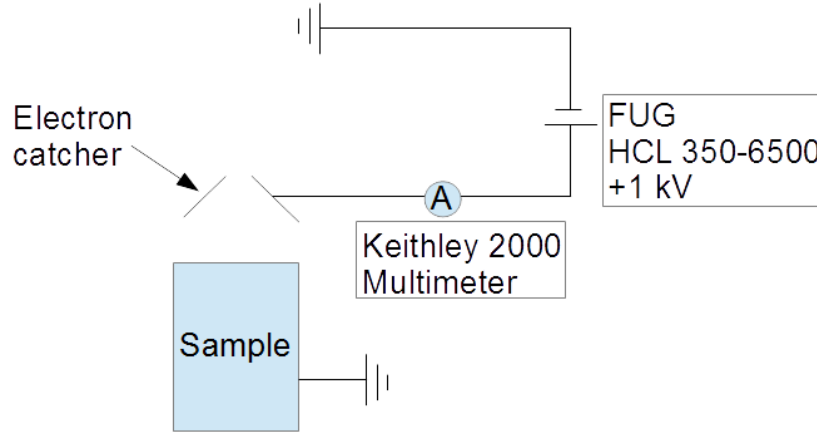


Figure 4.7: Electrical circuit to measure the electron emission current. The transfer line and hence the samples are heated by resistive heating with a Delta elektronika SM-400 power supply (not shown). The drain current of the voltage supply for the electron catcher is then measured by a multimeter.

4.2.3 Design and simulation of the extraction flange

In order to create the possibility of ion source testing and beam extraction on the test stand, an extracion flange was designed. The design was done using Autodesk Inventor 2016, a common 3D CAD design software. Ion beam trajectories were simulated using SIMION 8.1 and the particle tracking solver of CST studio suite 2016.

SIMION is used to calculate electric fields and charged particle trajectories. 3D models in the *.stl* data format can be imported and converted to electric potential arrays, which are used to calculate the electric fields by solving the Laplace equation.

CST Studio allows to import and create 3D structures with specific material properties. It is partitioned in various workflows and solvers for different applications. Particle trajectories are produced by the particle tracking solver which calculates the static electric and magnetic fields assigned to metallic parts of the 3D structure. Particles are then emitted from a chosen surface by a specific emission model and their interaction with the fields are displayed. Space charge of the beam can be accounted for by the gun iteration mode.

This is an iterative process, where the initial step is to produce the trajectory of the

particles only using the surrounding electromagnetic fields. The charge distribution of the particle beam is then included in the next step of the calculation. This is repeated until the difference between the resulting beam of two consecutive iterations is lower than a limit given by the user.

For the design of the extraction flange a thermionic emission model from a surface at 1500 K with a work function of 2.6 eV is used.

Due to the geometry of the target and the front-end, a long extraction electrode was necessary with its mounting plate being isolated from the rest of the flange, which is grounded. This was achieved by connecting the "first level" with the extraction electrode via isolating poly-acryl rods. A picture of the assembled flange as well as simulated trajectories from CST are shown in figure 4.8.

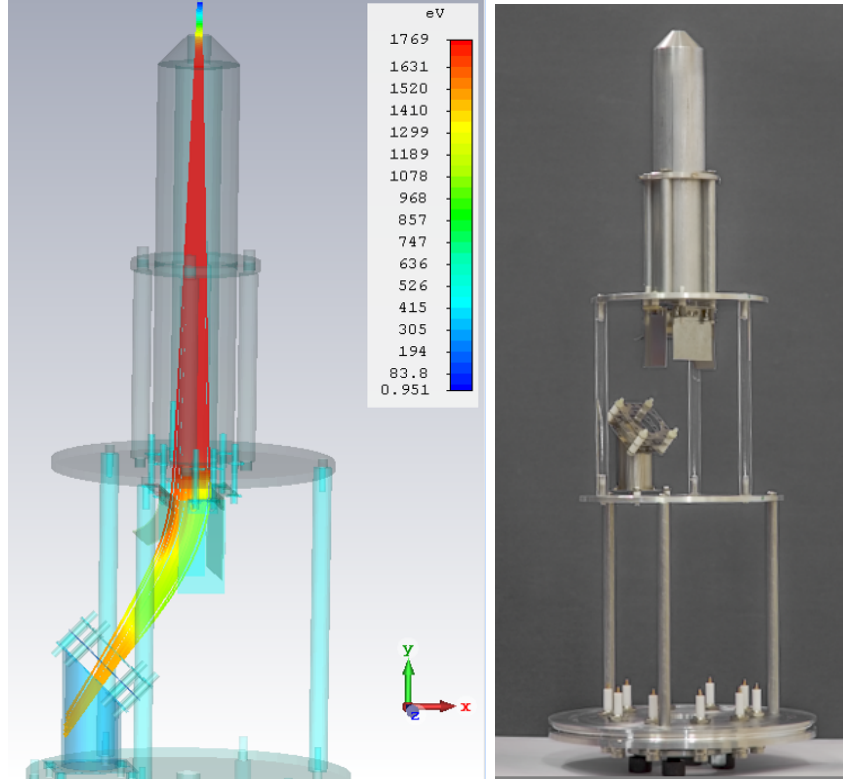


Figure 4.8: Simulation of the ion beam trajectory with the extraction flange made with CST studio(left). Photograph of the assembled extraction flange (right).

Bend plates were added in order to measure the ion beam current with an off-axis Faraday cup. This enables temperature measurements with a pyrometer and further creates the possibility to perform source optical spectroscopy of plasma ion sources. This also allows the testing of all ion sources which include or can be combined with laser ionization such as the VADLIS and positive surface ion sources as well as the development and testing of RILIS schemes.

For the purpose of simulating the ion beam path, the ions are created at the same distance as the source distance from the extraction electrode in the test stand. A thermionic emission model at a temperature of 1500K with a material of a work function of 2.6 eV, which corresponds to LaB₆ was used. The electrons or ions (here iodine was chosen) are emitted at ground potential and the extraction and bend plate voltages were tuned. As the source is grounded, it is necessary to keep the faraday cup on a positive potential. Due to the maximal floating voltage of the Keithley 6487 picoamperemeter, the Faraday cup was placed at 500V and the other potentials were adjusted accordingly.

Table 4.1 shows the optimal voltages for the extraction and bending of the ion beam such that the ions could reach the faraday cup.

Table 4.1: Simulated voltages of the extraction flange.

electrode	simulated Voltage [V]
extraction	900
bend plate	900
straight bend plate	550
left steer	0
right steer	0
Faraday cup	500
Faraday cup suppression	480

4.3 Negative ion source materials

The materials to be investigated were chosen on the basis of different properties such as a low work function, and stability under the expected operating conditions. This means that the materials are required to have a high melting point and a low vapor pressure as well as low chemical reactivity with expected surrounding elements.

Generally, two types of materials seem to exhibit a low work function, namely oxides and hexaborides. It was shown that LaB₆ is one of the most suitable hexaborides, which is why it is widely used as an electron emitter and in negative ion surface sources like the MK4 at ISOLDE. Hence, it was used as a benchmark material in this work.

GdB₆ is another hexaboride candidate with reported work functions between 1.5 and 2.78 eV ([50, 28]).

Many oxides such as BaO, CaO and SrO have measured work functions of under 2 eV, but their chemical properties make them not particularly suitable since they tend to react to a hydroxide when in contact with the humidity of air. BaO is often used as coating on electron emitters, but it has shown to evaporate at higher temperatures. A promising candidate is strontium vanadate (SrVO₃) with a predicted work function in the range of 1.79-1.86eV [17, 18].

A possible drawback of SrVO₃ is the stability at oxidizing atmospheres in high temperatures. Jacobs *et al.* predict SrVO₃ to be stable at 800°C with an oxygen partial

pressure of 10^{-10} mbar [17]. Experimental results show stability of pure SrVO_3 in an oxygen partial pressure in the range of 10^{-17} to 10^{-12} mbar at temperatures around 800°C [51, 52]. However, Jacobs et al. predict that by doping the SrVO_3 with Mo, Mn, Cr or Fe, it is largely stabilized, while its metallic character is preserved [18]. The addition of small amounts of barium is even predicted to drastically lower the work function from 1.79 eV to 1.1 eV if the barium is at the surface of the emitter [18].

4.4 Results

4.4.1 Material production and classification

All investigated materials were classified using a Siemens D5000 X-ray diffractometer. The compounds and their phases were identified using the software DIFFRAC EVA 4.0 and the database PDF-2 1991 from ICDD. LaB_6 and GdB_6 were purchased as powders from Sigma Aldrich and in tubular form from Huizhou Tian Yi Rare Material Co. Ltd, whereas SrVO_3 was attempted to both be produced in-house and purchased in powder form. The tubular samples were also investigated via scanning electron microscope to investigate their surface structure and composition. Self-produced samples were heated in an Carbolite Gero STF, with heating capabilities up to 1500°C .

Production of SrVO_3 as described in literature

According to literature (see [53, 54, 51]), SrVO_3 can be produced by a solid state reaction of SrCO_3 and V_2O_5 , which were both obtained from Sigma Aldrich. The raw materials were mixed stoichiometrically, so that $\text{Sr} : \text{V} = 1$. To achieve a homogeneous mixture, the powders are ground with mortar and pestle and then pressed into a pellet using a hydraulic press with a pressure of 2 T/cm^2 . The pellet is then put in an oven and heated in three steps, as indicated in table 4.2. The first step should initialize a reaction of the compounds in air, thereby preventing melting of vanadium pentoxide (melting point of 690°C). The second step of the calcination at 800°C in air produces an oxygen excess strontium vanadate phase [53, 55]. This is then reduced to SrVO_3 in a reducing atmosphere at a high temperature. This last step requires a reductive atmosphere, in the literature created by a mixture of hydrogen and nitrogen. Due to missing safety infrastructure, the use of hydrogen was not possible.

Table 4.2: Temperature procedure to produce SrVO_3 [53, 54, 51].

step	Temperature [$^\circ\text{C}$]	holding time	atmosphere
1	600	10h	air
2	800	10h	air
3	1300	12h	94% N, 6% H (reductive atmosphere)

Table 4.3: Production procedure and results of the strontium vanadate production.

Sample	protocol	atmosphere	Observation
S1	600 °C for 10h 800 °C for 10h 1300 °C for 12h in Mo boat	air	Sample reacted with Mo boat, therefore mainly SrMoO_4 , V_3O_5 , $\text{SrV}_6\text{O}_{11}$
S2	600 °C for 10h 800 °C for 10h in ceramic bowl	air	reacted with tantalum wire
S3	600 °C for 10h 800 °C for 10h 1100 °C for 12h in ceramic bowl	air	mixture of $\text{Sr}_2\text{V}_2\text{O}_7$, $\text{Sr}_3\text{V}_2\text{O}_8$ and $\text{Sr}_6\text{V}_6\text{O}_{19}$
S4	600 °C for 10h 800 °C for 10h 900 °C for 12h in ceramic bowl	air	mixture of $\text{Sr}_2\text{V}_2\text{O}_7$, $\text{Sr}_3\text{V}_2\text{O}_8$ and $\text{Sr}_6\text{V}_6\text{O}_{19}$
S5	600 °C for 10h 800 °C for 10h 1000 °C for 12h in graphite tube	reductive	predominant $\text{Sr}_3(\text{VO}_4)_2$, also $\text{Sr}_6\text{V}_6\text{O}_{19}$
S6	600 °C for 10h 800 °C for 10h 1000 °C for 12h in ceramic bowl	air	$\text{Sr}_3(\text{VO}_4)_2$ and $\text{Sr}_6\text{V}_6\text{O}_{19}$
S7	600 °C for 10h 800 °C for 10h 1000 °C for 12h in graphite box	reductive, last step in vacuum	mixture of $\text{Sr}_3(\text{VO}_4)_2$ and $\text{Sr}_6\text{V}_6\text{O}_{19}$ (temperature control malfunctioned)
S8	600 °C for 10h 800 °C for 10h 1100 °C for 12h in graphite box	reductive, last step in vacuum	main phase: $\text{Sr}_3(\text{VO}_4)_2$, also $\text{Sr}_2\text{V}_2\text{O}_7$ and a small amounts of $\text{Sr}_2\text{V}_3\text{O}_9$

Therefore, alternative ways to attempt the production of SrVO_3 were made in this thesis. By varying the sample containers and atmospheres, eight samples were produced in total.

An overview of the production protocol of the samples, which will be discussed in the following, is given in table 4.3. A first attempt was to proceed all three steps from table 4.2 in vacuum of about 10^{-6} mbar, which resulted in the evaporation of the sample. In order to verify our capabilities to produce samples at all, the next sample was left under air at normal pressure throughout the full process.

This lead to the first two samples, S1 and S2, surviving the heat treatment. The heat treatments were conducted using a Carbolite Gero STF 15/450 oven with heating capabilities up to 1500 °C.

Table 4.3 shows a summary of the produced samples with their production procedure and the resulting phases from XRD analysis.

Sample S1

The pellet with the first sample, S1, was put in a molybdenum boat to avoid the reaction with the oven. As shown in figure 4.9 this seemed to conclude in a reaction of the pellet with the molybdenum.

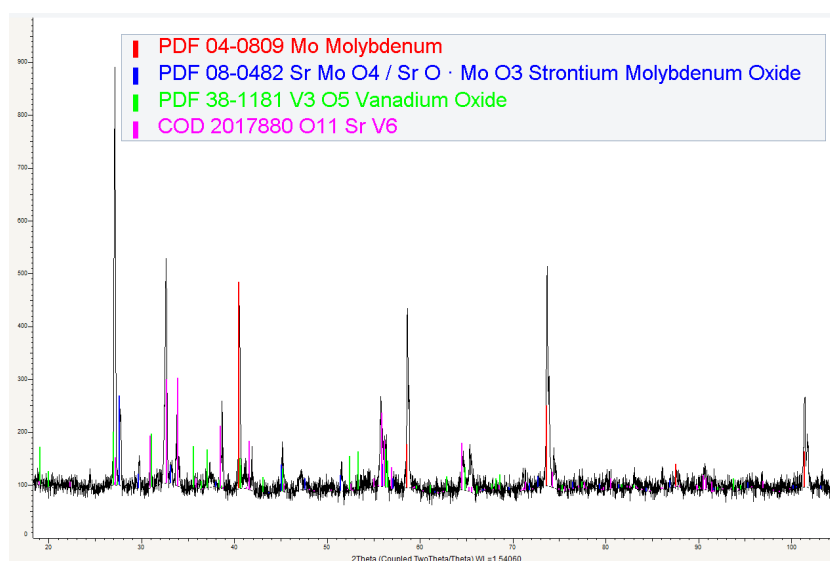


Figure 4.9: X-ray diffraction of S1. It shows a mixture of vanadium oxide, $\text{SrV}_6\text{O}_{11}$ and SrMoO_4 , with molybdenum oxide being the dominant species.

S1 exhibits pure molybdenum as well as vanadium oxide V_3O_5 , resulting from V_2O_5 reacting with O_2 from air. Despite that, a phase of strontium vanadate, $\text{SrV}_6\text{O}_{11}$ was formed. The rest of the SrCO_3 seems to have reacted with the molybdenum to SrMoO_4 .

Sample S2

As a consequence of the reaction of S1 with the molybdenum boat, S2 was put in a ceramic bowl. Unfortunately, this time the sample reacted with the tantalum wires used to fix the heat shields of the oven which were therefore left out in the following experiments.

An investigation via XRD, shown in figure 4.10, revealed that most of the sample disappeared, leaving mostly tantalum oxides from the oxidized tantalum wires and SrCO_3 ,

a starting ingredient from the pellet. S2 seems to mainly consist of the oxidized tantalum wires from the heat shields and some left overs of SrCO_3 . The pellet does not seem to have reacted or evaporated leaving mostly tantalum-oxides.

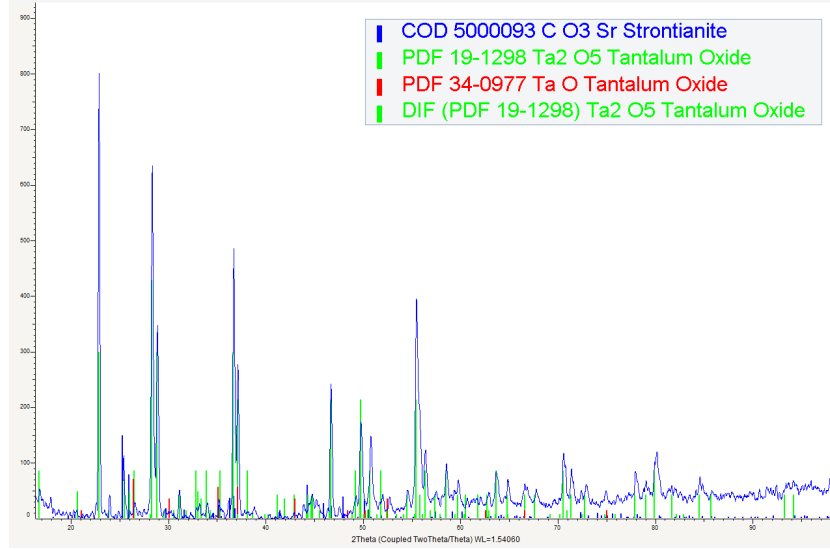


Figure 4.10: X-ray diffraction of S2, which seems to consists mainly of oxidized tantalum.

Sample S3

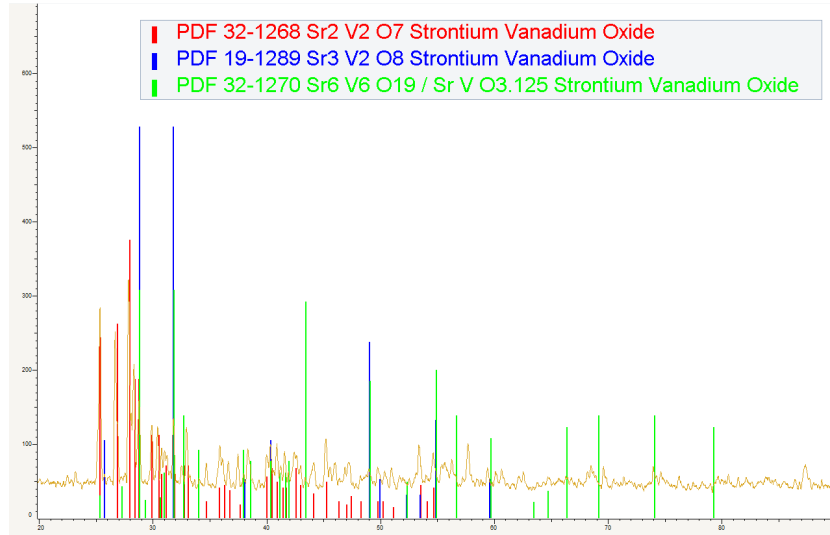


Figure 4.11: X-ray diffraction of S3 which shows three different phases of strontium vanadate, $\text{Sr}_2\text{V}_2\text{O}_7$, $\text{Sr}_3\text{V}_2\text{O}_8$ and $\text{Sr}_6\text{V}_9\text{O}_{19}$.

In order to confirm the reactions of the first two steps leading to strontium vanadate phases with high amounts of oxygen, a sample was produced with only step 1 and 2 from table 4.2, which resulted in sample S3. Half of the pellet was then put in air at the reduced temperature of 1100°C, but it evaporated also in this case. The remaining half was investigated with XRD. It showed multiple phases of strontium vanadate identified as $\text{Sr}_3\text{V}_2\text{O}_7$, $\text{Sr}_3\text{V}_2\text{O}_8$ and $\text{Sr}_6\text{V}_6\text{O}_{19}$ which is shown in figure 4.11.

Sample S4

After S3 seemed to confirm the desired reaction of steps 1 and 2 from table 4.2, the next samples were prepared in air with lower temperatures in the final step of the reaction. S4 was prepared at 900 °C in air as a last step. However, it did not show any difference in composition compared to S3, as shown in figure 4.12.

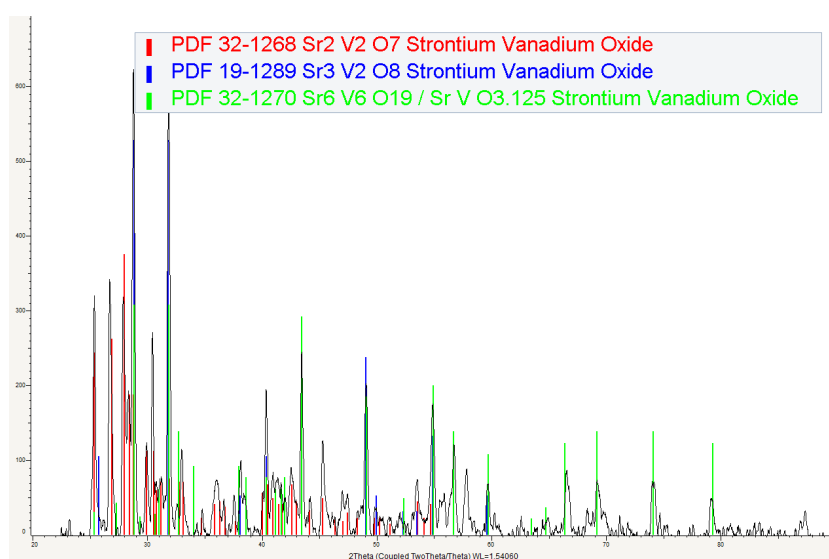


Figure 4.12: X-ray diffraction of S4.

Sample S5

As a next step after the production of S4, the temperature during the last step of the production of sample S5 was increased to 1000°C. As an additional change, S5 was put inside a graphite cylinder of about 1.5 cm diameter and about 3 cm height to produce a more reductive atmosphere in the vicinity of the sample. The XRD results of S5 are shown in figure 4.13.

While mechanically remaining its form, S5 showed the two strontium vanadate phases $\text{Sr}_3(\text{VO}_2)$ and $\text{Sr}_6\text{V}_6\text{O}_{19}$. The peaks of those two phases are very similar and overlap often, but it seems that $\text{Sr}_3(\text{VO}_2)$ is the slightly more abundant phase.

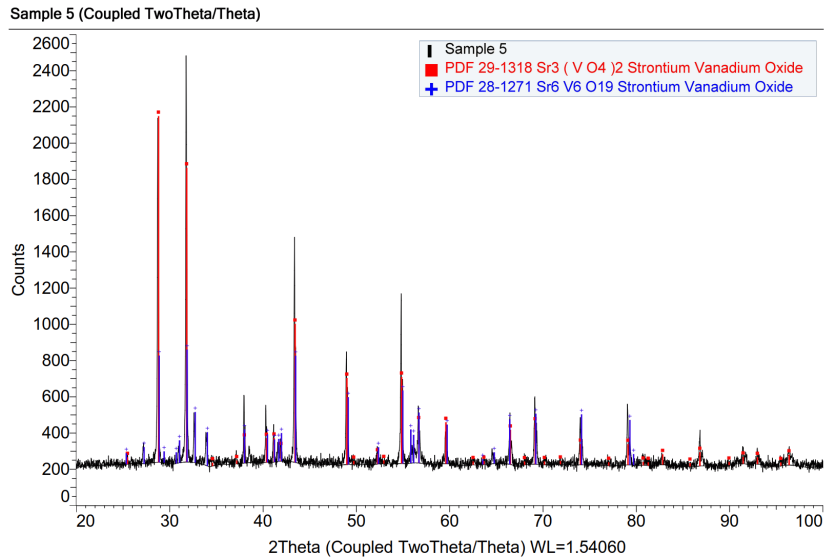


Figure 4.13: X-ray diffraction of S5 which shows the strontium vanadate phases $\text{Sr}_3(\text{VO}_2)$ and $\text{Sr}_6\text{V}_6\text{O}_{19}$.

Sample S6

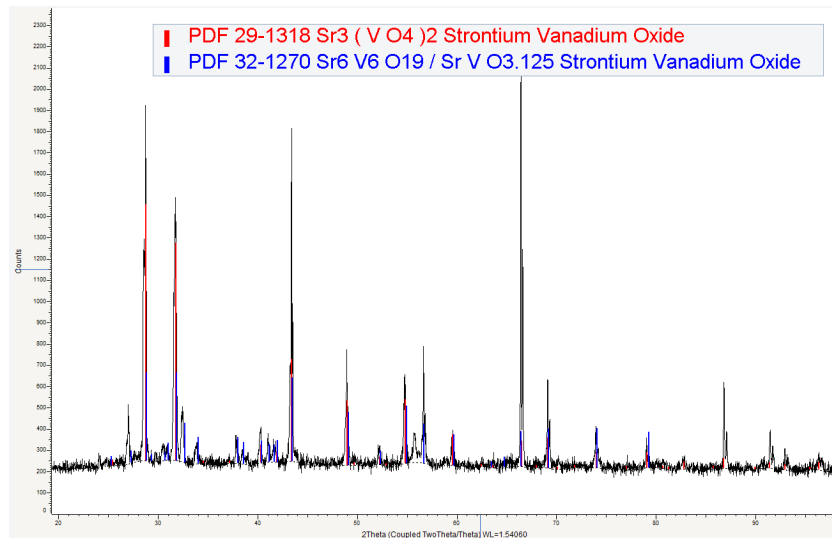


Figure 4.14: X-ray diffraction of S6 which show the strontium vanadate phases $\text{Sr}_3(\text{VO}_2)$ and $\text{Sr}_6\text{V}_6\text{O}_{19}$, as in S5.

S6 was produced with the same conditions as S5, with the only difference being that it was placed in an alumina bowl instead of the graphite tube.

As a result, the pellet was deformed and partially melted onto the bowl. However, the sample could be investigated via XRD, which is shown in figure 4.14. As in sample S5, the two main phases are identified as $\text{Sr}_3(\text{VO}_2)_4$ and $\text{Sr}_6\text{V}_6\text{O}_{19}$, with $\text{Sr}_6\text{V}_6\text{O}_{19}$ being more present in S6 than S5.

Sample S7

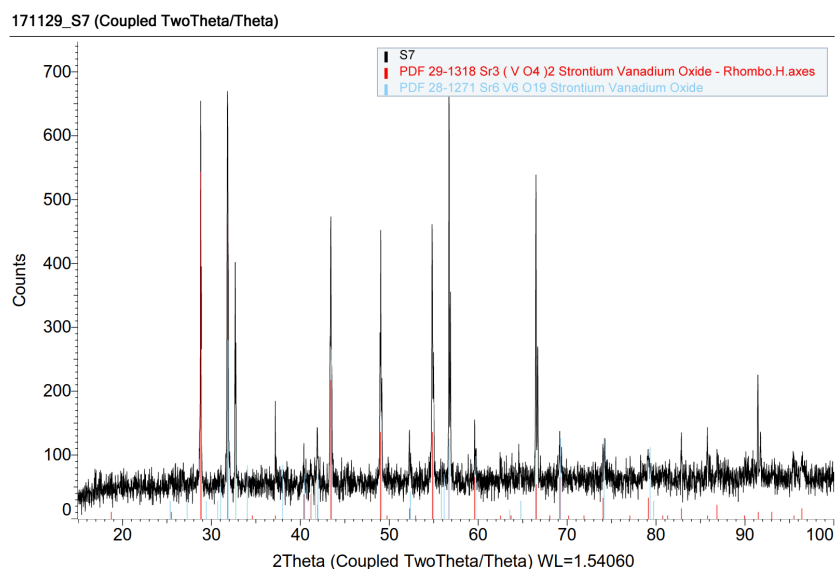


Figure 4.15: XRD results of S7. Two strontium vanadate phases, $\text{Sr}_3(\text{VO}_4)_2$ and $\text{Sr}_6\text{V}_6\text{O}_{19}$ are mainly produced.

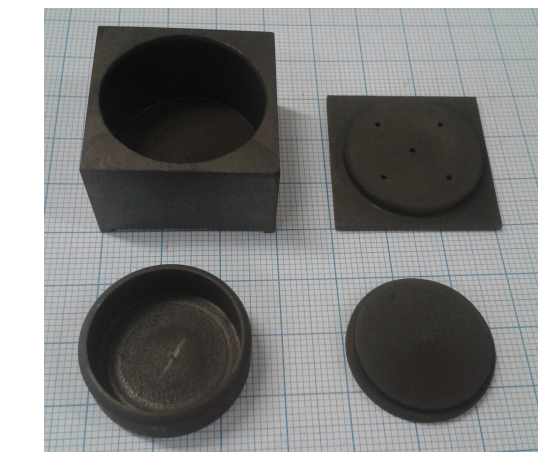


Figure 4.16: Graphite boxes used to produce S7 and 8. The pellet was placed in the inner round box, which is then put inside the bigger box. The top lid has holes with 1 mm diameter to allow gas evacuation of the crucible.

Due to the results of S5 compared to S6, the following samples were all prepared in graphite substrates. For sample S7, the pellet was first put inside the graphite tube used for S5 for the first two reaction steps and heated in air. Afterwards the pellet was put in a graphite box designed for this purpose (shown in figure 4.16) and heated to 1100°C under a vacuum in the order of 10^{-7} mbar for 12 h using a Pfeiffer turbo pump. The box consists of one graphite container in which the pellet is placed and an additional surrounding graphite cylinder with small holes. A similar approach was described previously for the production of TiC [56].

Unfortunately, there was a loose contact at the thermocouple of the oven which lead to an uncertainty of how long the sample had been heated after the first two steps. Despite these circumstances, the pellet survived and could be investigated with XRD, shown in figure 4.15. The resulting sample consisted of the $\text{Sr}_3(\text{VO}_4)_2$ and $\text{Sr}_6\text{V}_6\text{O}_{19}$

Sample S8

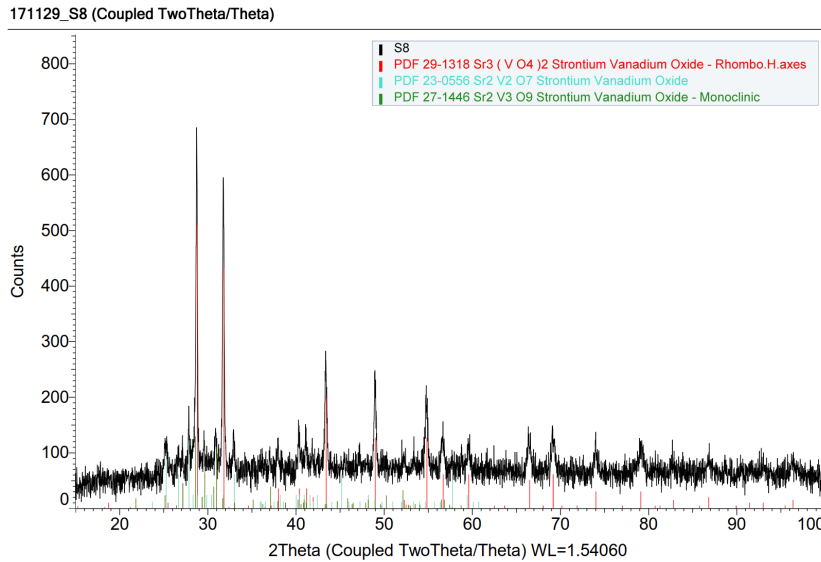


Figure 4.17: XRD results of S8. There are three strontium vanadate phases present, the dominant being $\text{Sr}_3(\text{VO}_4)_2$, $\text{Sr}_2\text{V}_2\text{O}_7$ and $\text{Sr}_2\text{V}_3\text{O}_9$.

The same procedure was applied as for S7, but this time with a repaired thermocouple and therefore the correct time spans. Its composition is shown in figure 4.17. Besides the dominant phase of $\text{Sr}_3(\text{VO}_4)_2$, $\text{Sr}_2\text{V}_2\text{O}_7$ and $\text{Sr}_2\text{V}_3\text{O}_9$ are present. These two residual phases are not very abundant and therefore hard to identify. Surprisingly, the $\text{Sr}_6\text{V}_6\text{O}_{19}$ phase is not seen in this sample. Instead, there are phases with a higher oxygen ratio.

4.4.2 SrVO_3

In addition to the self-made samples, SrVO_3 was bought from American Elements, USA. To confirm its composition, the powder was investigated by XRD, which showed that it contained no SrVO_3 at all. Instead it seems to consist of the initial ingredients SrCO_3 and V_2O_5 and vanadium hydroxides. The product was therefore returned to the manufacturer. The underlying structure in 4.18 results from the quicker scan speed and reflections from the sample holder.

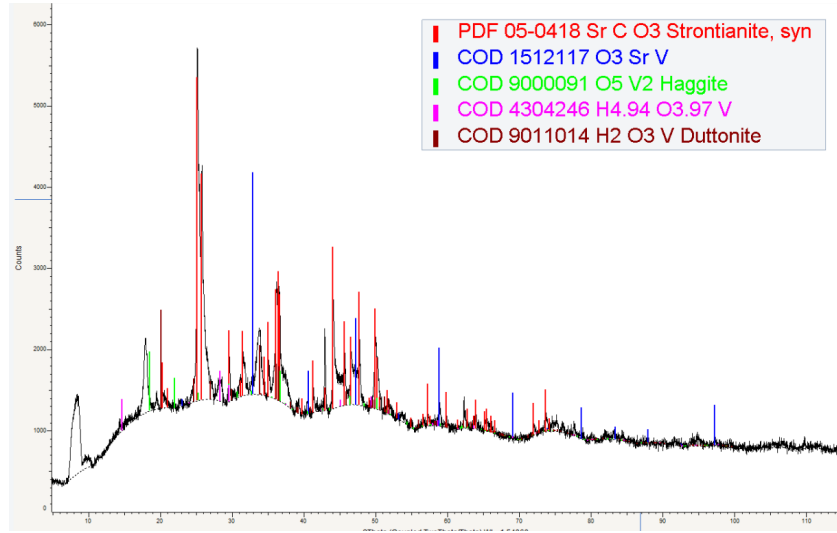


Figure 4.18: The composition of the supposed SrVO_3 powder.

4.4.3 Gadolinium hexaboride- GdB_6

In addition to the strontium vanadate samples, LaB_6 and GdB_6 were used for electron emission tests. GdB_6 was available as a tube (acquired from Huizhou Tian Yi Rare Material Co.,Ltd) and as a powder (acquired from Sigma Aldrich).

In order to enable testing of GdB_6 before the arrival of the powder, one of the tubes was first investigated with a Carl Zeiss SMTSigma secondary electron microscope (SEM) and via energy dispersive X-ray spectroscopy (EDX) to determine the bulk and surface structure and then ground down to a powder. The electron emission of the powder was then investigated at the test-stand.

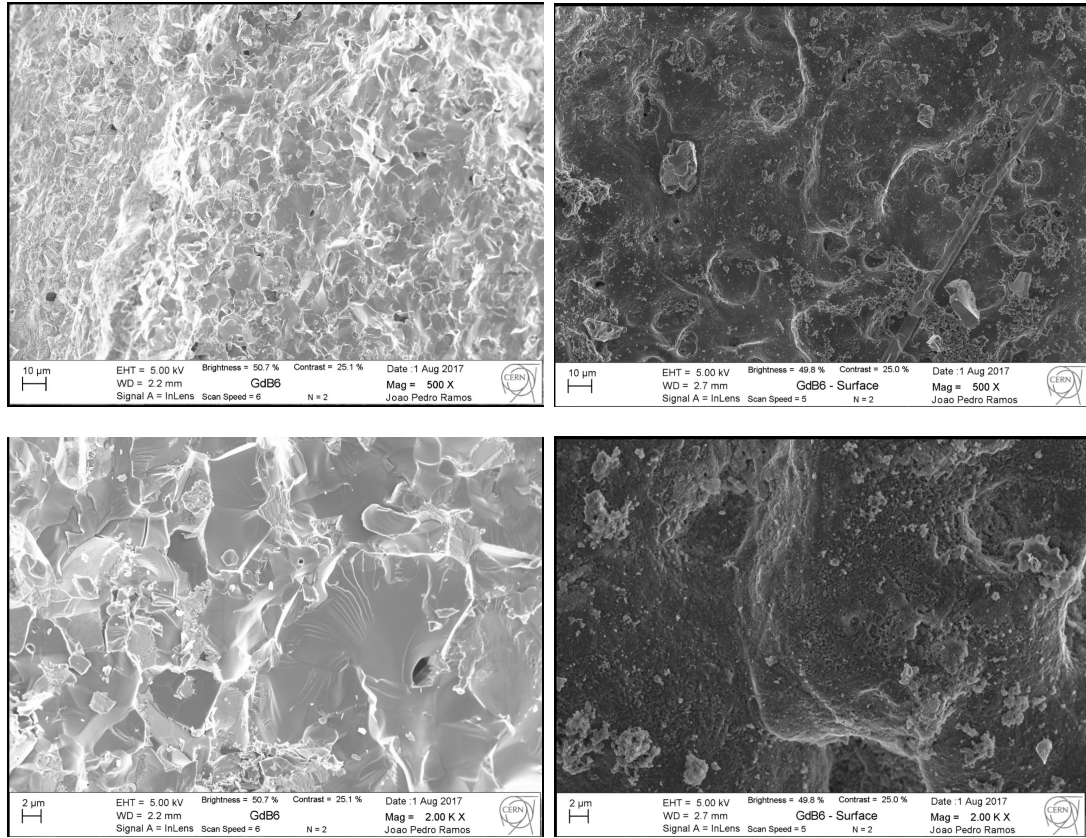


Figure 4.19: SEM pictures of the bulk (left) and the surface (right) of the GdB_6 tube.

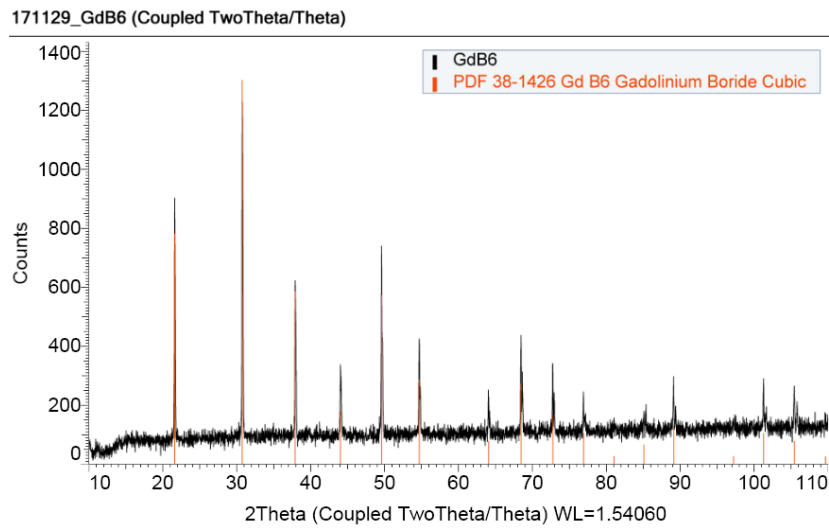


Figure 4.20: Results of the x-ray diffraction measurements of GdB_6 , which was verified to be pure.

For the investigation of the bulk, one tube was broken and measurements at the fracture spot were taken. The fracture is transgranular, which means it does not follow the grain boundaries but instead goes through the crystalline lattice. This is characteristic for a brittle material.

Comparing the resulting images of the bulk and surface in figure 4.19, it is noticeable that the morphology of the surface and bulk are completely different. There is a nanostructured layer on the surface of the sample, while in the bulk grains of a few μm can be seen.

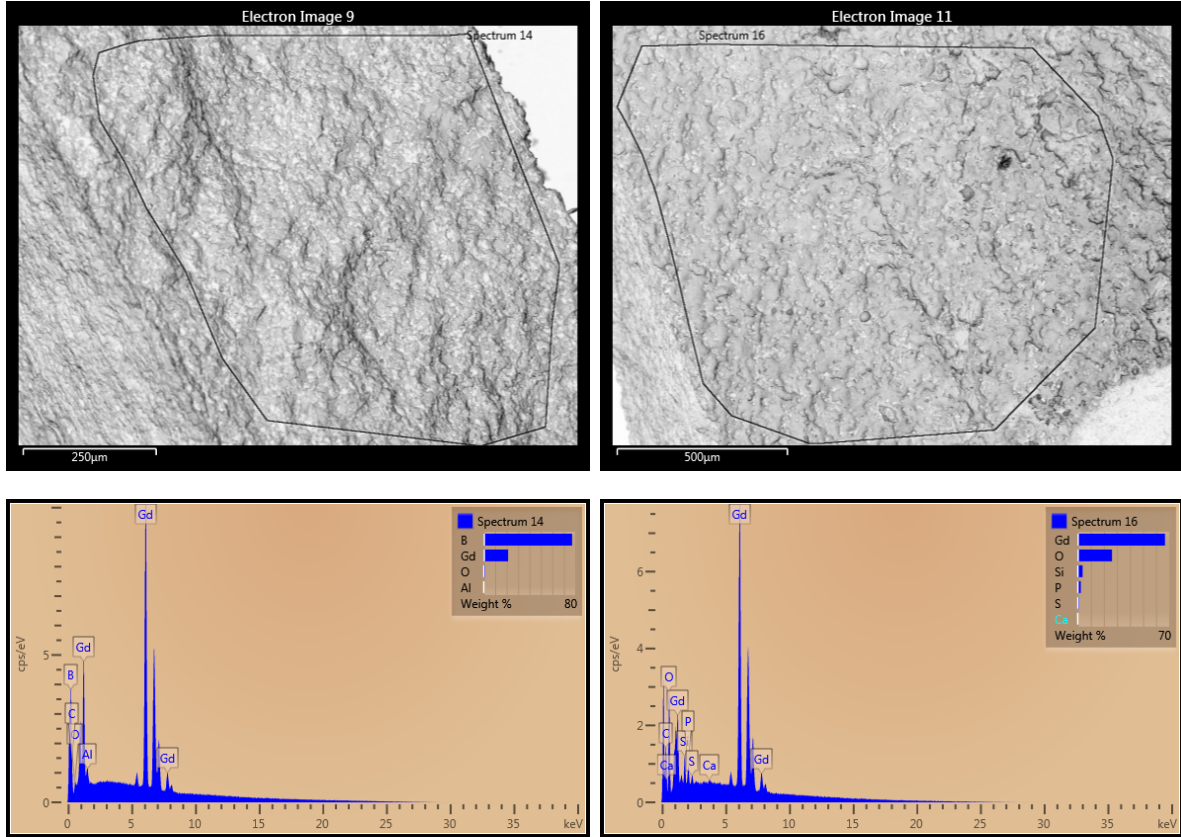


Figure 4.21: Picture and composition of the bulk (left) and the surface (right) of the GdB_6 tube.

The results of the EDX of the bulk and the surface of the GdB_6 tube are shown in figure 4.21.

While the bulk material shows the expected elements Gd and B with small contaminations, the surface of the tube exhibits no boron but oxygen, phosphorus and silicon. Due to their low concentration, the latter are probably contaminants while the big amount of oxygen probably means the existence of gadolinium oxide at the surface instead of GdB_6 .

To ensure the composition of the GdB_6 powder acquired from Sigma Aldrich, it was

investigated using XRD, as shown in figure 4.20. Within the detection limit of the XRD, the powder seems to consist only of GdB_6 .

4.4.4 Lanthanum hexaboride- LaB_6

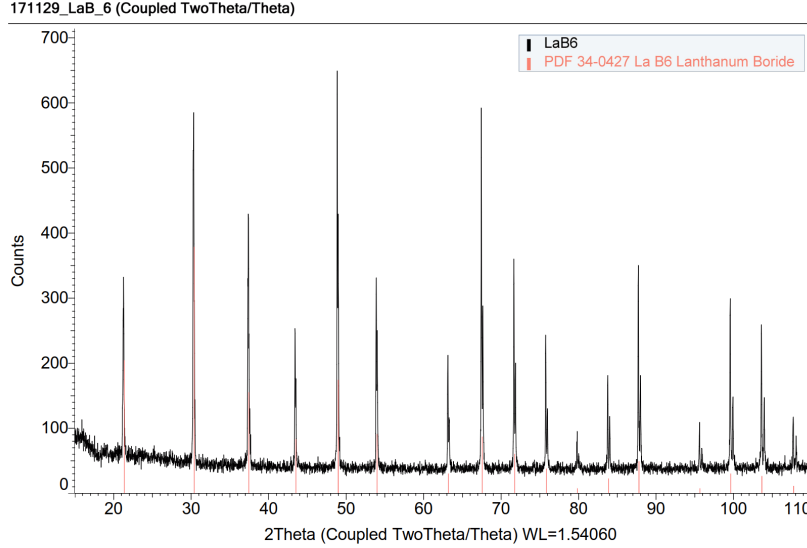


Figure 4.22: Results of the x-ray diffraction measurements of LaB_6 which can be verified to be LaB_6 within the detection limit of the XRD.

The LaB_6 powder, acquired from Sigma Aldrich, was also investigated with XRD. Before the measurement, the sample was heated up to 1400°C in an oven at air of normal pressure in order to verify that it does not dissociate under high temperatures. As shown in figure 4.22, the powder clearly consists only of LaB_6 .

4.5 Characterization through electron emission

In order to infer the potential performance of the different materials as negative surface ion source, the samples were initially characterized in terms of their electron emission capabilities. The samples were placed in the location of the pellet in the MK4 negative ion source and the electron current was measured using the electron catcher.

4.5.1 Temperature calibration

Prior to the investigation of the different material samples, the temperature of the ion source was calibrated using a pyrometer. Since the target #316 used in this thesis was

changed due to necessary repairs, the target calibration was repeated when necessary.

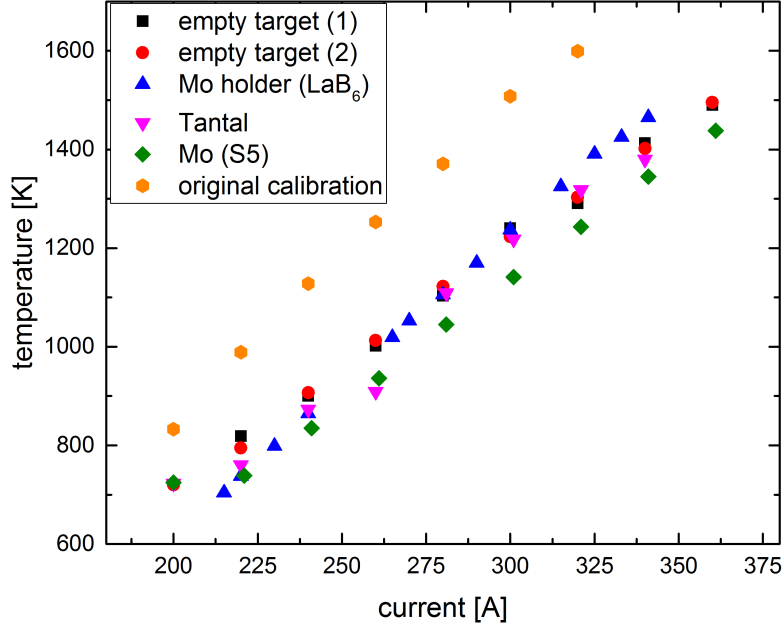


Figure 4.23: Temperature calibration of the original (orange) and refurbished 316. The refurbished version was calibrated empty as well as with tantalum and molybdenum sample holders. The samples contained are given in the brackets.

While both temperature calibrations were performed using a Microtherm disappearing filament type optical pyrometer, there were some important differences. The original calibration was done at the hottest point of the empty transfer line. The second calibration, performed by a different person, was done with empty as well as filled sample holders placed at the front of the transfer line. This temperature calibration therefore was performed at the spot of the sample, which is why it is believed to represent the actual sample temperature better. The result of the performed calibrations, both for the original and refurbished target, are shown in figure 4.23.

Additionally, figure 4.23 also shows, that different sample holder materials have only little impact on the sample temperature. Since the applied line heating current was the same for all samples, in the following discussion all graphs are made with the newer temperature calibration which seems to present the actual sample temperature more accurate. It is worth mentioning that the temperature is serving only as a reference point for comparing the electron emission, an exact determination of the work function of the compounds is not necessary at this point.

4.5.2 Electron emission of LaB₆

LaB₆ is the standard material for the negative ion source at ISOLDE, and can therefore be used for benchmarking possible alternatives. The samples were prepared by filling the sample holder completely and then pushed to the end of the transfer line. If not indicated otherwise, all heating cycles were performed with a $0.05 \frac{A}{s}$ current ramp to heat the samples in target #316. In some cases, a dwell time at the maximum temperature was added.

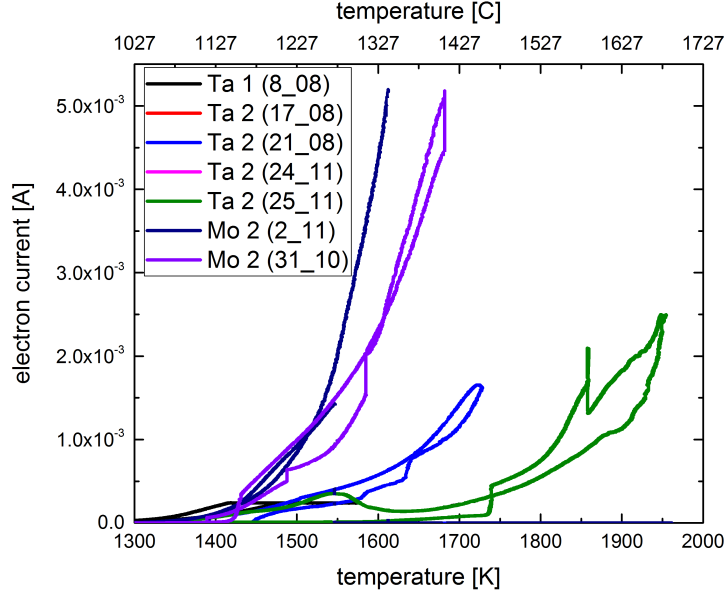


Figure 4.24: Electron emission vs. temperature of three different laB₆ samples. The sample holder material and sample number is given in brackets. The Sample Ta 2 was already heated multiple times and recreated the same curve twice. For the samples Ta 1 and Mo the current limit of the used voltage supplies was reached at the maximum of the current, which is why these data points are left out.

Figure 4.24 gives an overview of the electron emission of various samples plotted against the temperature for both before and after the refurbishment of the target #316. Sample Ta 2 turned out to not being properly filled, so that some LaB₆ fell out during the sample insertion. The maximum current reached is in the order of a few mA.

It seems that the emission curves change with the different samples but always reach an electron current of above 1 mA. This could be an effect of differences in surface structure of the prepared samples since all were containing pure LaB₆, which was verified with the XRD, as discussed in the section 4.4.

Additionally, during the temperature calibration with the pyrometer it was visible that the sample surface was not heated homogeneously since there were cold spots visible in

the beginning. This could also add to the difference in the curves. Sample Ta 1, the first investigated sample in a tantalum sample holder shows a similar electron current during heating as the samples in the molybdenum holder in the beginning.

Unfortunately, during the measurement of Ta 1 the current limit of the voltage supply for the electron catcher was reached, which is why the curve is constant at $250\text{ }\mu\text{A}$ starting at a temperature of about $1430\text{ }^{\circ}\text{C}$. Sample Ta 2 seems to perform worse with ongoing heating cycles. Since the measurements from the 21st of august and 24th of November are identical, there could be a difference of the surface if this sample in respect to the other samples, possibly caused during the sample preparation. After the initial two measurements, the sample seems to degrade. This is indicated by the decrease of the maximum currents at the measurements on the 25th and 27th of November. The residual gas analyzer did not show any increase in lanthanum or boride, but it would not detect LaB_6 since its mass is above the limit of 200 amu of the detector. Doubly positive LaB_6 was not detected.

The highest current was reached by the last measured sample, Mo 2, which reached a current of 5 mA at 1600 K . Mo 2 also reached the current limit of the voltage supply at 5 mA , which is why there is no additional data at higher temperatures. In total, the electron current seems to depend a lot on the sample for LaB_6 , which could indicate that the difference in the surface structure was substantial. This indicates that the careful manufacturing of the sample is critical. Theoretically, at 1600 K an electron current of 7.3 mA is expected from a LaB_6 surface area of 3.14 mm^2 with a work function of 2.7 eV , which is close to the sample results shown in figure 4.24.

Generally, all samples show a hysteresis between cooling down and heating. This may result from not reaching thermal equilibrium during the heating due to the fast increase of the temperature or small changes in the sample structure and resulting inhomogeneities in the electron emission. Heating with slower increase of the temperature reduces the hysteresis, as shown later for sample S7 in figure 4.34.

4.5.3 Electron emission of tantalum

In order to investigate the heating procedure and to test a material with a known work function as well as the setup, tantalum was investigated. This was conducted with an empty transfer line as well as a tantalum sample holder. The resulting electron emission curves are shown in figure 4.25.

The electron current of the empty transfer line was significantly less then with a tantalum sample holder inserted in the front of the line. This results from an increased surface and greater vicinity of the sample holder to the electron catcher, which leads to a more efficient extraction of the emitted electrons. Fits of the Richardson law of the heating cycles, corrected for emission from tantalum, resulted in a work function of about $4.01 \pm 0.1\text{ eV}$, which is in the expected range of the literature value 4.12 eV . The surface was estimated to be 3.14 mm^2 radius. The result is a good indicator that the assumptions made are valid.

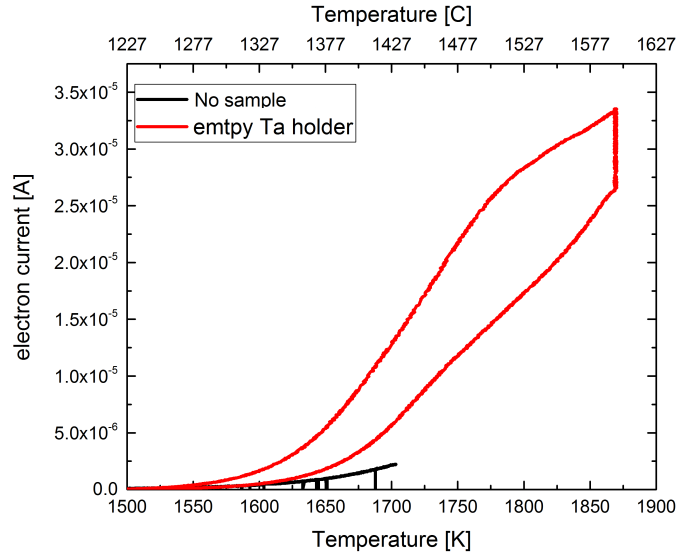


Figure 4.25: Electron emission measurements for tantalum from the empty transfer line and an empty tantalum sample holder.

4.5.4 Electron emission of molybdenum

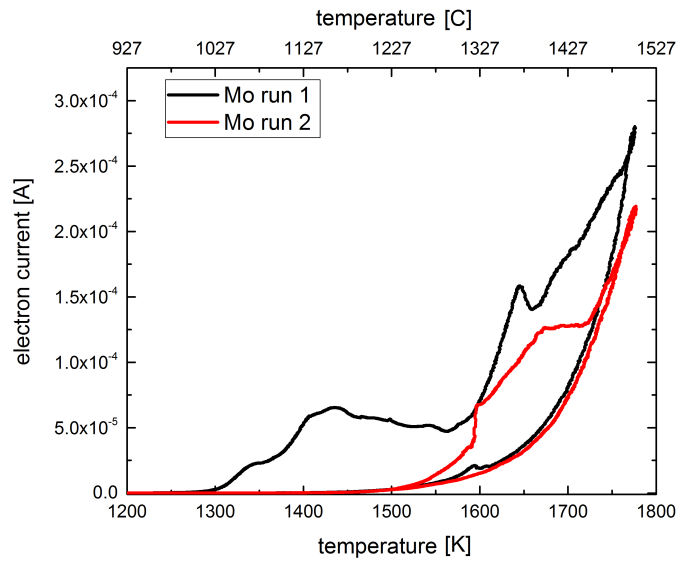


Figure 4.26: Electron emission measurements for molybdenum. During heating, molybdenum shows unexpected increase of the electron current, which seems to result from evaporation of material from the surface at certain temperatures.

A second element with known work function, molybdenum, was investigated in order to test and verify the feasibility of the measurements with the electron catcher.

As expected, molybdenum shows a low maximum electron emission in the order of $100 - 200 \mu\text{A}$, similar to tantalum. The electron emission current plotted against the temperature is shown in figure 4.26. In most cases, the cool down curve shows the expected behavior described by the Richardson law, while there are some interesting features during heating: in both cases shown in figure 4.26 the electron current shows an unstable behaviour, resulting in a temporarily higher electron emission current in the temperature range between 1300°C and 1650°C .

There are much more irregularities in run 1 than in run 2 of the sample where they start at higher temperatures. Therefore, it can be assumed that these irregularities result from surface or target contamination which is evaporating due to the heating. Fitting the current density with the Richardson law results in a work function between 3.4 eV and 3.6 eV for molybdenum, which is about 0.4 eV less than the literature value.

4.5.5 Electron emission of GdB_6

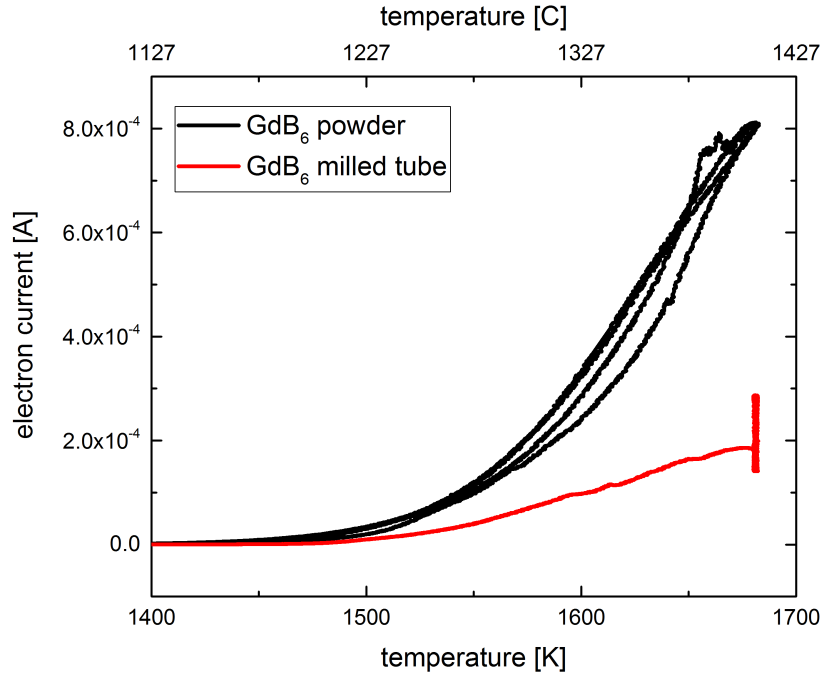


Figure 4.27: Electron emission current of the GdB_6 powder (black line) and the milled GdB_6 tube.

As one can see in figure 4.27, the commercial GdB_6 powder showed good agreement with the expected shape of the emission current and displays almost no hysteresis throughout two consecutive heating cycles despite the same heating speed. This seems to indicate a

very homogeneous surface of the sample. However, the maximum current reached with about $800\ \mu\text{A}$ was surprisingly low. The pulverized GdB_6 tube performed significantly worse with a maximum current of about $200\ \mu\text{A}$. A richardson law fit of the current density of the powder, shown in figure 4.29 on the right, gives a work function of about $2.95(9)\ \text{eV}$, which is higher than the $1.5\ \text{eV}$ from [50] and slightly above the effective work function of $2.78\ \text{eV}$ given in [28]. The SEM and EDX results in the previous section showed that the surface of the tube consists not of pure GdB_6 but is oxidized, which might be the cause of the lower electron current than for the pure powder. Additionally, the sample might have consist of larger grains then the pure powder since the tube was hard to ground into pieces. The straight line of the pulverized tube at the maximum current in figure 4.27 results from fluctuations of the current during a dwell time at that temperature. Hence, the time dependent electron current is shown in figure 4.28.

There is a dip directly after reaching the end temperature, followed by an increased emission current, which falls off at the end of the dwell time.

The dip could be the result of a part of the surface reacting or evaporating, the following increase in current could be the result of inhomogeneous heating of the surface. Despite that, the electron current behavior during heating up and cooling shows no hysteresis.

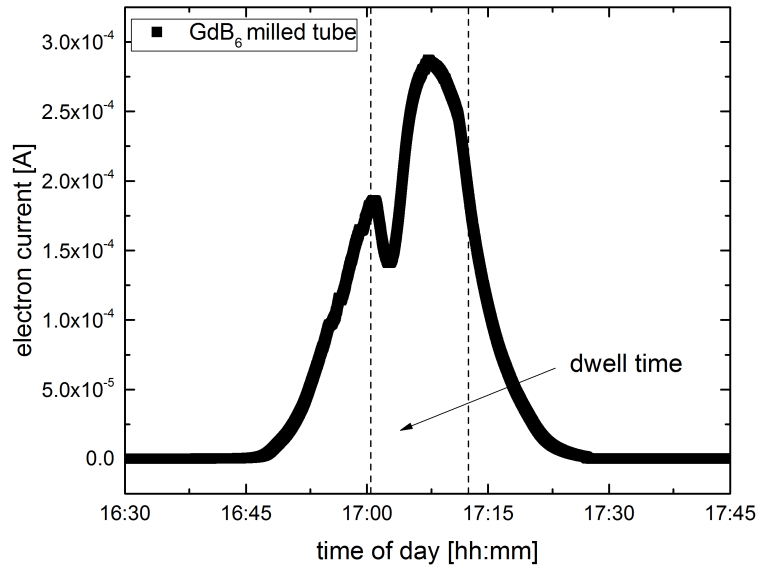


Figure 4.28: Time dependent electron current. There is a dip at the beginning of the dwell time, after which the current increases slightly and falls off again towards the end of the dwell.

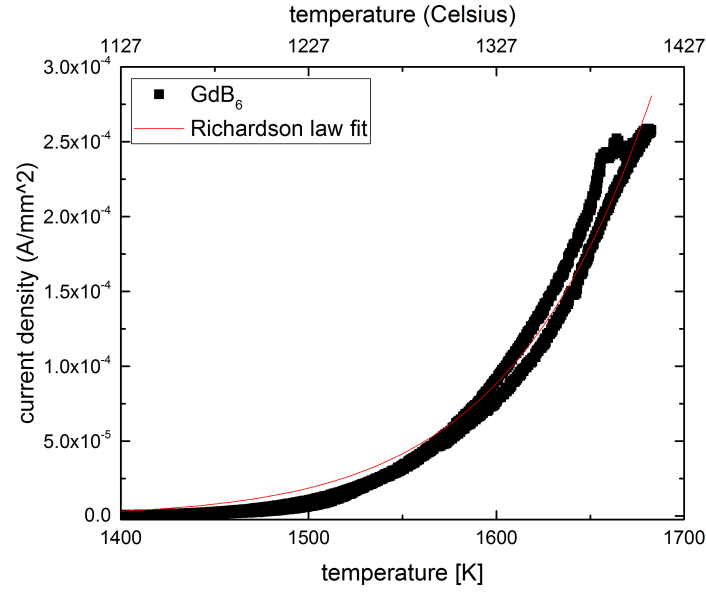


Figure 4.29: Current density of GdB_6 powder with richardson law fit (red line). The resulting work function is 2.95 eV.

4.5.6 Electron emission of sample S1

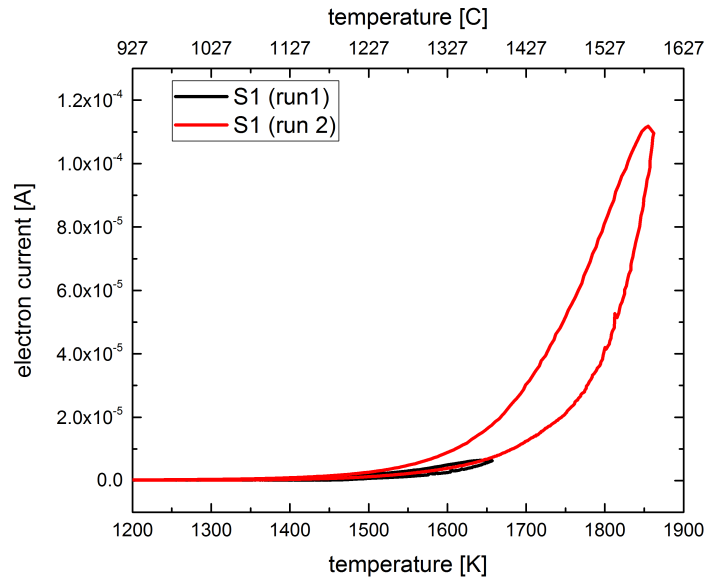


Figure 4.30: Electron emission of sample S1. The maximum current of $110 \mu\text{A}$ was observed at a temperature of 1850 K.

The first produced sample, S1, consisting of a mixture of V_3O_5 , $SrMoO_4$, SrV_6O_{11} showed a maximum electron emission current of about $115 \mu A$, which is an order of magnitude lower than LaB_6 . Due to the composition of the sample, a low current was expected.

Besides the hysteresis of the heating and cool down, which is seen at all samples. This hysteresis can be explained by the speed of the heating and therefore the surface of the sample not being in thermal equilibrium.

4.5.7 Electron emission of sample S5

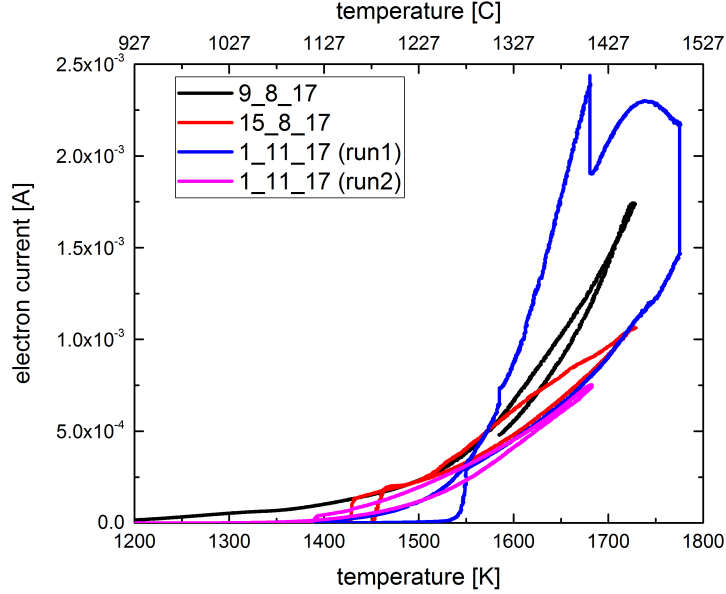


Figure 4.31: Electron emission of S5. The maximum current, achieved in the first measurement, was about 1.8 mA. In later measurements, the maximum electron current decreases. This seems to have been reversed during a dwell at about 1770 K.

This sample was a more promising candidate since it showed only two strontium vanadate phases, $Sr_3(VO_4)_2$ and $Sr_6V_6O_{19}$, with $Sr_3(VO_4)_2$ being slightly more abundant. The electron emission current, shown in figure 4.13 is with a maximum current between 1 mA and 2 mA comparable to LaB_6 . However, this sample seemed to degrade with the number of heating cycles. In the last heating cycle though, there was a peculiar behaviour at the highest temperature: during a dwell time, the electron current increased, dropped during cool down and immediately spiked. Following this, the sample proceeds with the typical slow drop of the current during cool down. This could indicate that the surface layer was covered or contaminated. During the dwelling at high temperature, this layer or parts of the sample could have baked out, revealing a fresh hot sample surface which then was cooled down.

4.5.8 Electron emission of sample S6

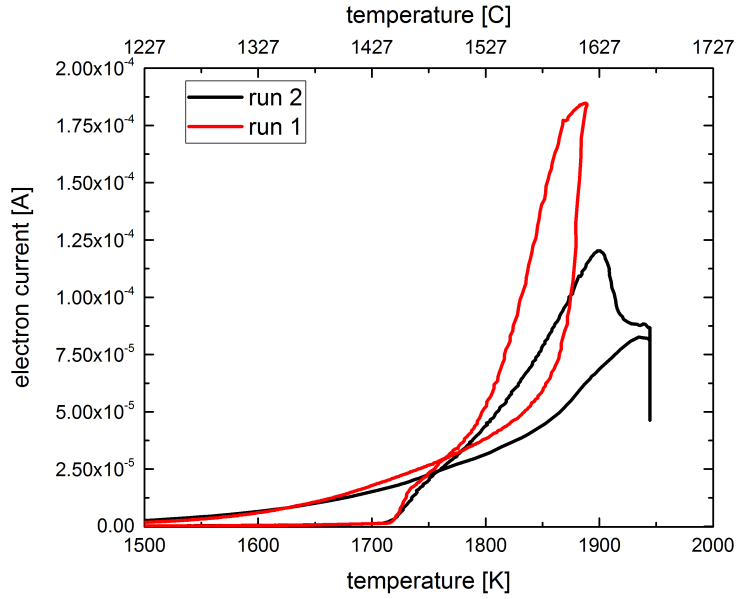


Figure 4.32: Temperature dependent electron emission of sample S6.

In figure 4.32 the electron emission current of sample 6 is shown. The first heating cycle resulted in a slightly better electron current than the second, possibly indicating changes on the surface of the sample during the first heating cycle.

Sample S6 consists of the same two strontium vanadate phases as S5, $\text{Sr}_3(\text{VO}_4)_2$ and $\text{Sr}_6\text{V}_6\text{O}_{19}$. However, the performance regarding the electron emission was with 2 mA an order of magnitude lower than for S5. Since $\text{Sr}_3(\text{VO}_4)_2$ seems more dominant in S5, this might indicate that this phase is the responsible for increased electron emission current in S5 and in return the increased amount of $\text{Sr}_6\text{V}_6\text{O}_{19}$ causing worse performance. Another explanation could be that there are contaminants at the surface of the sample which were not detected by the XRD.

4.5.9 Electron emission of sample S7

S7 was produced in a more reductive atmosphere inside a graphite crucible. The electron emission, shown in figure 4.33 rose up to 5 mA at about 2000 K, which is similar to S5. This was as expected, since both samples consist of the same two strontium vanadate phases, $\text{Sr}_3(\text{VO}_4)_2$ and $\text{Sr}_6\text{V}_6\text{O}_{19}$. In order to see if the hysteresis of the samples was due to the speed of the heating and cooling, a slow heating cycle of S7 was measured, shown in figure 4.34. Besides a slow drop off in the current during dwell time, no hysteresis can be seen. Additionally, the heating time did not change the maximum current. During two consecutive heating cycles (blue graph in figure 4.33) the sample seems to have

changed its surface structure which involved the production of CO and CO₂, as shown in figure 4.5.9. Here, the partial pressure of CO and CO₂, detected with the residual gas analyzer, are shown. After the initial decrease during pump down, both spike at the same time during the heating cycle.

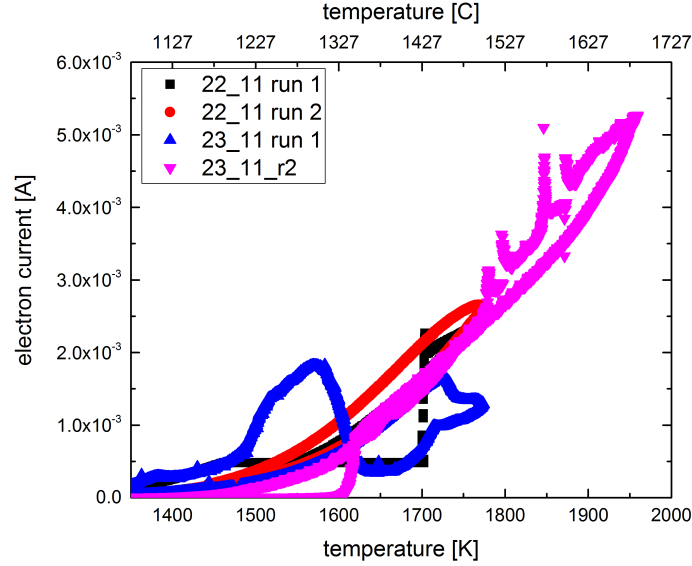


Figure 4.33: Electron current of S7, the maximum current is about 5.1 mA at 1900 K.

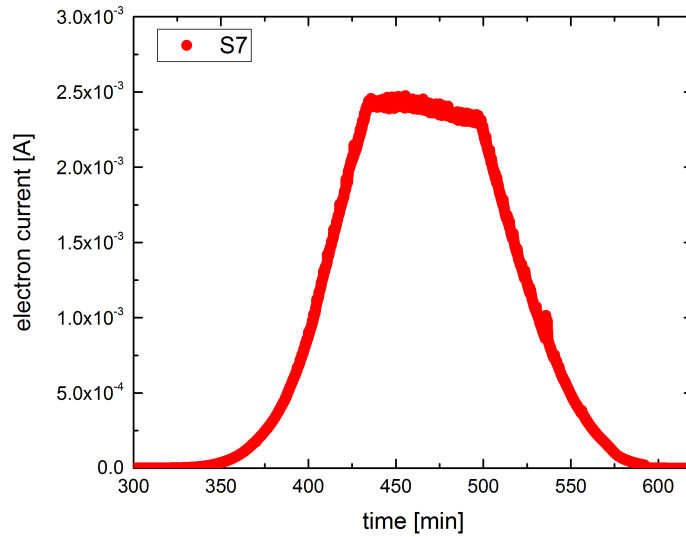


Figure 4.34: Time dependent electron emission of S7. The plot shows no hysteresis in comparison to the samples with faster heating cycles but reaches a similar maximum electron current of about 4.1 mA.

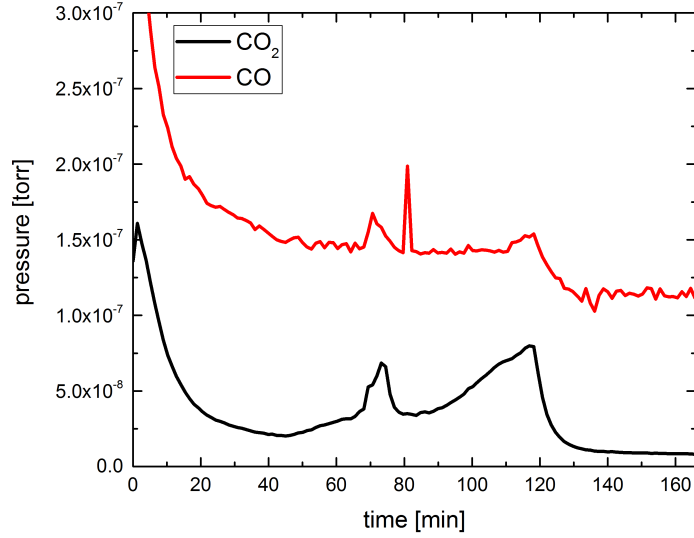


Figure 4.35: Partial pressure of CO and CO₂ during the heating cycle of S7 (run 1 on the 23rd of November). Both graphs exhibit spikes after 70 minutes and a decrease during cool down after 2 hours. This indicates decomposition of the sample.

4.5.10 Electron emission of sample S8

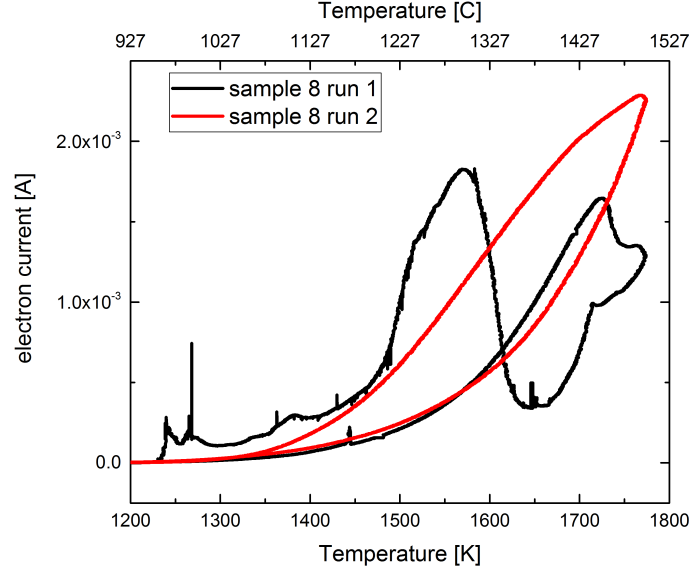


Figure 4.36: Electron emission of sample 8. During the first consecutive heating cycles the sample seems to have underwent temperature dependent surface changes.

The electron emission from sample S8 is expected to be similar to S7 since there almost identical production procedure. In both samples the main phase was $\text{Sr}_3(\text{VO}_4)_2$, with sample S8 having traces of $\text{Sr}_2\text{V}_2\text{O}_7$ and $\text{Sr}_2\text{V}_3\text{O}_9$, which was hard to identify. However, the resulting electron emission, shown in figure 4.36 is very similar to S8, with its maximum being around 2.2 mA. Figure 4.36 shows a strange behavior during the first two heating cycles. This could be explained by a chemical reaction of the sample similar to S7.

4.5.11 Discussion

In general the phase identification, especially of the first four samples, was difficult due to the similarities in the crystal structures of different phases and the wide variety of the possible fits. This often resulted in an overlap of multiple phases, which could not be distinguished.

The samples produced within a reductive atmosphere, predominantly show two phases of SrVO: $\text{Sr}_3(\text{VO}_4)_2$ and $\text{Sr}_6\text{V}_6\text{O}_{19}$. Especially the latter compound is already very close to the desired element ratio of SrVO_3 , but surprisingly, $\text{Sr}_3(\text{VO}_4)_2$ seems to contribute more to the electron emission. This is especially in the case of S5 and S6, which are both showing the same two phases with just a slight difference in abundance of $\text{Sr}_6\text{V}_6\text{O}_{19}$.

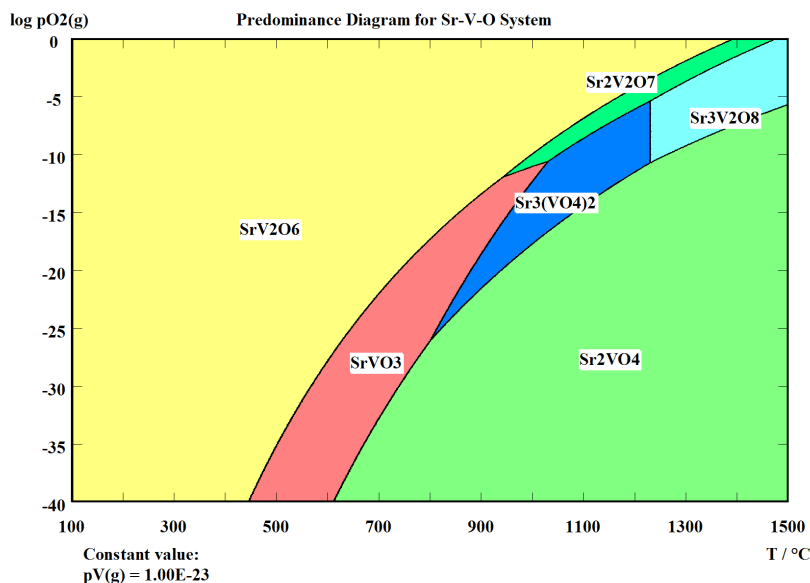


Figure 4.37: Predominance diagram of strontium vanadate phases. The samples S1-8 are in a regime with slightly higher oxygen partial pressure and temperature than the desired SrVO_3 . This diagram was made with HSC 7.11.

In figure 4.37 a predominance diagram of the Sr-V- O phases is shown, created with HSC 7.11. The V partial pressure is fixed at $1 \cdot 10^{-23}$ mbar while the x-axis is the

temperature and the y-axis the logarithm of the oxygen partial pressure. The vanadium partial pressure was adjusted to be very low since vanadium is not very volatile, also considering the production temperature of the samples and the corresponding strontium vanadate phases.

This theoretical graph indicates, that the regime in which the sample production took place was too hot and at a too high oxygen partial pressure. This resulted in the production of $\text{Sr}_3(\text{VO}_4)_2$ and $\text{Sr}_2\text{V}_2\text{O}_7$, which both occur in the produced samples. However, the processes considered by HSC in this case are thermodynamic, which means that the reaction speed is not accounted for.

For future production attempts the atmosphere should be slightly more reductive. This could be achieved in a metal oven, an airflow filtered by additional graphite sponge or a hydrogen atmosphere, as indicated in the literature [53, 54, 51].

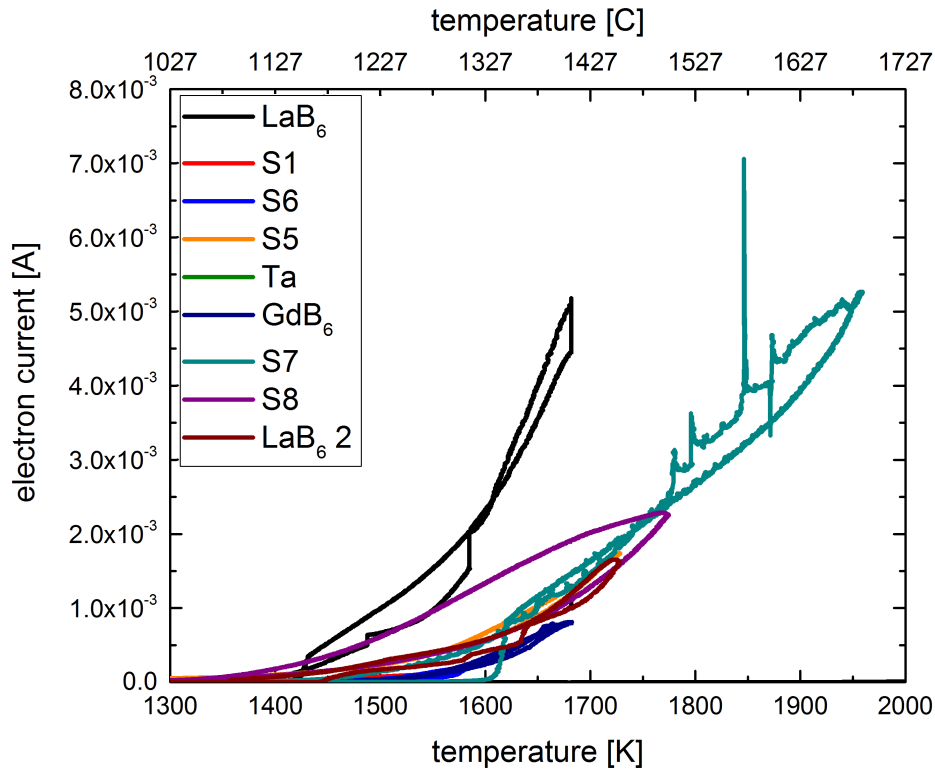


Figure 4.38: Summary of the electron emission of all investigated samples.

In figure 4.38 the electron emission of all samples is shown. The last LaB_6 sample seems to have performed the best, while one previous sample of the same material shows little difference to the self-produced strontium vanadate phases. Generally, it seems that small differences of the structure of the sample surface is of high importance, since there are differences between the various LaB_6 samples. However, in the case of LaB_6 , homogeneous sample preparation was especially difficult, since the powder is not easily

pressed to a pellet. Therefore, small losses and differences between samples are more likely for LaB_6 .

The GdB_6 powder, which was expected to be in the same range as LaB_6 had an order of magnitude less electron emission current. Since the ground tube with an oxide layer on the surface showed even lower electron current, one can assume that the powder sample either had contaminations on its surface too small to detect for the XRD or that GdB_6 simply is no suitable alternative for LaB_6 .

The samples of strontium vanadate phases produced in a reductive atmosphere, S5, S7 and S8 are with a few miliampere maximum current closer to the electron current of LaB_6 . These are all samples containing the $\text{Sr}_3(\text{VO}_4)_2$ compound, which is close to the desired SrVO_3 , as discussed in a previous section. However, S7 and S8 also seem to react during heating. This could indicate a temporary change of the sample surface which would result in the production of CO_2 and CO , as detected with the residual gas analyzer. However, both samples seem to be able to recover degradation and reached the maximum current measured in the initial heating cycles.

5 GANDALPH

5.1 Setup

The Gothenburg ANion Detector for Laser PHotodetachment (GANDALPH) is an experimental beam line designed to measure the electron affinity of negative ions of radioactive isotopes. The setup is shown in figure 5.2. GANDALPH was built at Gothenburg for the measurement of the EA of astatine and was installed at the GLM beamline of CERN-ISOLDE during the initial At^- campaigns [16]. GANDALPH consists of several ion optics and a neutral particle detector which is shown in figure 5.2. The ion beam enters through a 10 degree flange where it is deflected into the main chamber. The beam then passes a steering box and is aligned to pass through two apertures, in between which the ions are photodetached by a laser beam. The neutralized atoms then enter the neutral particle detector, which is shown in its upgraded form in figure 5.3. The neutral particle detector itself consists of two stages. After an initial aperture, residual charged particles can be bent by 45° into a Faraday cup for beam tuning purposes or detection of residual negative ions.

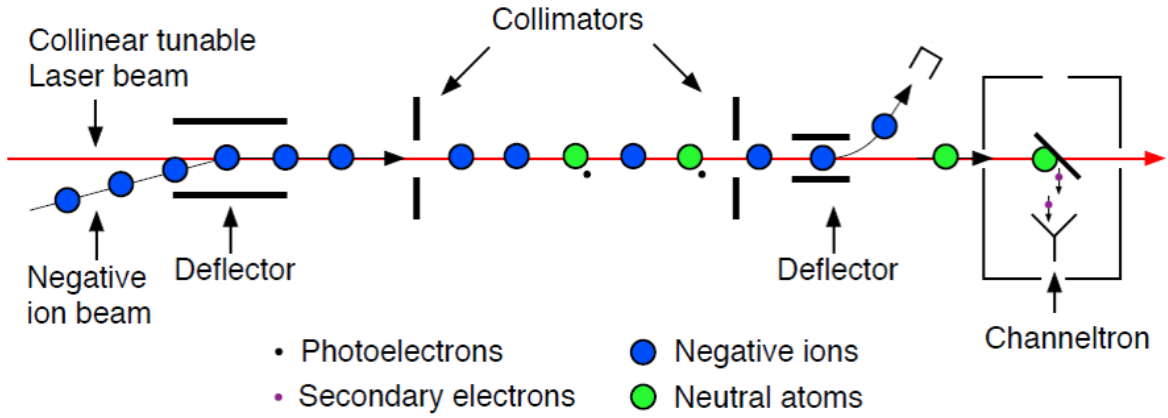


Figure 5.1: The GANDALPH setup (schematic). Incoming ions are bent to overlap with the laser beam in the interaction region between deflector and neutral particle detector. Neutralized particles are detected by the neutral particle detector. Residual negative ions are bent into the Faraday cup.

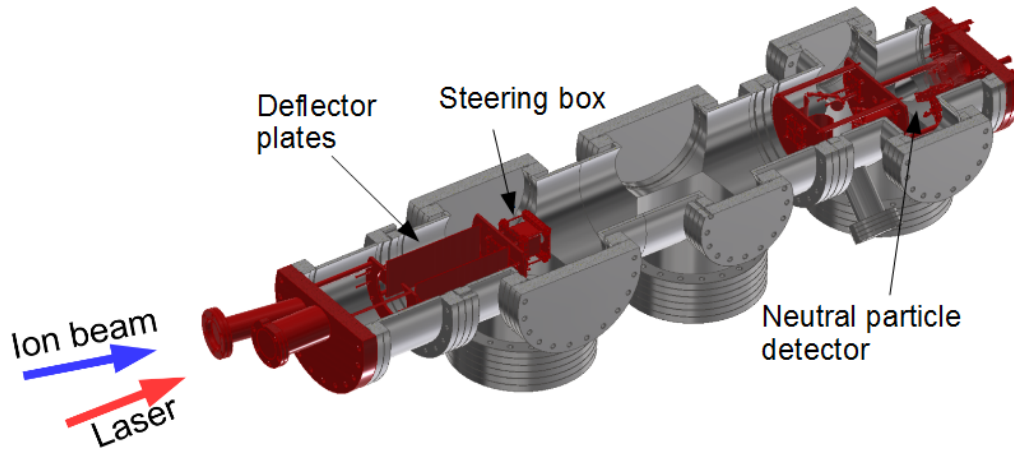


Figure 5.2: 3D model of the GANDALPH setup.

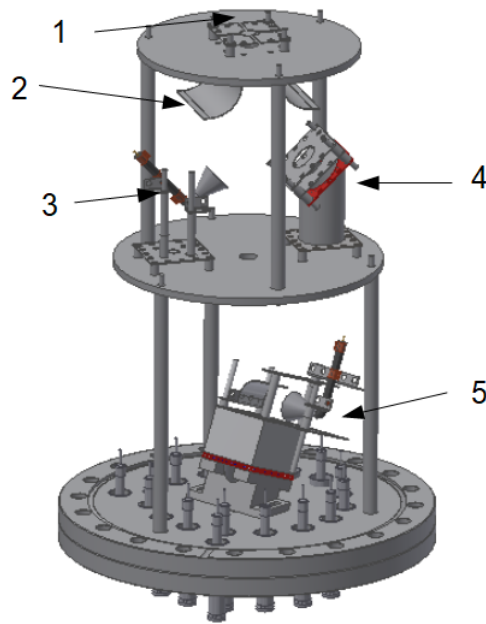


Figure 5.3: Neutral particle detector of GANDALPH. Charged particles passing through the segmented aperture (1) can be bend away (2) into the Faraday cup (4) or the CEM (3). Neutral particles hit a indium-doped tin oxide (ITO) coated glass plate within a metal box. The resulting emitted electrons are detected with an CEM (5).

5.2 GANDALPH Upgrades

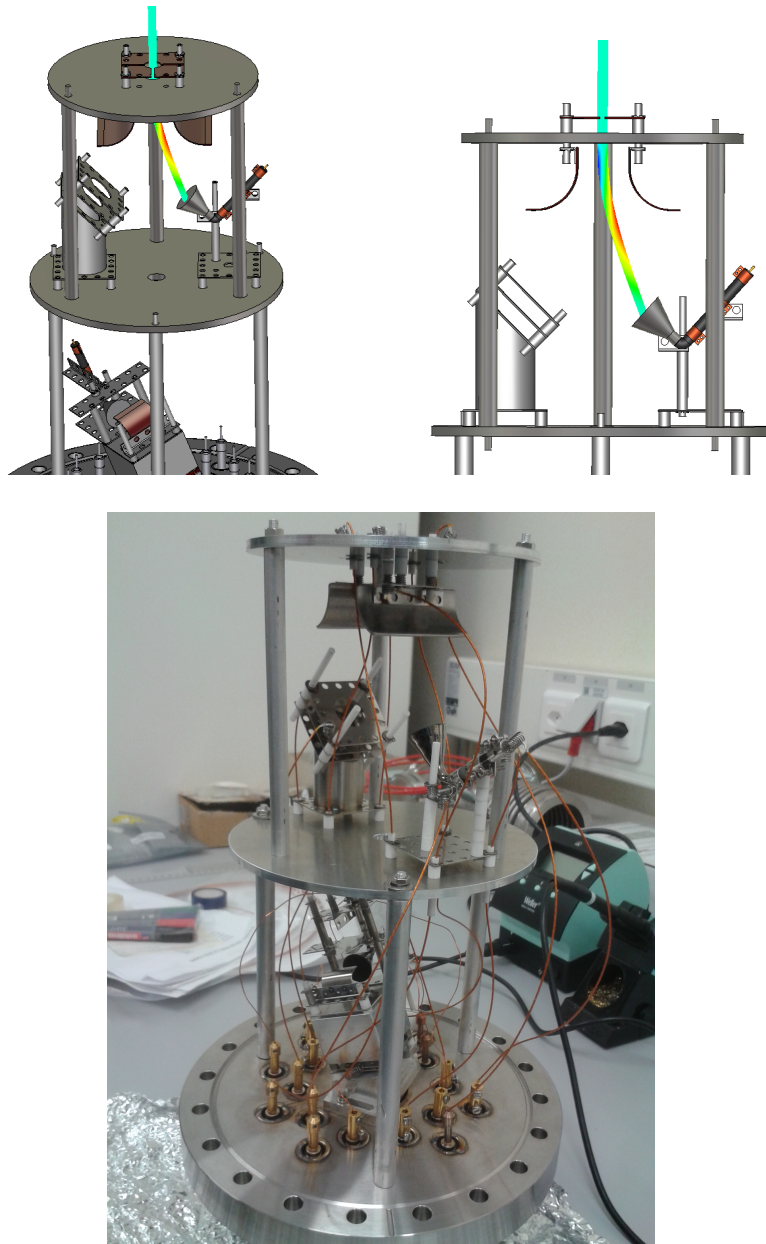


Figure 5.4: upper part: Simulation of the ion beam trajectory into the added SEM with CST Studio. lower part: Photograph of the built new neutral particle detector.

As a part of this thesis, several upgrades for GANDALPH were conceived, designed and integrated in order to improve ion beam tuning with ion currents lower than 1pA.

In order to facilitate the initial beam tuning, the apertures were segmented and dedicated picoampere-meters added. Additionally, the first stage of the neutral particle detector was modified with an additional CEM to be able to detect low current ion beams for which the faraday cup is not sensitive enough. The issue with the sensitivity of the faraday cup was seen in previous on-line experiments [57] which resulted in using the neutral particle detector for beam tuning. This led to contamination of the detector thereby increasing the background noise. For mechanical design and the simulation of the ion beam trajectories, Autodesk Inventor, SIMION and CST Studio were used. The result of the simulations are shown in figure 5.4, where a 20 keV ion beam is bend into the added CEM. The voltages at the bending plates are ± 4500 respectively, depending on whether the faraday cup or the SEM is used.

5.3 Off-line ion Source for GANDALPH

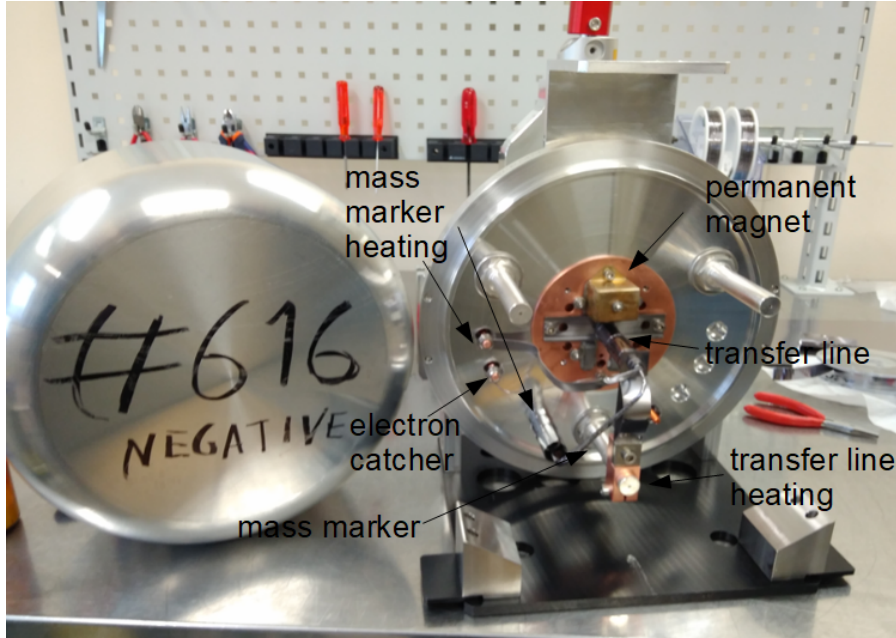


Figure 5.5: Inside view of target unit #616. Potassium iodide is inserted in the mass marker, which can be heated in order to release iodine. The permanent magnet aids the deflection of the electrons towards the electron catcher. The mass marker is connected to the transfer line. Both can be independently heated resistively.

To ensure optimal performance of GANDALPH during an on-line measurement of astatine, an off-line test run with the complete setup and a negative ion with comparable characteristics as the expected astatine beam is desirable. For this purpose, an off-line ion source, shown in figure 5.7, was designed and commissioned. For the GANDALPH

Ion Source (GANDIS) the ISOLDE target unit #616, shown in figure 5.5, was configured as a negative ion source.

This has the advantage that the conditions and geometry in the source are as close as possible to an on-line measurement. The ion source of target #616 was a LaB_6 tube put inserted to the transfer line. In order to obtain an ion beam of iodine, a so called mass marker was added and filled with macroscopic amount of potassium iodide (KI). The mass marker can be heated separately, thereby releasing iodine into the transfer line.

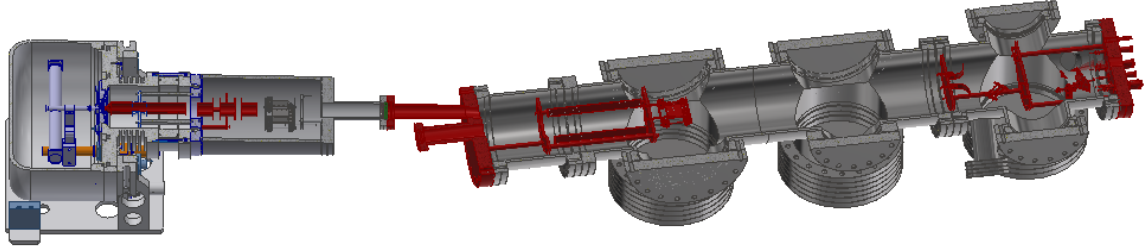


Figure 5.6: A 3D model of GANDIS connected to GANDALPH.

5.3.1 Ion extraction

In order to be able to extract an ion beam from the source, a vacuum flange with extraction and steering electrodes was designed.

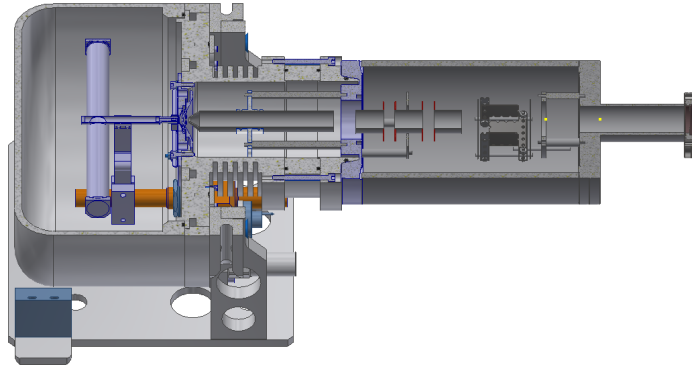


Figure 5.7: 3D model of GANDIS. Parts were designed using Autodesk Inventor.

This can be coupled directly to any target unit, thereby creating synergies regarding the testing of different sources as well as increase capabilities of the on-line target production. A 3D model of the envisioned setup with the ion source coupled to GANDALPH is shown in figure 5.6

In order to avoid building a faraday cage for the ion source, it had to be kept at ground potential, which made it necessary to put the ion optics at higher potential.

Simulations using CST showed that simply putting all ion optics at high voltage might not result in a sufficiently intense beam reaching the detector of GANDALPH. The critical point hereby was the region connecting the ion source and GANDALPH.

A 3D model and a photograph of the assembled ion source is shown in figure 5.7. Figure 5.8 shows a picture of the assembled version coupled to GANDALPH. Hence, the alternative was to use the extraction electrode in a pulsed drift tube configuration, using a Behlke GHTS solid state high voltage switch. The extraction potential is switched from +2kV to -2kV while the ions are travelling inside the volume of the extraction electrode. Given a correct timing, the ions are at a potential of -2kV after exiting the extraction electrode. This makes it possible to leave all following ion optics at a low potential, with the disadvantage of reduced ion beam intensity.

This is acceptable for this setup, where intense beams of stable iodine ions can be produced and low ion beam currents are expected in the on-line run. Following the extraction electrode, an Einzel lens and a steering box are added for additional beam tuning. Pictures of the assembled steering box and extraction flange with Einzel lenses are shown in figure 5.9.

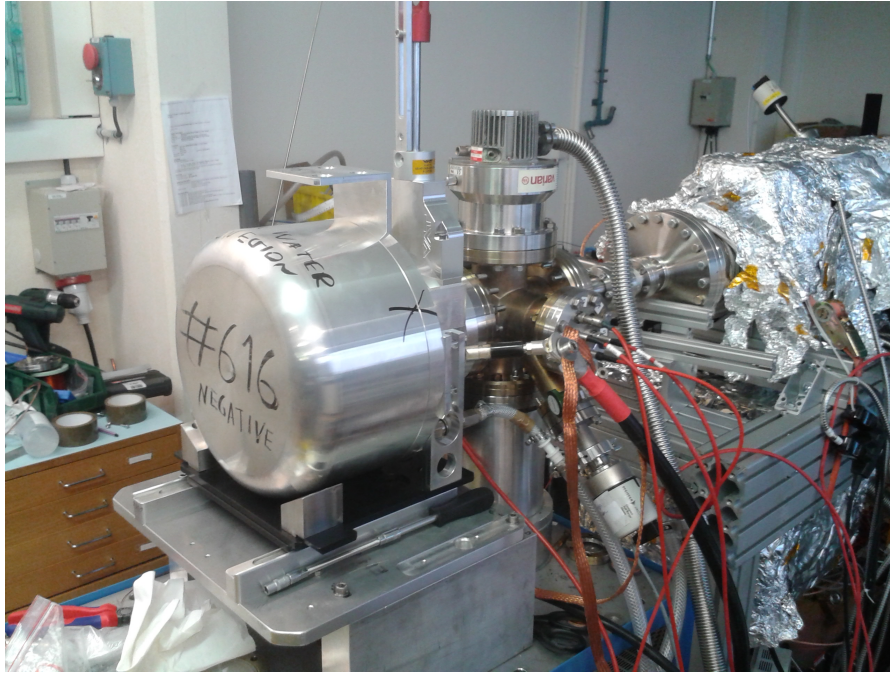


Figure 5.8: Photograph of GANDIS coupled to GANDALPH.

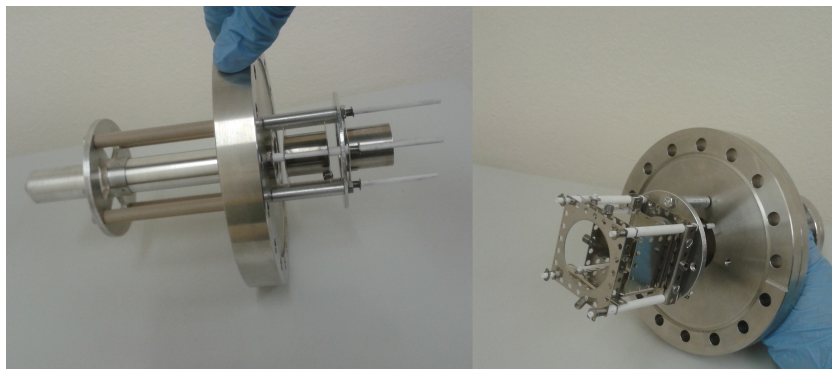


Figure 5.9: Photographs of extraction flange (left) and steering box(right) for GANDIS.

5.4 Results

5.4.1 Target unit #616

After assembling target unit #616 with an iodine mass marker it was briefly tested at ISOLDE's off-line separator.

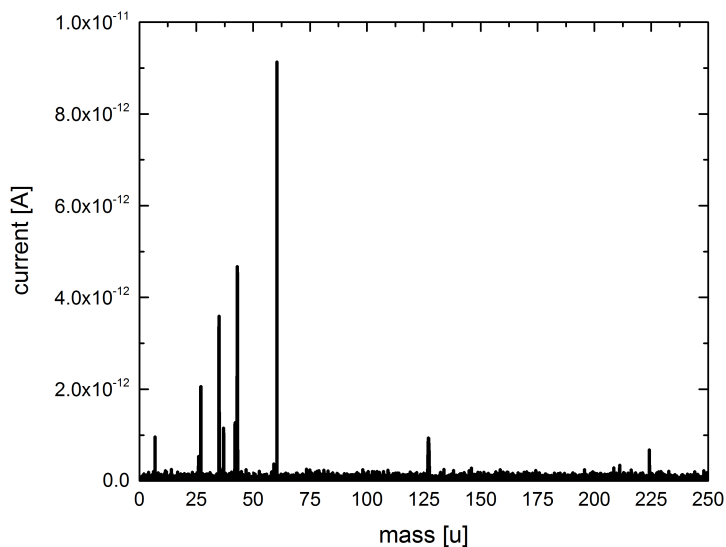


Figure 5.10: Mass scan of target #616 at the offline separator. Besides the expected iodine peak at 127 u, there seems to be a variety of contaminants at lower masses.

A mass scan showed the expected ^{127}I . The mass marker was heated up to 20 A, since

this was the maximum current available. As a result, the KI sample was placed in the center of the mass marker capillary.

5.4.2 Initial tests with GANDIS

As a first proof of concept, the newly built GANDIS was coupled to the GANDALPH beam-line for initial tests and trouble shooting. Unfortunately, essential vacuum feedthroughs of the angle flange of GANDALPH were damaged. Therefore, GANDIS was coupled straight to GANDALPH with a reducer flange. This increased the difficulty of beam tuning, since there were no ion optics or detectors available until the neutral particle detector. Additionally, some SHV feedthroughs for the ion source optics were not vacuum tight and had to be replaced, so that in the end a pressure of about $5 \cdot 10^{-6}$ mbar in the ion source cross and about $2 \cdot 10^{-7}$ mbar in GANDALPH was achieved.

Despite these circumstances, it was possible to extract an ion beam from the source and detect it on the segmented apertures, with the Faraday cup in the neutral particle detector, and on the box top of the neutral detector. However, in this case the ion beam extraction was done using DC high voltage. The measured current at the apertures was about 120 pA with the mass marker current at 16 A. A screen shot of the aperture read-out is shown in figure 5.11. The ion current measured with the Faraday cup is shown in figure 5.12 and was about 13 pA. In both cases, fluctuations of the ion current are visible. These may originate from discharges in the ion extraction region. Nevertheless, the signal reacted to changes of the mass marker heating as well as to the voltage settings of the ion optics, which is why it was considered to be originating from ions emitted by the source.

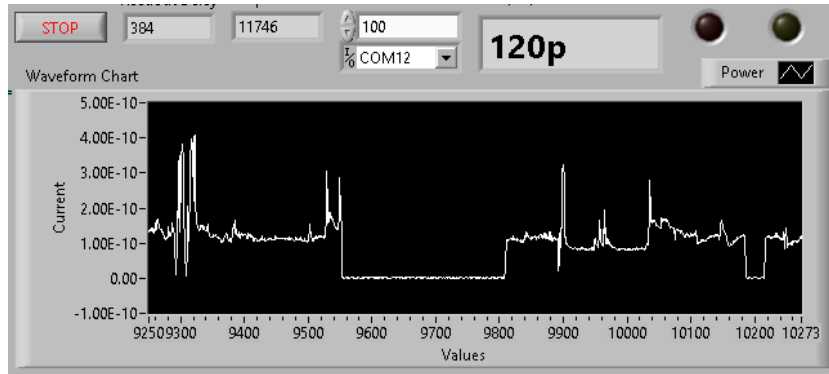


Figure 5.11: Ion beam current at the aperture of the neutral particle detector. The current of about 120 pA decreased to zero when turning off the mass marker heating.

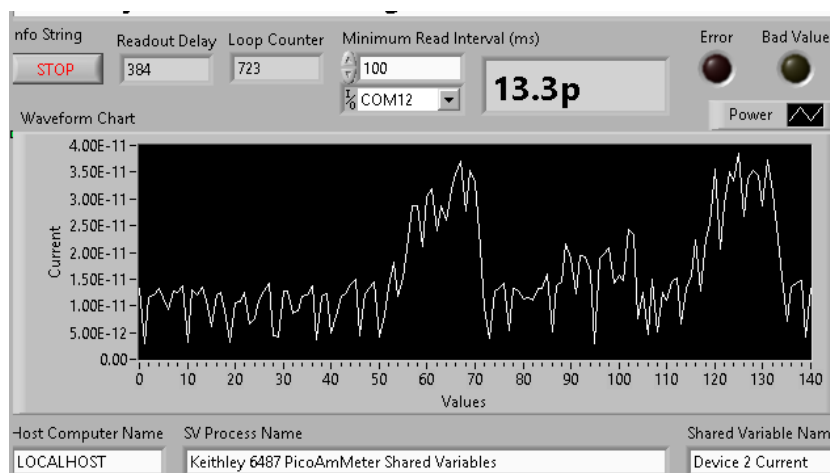


Figure 5.12: Ion beam current at the Faraday cup. Bend plates were at -1 kV and 300 V respectively.

Unfortunately, the additional CEM was damaged, since the drain current of the voltage supply was with about 2 mA uncharacteristically high. The CEM was therefore not used.

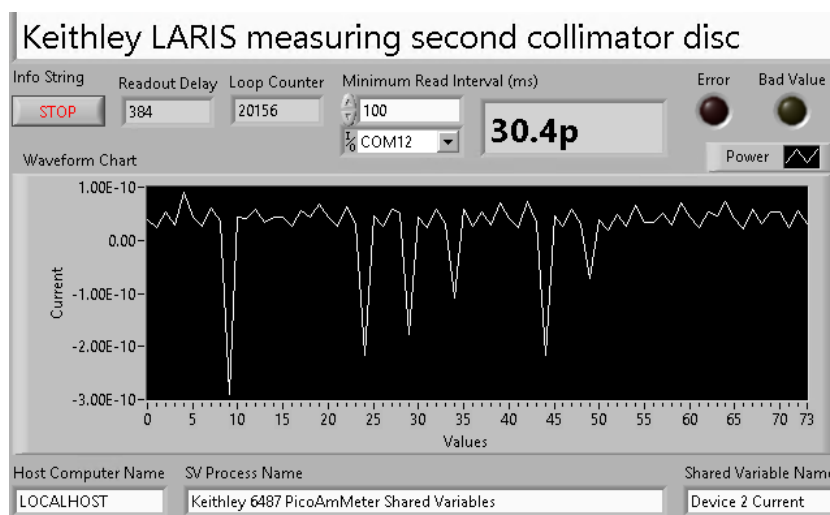


Figure 5.13: Ion beam at the box top of the neutral particle detector. The baseline of 30 pA is interrupted by discharges, possibly coming from the voltage supplies of the ion optics.

Additionally, it was attempted to measure photodetachment of iodine with the remaining SEM of the neutral detector, but despite seeing dark counts and the laser pulse, it was unfortunately not possible to detect a photodetachment signal.

6 Conclusion and outlook

In this thesis steps were taken towards the measurement of the electron affinity of astatine. For the improvement of the MK4 negative surface ion source at ISOLDE the production of SrVO_3 as an ultra-low work function material was attempted. A new low work function material would not only benefit the measurement of the electron affinity of astatine but in general create new possibilities for measurements with low electron affinity elements. The samples resulting from the production experiments were classified with X-ray diffraction and their electron emission measured against GdB_6 and LaB_6 . For the purpose of those test, a dedicated ion source test stand was built for which an ion beam extraction flange was designed and constructed. Aside from the measurements conducted in this thesis, this test stand will facilitate the investigation of source poisoning and regeneration as well as long-term performance studies, thermal stress tests and destructive tests of all ion sources at ISOLDE.

Although SrVO_3 could not be produced yet, the samples produced in reductive atmospheres, showed promising results: these samples all exhibit the $\text{Sr}_3(\text{VO}_4)_2$ phase of strontium vanadate, which seems to be responsible for an electron emission close to those of LaB_6 , the currently used negative surface ion source material. For future production attempts, there is strong indication that SrVO_3 can be produced by reducing the oxygen partial pressure slightly more. This could be achieved by filtering the airflow through a graphite plug, producing the samples in a metal oven or in a hydrogen atmosphere. The development of the negative surface ion source will continue with attempts to improve the source geometry additional to the search of other new low work function materials.

In order to increase the beam tuning capabilities of the GANDALPH beam line, its neutral particle detector was upgraded with a second CEM, which required the redesign of the bending plates. Additionally, the apertures of the neutral detector were segmented. For off-line tests of the GANDALPH beam-line, a dedicated ion source was built. It consists of an ISOLDE target unit with a negative LaB_6 surface ion source and a potassium iodide mass marker which produces iodine when heated. A flange for the coupling of the target to a vacuum cross was developed, which was completed with an extraction electrode and ion beam optics for beam tuning. The ion source was assembled and coupled to GANDALPH. Initial tests verified the capability to produce an ion beam which was extracted and sent to the neutral particle detector in GANDALPH.

For future test runs, the ion source will be more thoroughly characterized and a Faraday cup for the measurement of the ion beam current added. The upgraded GANDALPH will be fine tuned in an off-line, thereby facilitating the attempt of an on-line measurement of the EA of astatine for which beam-time has been granted.

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Acknowledgement

At this point I would like to express my appreciation to the many people who made it possible to create this thesis. First and foremost, I would like to thank Prof. Dag Hanstorp for introducing me to the world of negative ions and for giving me the opportunity to do this thesis as well as his advice, knowledge and support during the last 15 months. I would also like to thank Prof. Andreas Schrimpf very much for his support and supervision.

For his countless great ideas and solutions, his support even on weekends and during late nights in the lab and the beer I would like to express a particular thanks to Dr. Sebastian Rothe, my supervisor at CERN.

Additionally, I would like to thank Dr. Joao Pedro Ramos and Jochen Ballof for the great atmosphere in the office, good advice and their willingness to help and discuss even during some weekends.

Most of the mechanical components used in this thesis were built at the ISOLDE target workshop and I am very thankful for the advise and expertise from Andres Vieitez Suarez, Bernard Crepieux and Ermano Barbero. I would also like to thank Jan-Ake Wiman, who built the flange and parts for the GANDALPH detector. Also, the introduction and help with the XRD from Josep Busom Descarrega was much appreciated. For the financial support throughout my time at CERN I would like to thank the EN department. I would also like to thank my family, especially my parents and Kathy and Guido Schlitzer for their financial and general support throughout my studies. Last but certainly not least I would like to thank my girlfriend Le Anh Nguyen for her love and support throughout the last years.