Applied Radiation and Isotopes 217 (2025) 111642

Contents lists available at ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

Preparation of a ^{73}As source sample for application in an offline ion source

Andrew C. Candia [a,b], Georg Bollen [a], Suvan Campbell [c], Ana Henriques [a], Alain Lapierre [a], Samuel Nash [a], Stefan Schwarz [a], Chandana Sumithrarachchi [a], Antonio C.C. Villari [a], Katharina A. Domnanich [a,b,*]

[a] Facility for Rare Isotope Beams, Michigan State University, 640 South Shaw Lane, East Lansing, 48824, MI, USA
[b] Department of Chemistry, Michigan State University, 640 South Shaw Lane, East Lansing, 48824, MI, USA
[c] Andrews University, 8975 Old 31, Berrien Springs, 49104, MI, USA

ARTICLE INFO

Keywords:
As-73
Batch-Mode Ion Source (BMIS)
Source sample
Facility for Rare Isotope Beams (FRIB)
Radiochemical precipitation

ABSTRACT

For the generation of beams with the offline ion source at the Facility for Rare Isotope Beams (FRIB), suitable source samples are required. Arsenic-73 is a frequently requested user beam due to its significance in nuclear structure studies and astrophysics. In this work, we outline the process of preparing a ^{73}As source sample, containing $(5.76 \pm 0.37)*10^{14}$ atoms of ^{73}As, which was successfully used to generate a ^{73}As beam for a multi-day user experiment. Silver arsenate was chosen as the chemical form, due to its favorable volatility within the designated operating temperature range. We refined the precipitation method using stable arsenic prior to its application with the ^{73}As sample, resulting in precipitation yields of (99.4 ± 4.5)%.

1. Introduction

The Facility for Rare Isotope Beams (FRIB) is a new national user facility for cutting-edge nuclear science research, where the desired rare isotope beams are typically created by fragmentation of a stable primary beam (Sherrill, 2018). Next to fast beams, stopped beams and beams reaccelerated to around Coulomb barrier energies are available for nuclear science experiments at FRIB (Glasmacher et al., 2024). However, ion beams for selected user experiments can alternatively be generated in so-called ‘offline mode’ by utilizing radioactive or stable source samples (Sumithrarachchi et al., 2023). The radioisotope ^{73}As is characterized by a half-life of 80.3 days and a primary gammy ray at 53.437 keV ($I_\gamma = 10.6\%$) (Singh and Chen, 2019). Beams and samples of ^{73}As are of interest for nuclear data studies, as well as for cross-section measurements in nuclear astrophysics (Rauscher et al., 2016; Ten Brink et al., 1980). A feasible route to provide ^{73}As beams for user experimentation at FRIB is by employing source samples of ^{73}As, which are inserted into the Batch-Mode Ion Source (BMIS). The BMIS is an oven-ion source combination, where the samples are placed into the oven. There they are evaporated and atomized, followed by the effusion of the atoms into the plasma ion source where they are ionized. Following acceleration to a few tens of keV, the ion beams from BMIS are selected by a magnetic mass analyzer. The generated beams can be delivered to the stopped-beam area, which houses the Low-Energy Beam and Ion Trap facility (LEBIT), the Beam Cooler and Laser Spectroscopy facility (BECOLA), and beamlines for on-demand experimenter instrumentation (Minamisono et al., 2013; Sumithrarachchi et al., 2023). Alternatively, beams can be delivered to user experiments at a few MeV/u energy using the ReAccelerator (ReA) (Villari et al., 2023). The BMIS is an offline setup, which allows an independent execution of the stopped and reaccelerated beam facilities, thereby facilitating parallel operation of multiple user experiments at FRIB. Since its commissioning in 2021, the BMIS team has been able to provide a selected number of offline-generated isotope beams for user experiments (Domnanich et al., 2023; Satija et al., 2024; Sumithrarachchi et al., 2023). A suitable sample material for BMIS needs to meet several requirements: Firstly, the samples have to be a solid that can be readily vaporized within the BMIS operating temperatures (starting at temperatures of about 400 °C and generally up to around 1000 °C, but temperatures up to 2000 °C are possible). Secondly, any volatile matrix components, as well as isobaric impurities, should be avoided or at least kept at a minimal level.

The FRIB user community expressed strong interest in utilizing a low-energy ^{73}As beam. In this paper, we describe the preparation of a ^{73}As source sample in support of the experimental user beam program at

---

* Corresponding author. Facility for Rare Isotope Beams, Michigan State University, 640 South Shaw Lane, East Lansing, 48824, MI, USA.
E-mail addresses: mracandia@gmail.com (A.C. Candia), bollen@frib.msu.edu (G. Bollen), suvanc@icloud.com (S. Campbell), henrique@frib.msu.edu (A. Henriques), lapierre@frib.msu.edu (A. Lapierre), Nash@frib.msu.edu (S. Nash), schwarz@frib.msu.edu (S. Schwarz), chandana@frib.msu.edu (C. Sumithrarachchi), villari@frib.msu.edu (A.C.C. Villari), domnanic@frib.msu.edu (K.A. Domnanich).

https://doi.org/10.1016/j.apradiso.2024.111642
Received 12 August 2024; Received in revised form 27 November 2024; Accepted 14 December 2024

FRIB. An acidic ^{73}As solution was converted into silver arsenate (Ag_3AsO_4) due to its favorable volatility within the designated operating temperature range of BMIS. This conversion was achieved through an optimized precipitation reaction after the addition of a stable arsenic carrier. A source sample with about 1.56 mCi ($5.76 \cdot 10^{14}$ atoms) of ^{73}As was prepared and successfully used in BMIS to deliver a reaccelerated ^{73}As beam to scientific users.

2. Materials and methods

2.1. Stable and radioactive arsenic isotopes for source sample preparations

The ^{73}As was obtained via the National Isotope Distribution Center (NIDC), with an initial stock activity of 3 mCi, containing less than 0.01 mCi of ^{74}As and in a matrix of 0.1 M hydrochloric acid (HCl). The stable arsenic originated from an arsenic +3 ICP standard solution obtained from High-Purity Standards (HPS) at a concentration of (1000 ± 20) ppm in a matrix of 2% HCl.

2.2. Chemicals

For the preparation of the source samples, hydrogen peroxide (H_2O_2, 30%, ACS grade, Fisher Scientific), acetic acid (glacial CH_3COOH, ≥99%, GR-ACS, Millipore Sigma), ammonium hydroxide solution (NH_4OH, 30%, Sigma Aldrich), hexane (C_6H_{14}, Supelco, Sigma Aldrich), and silver nitrate ($AgNO_3$, Reagent ACS, ChemPure Brand Chemicals) were used. The stable element analysis was performed in a matrix of 3% by volume of nitric acid (HNO_3, 70%, Sigma Aldrich). A 50 × 50 mm sheet of tantalum foil, 0.006 mm thickness (99.9% purity, GoodFellow) was used as the support material. Acetone (C_3H_6O, for liquid chromatography, Supelco, Sigma Aldrich) was used for rinsing. For all dilutions, MilliQ water with a conductivity of 18.20 MΩ*cm was used, obtained from a Thermo Scientific Barnstead MicroPure Water System. Solutions of ICP Arsenic Standard ((997 ± 4) mg/L, 5% HNO_3 matrix, Sigma Aldrich) and ICP Silver Standard (Transition Metal Mix 1 for ICP, 100 mg/L, 2% HNO_3 matrix, Sigma Aldrich) were used for the stable element analysis.

2.3. Instruments

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, Agilent 5900) was employed to analytically determine the concentration of stable elements. Gamma-ray spectroscopy with a Broad Energy Germanium Detector (BE2020, Canberra) was used to quantify the activity of ^{73}As using the characteristic gamma-line at 53.43 keV, $I_\gamma = 10.6\%$. The energy and efficiency calibration were performed with a set of point sources, encompassing europium-154 (Eu-154, Eckert & Ziegler, 1.054 μCi, reference date 15-Sep-2020, E_γ = 123.07 keV (40.4%), 247.92 keV (6.89%), 591.75 keV (4.95%), 723.30 keV (20.06%), 873.18 keV (12.08%), 1004.76 keV (18.01%), 1274.42 keV (34.8%)), and americium-241 (Am-241, Eckert & Ziegler, 1.040 μCi, reference date 15-Sep-2020, E_γ = 59.54 keV (35.9%)) at distances of 15 cm, 25 cm, and 100 cm. For the characterization of the prepared stable silver arsenate source samples, Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDS, JEOL 7500F, Oxford Instruments AZtec system), as well as X-Ray Photoelectron Spectroscopy (XPS, CasaXPS, Physical Electronics 5400 System) were performed. For the chemical processing, a benchtop vortex mixer (Digital Vortex Mixer, VWR), a hot plate (Cimarec, Barnstead Thermolyne), and a benchtop centrifuge (Sorvall ST8, ThermoFisher Scientific) were utilized.

2.4. Formation of stable silver arsenate precipitate

The arsenic in the stable standard solution was present in the +3 oxidation state. To transform the stable arsenic from the +3 to the +5 oxidation state, 1 mL of the 1000 ppm As^{3+} solution was first treated with 30% hydrogen peroxide at a 1:5 ratio (Molnár et al., 1994). The solution was covered and left at room temperature overnight. After this incubation, the solution was left to completely evaporate at 90 °C. The formed residue in the sample container was dissolved in about 500 μL MilliQ water and transferred to an Eppendorf tube. The beaker was rinsed three times and the rinse solutions were also added to the tube.

The precipitation followed a procedure similar to the one outlined by Curtman et al. (Curtman and Daschavsky, 1916). A stock solution of silver nitrate was prepared at a concentration of 3175 ppm Ag and kept in the dark. About 0.5 mL of the prepared As(V) solution that contained 80 μg arsenic was used for the precipitation reaction. The silver nitrate stock solution was added to three separate As(V) solutions to yield molar ratios of Ag:As of 1.3:1, 5.7:1, and 12.7:1, with the stoichiometric 3-to-1 ratio of Ag and As in silver arsenate already taken into consideration. The pH of these solutions was adjusted to 7–8 using a few drops of 1 M ammonium hydroxide and 10% acetic acid. After adjusting the pH and vortexing, a visible brown precipitate formed. The samples were wrapped in parafilm and left to react completely overnight. The tubes were centrifuged, and the supernatants were removed and transferred into other tubes. The concentrations of arsenic and silver in the supernatants were quantified via ICP-OES and used to assess the yield of precipitation.

2.5. Preparation of the stable source samples

The stable silver arsenate precipitate, prepared at the optimized Ag:As ratio of 5.7:1, was used for the preparation of the stable source samples. The tantalum foil was first cut in half to yield sheets of 50 × 25 mm and then cleaned with acetone and dried. The precipitate was transferred onto the foil, which was kept inside a small, in-house made aluminum boat on a hot plate set to 150 °C. Any residual silver arsenate precipitate was rinsed from the tube three times with about 0.6 mL hexane, pipetted onto the foil, and followed by evaporation of the solvent. The stable samples were used to develop the beam extraction from the BMIS and to optimize the ion beam delivery process. Furthermore, the prepared stable source samples were characterized via SEM-EDS and XPS to identify the present elements, their relative atomic percentages, and to obtain further information about the compound speciation.

2.6. Formation of the radio-silver arsenate precipitate and source sample preparation

The initial activity of the ^{73}As sample was quantified via gamma-ray spectroscopy. The activity was checked throughout the precipitation process to track the activity and to account for any losses. A volume of 0.259 mL ^{73}As solution that contained (2.27 ± 0.08) mCi of ^{73}As was used for the reaction. To quantitatively precipitate the radio-arsenic, the ^{73}As sample was spiked with 80 μg stable arsenic (27.2 μL of a 2949 ppm stable As solution; This As solution was the same one previously prepared for the formation of the stable silver arsenate precipitate. However, only the volume was reduced by evaporation, and the arsenic concentration determined via ICP-OES measurement to be 2949 ppm. Using a smaller initial volume facilitated the subsequent evaporation step.) The oxidation with H_2O_2 and other steps were performed by following the optimized procedure for the stable precipitate formation. Briefly, after the oxidation and evaporation steps, the reconstituted solution (0.287 mL) was used for the precipitation reaction. This was done by using the previously optimized 5.7:1 ratio of Ag:As and adjusting the solution pH to 7–8. Once a visible precipitate formed and incubated, the precipitate was centrifuged and the supernatant was separated off. The formed precipitate was used for the preparation of the source sample. The silver arsenate precipitate was transferred onto a clean sheet of tantalum foil (50 × 25 mm) placed inside an aluminum boat on a hot plate set to 150 °C. During the transfer and subsequent rinsing of the tube using hexane, the activity of the sample was checked so that about (1.556 ± 0.10) mCi of ^{73}As (($5.76 \cdot 10^{14} \pm 3.74 \cdot 10^{13}$) atoms) were transferred onto the tantalum foil. The remaining portion of the initial ^{73}As activity could not be transferred, which is explained in detail in the Results & Discussion section. The prepared source sample was used for the generation of the ^{73}As beam.

2.7. ^{73}As beam delivery

The ^{73}As deposited Ta foil was folded tightly and inserted into the BMIS oven. The oven was heated to 500-1000 °C, whereby the sample material evaporated, followed by effusion into the ion source. Through ionization, the monovalent $^{73}As^{+}$ ion was formed and the ion beam, containing the $^{73}As^{+}$ as well as stable ^{75}As and other contaminants, was extracted. After acceleration to 30 keV, the beam was mass separated, where the desired $^{73}As^{+}$ ions were selected. Finally, the selected ion beam was accelerated to 3.1–3.7 MeV per nucleon in the ReA after charge breeding to the 23^{+} charge state. The ^{73}As beam was successfully delivered to the scientific user beam experiment, with a more in-depth discussion of the outcomes provided later in this publication.

3. Results and discussion

3.1. Stable silver arsenate source sample preparation

Arsenic +3 compounds are usually highly volatile, which could result in significant losses during the subsequent sample preparation procedure (Smedley and Kinniburgh, 2002). Preliminary investigations involving the evaporation of about 1 mL aliquots of the 1000 ppm As^{3+} ICP solution showed recoveries below 0.5%. With the addition of hydrogen peroxide at a 5-times molar excess, the As^{3+} in solution was oxidized to the less volatile +5 oxidation state. This was confirmed by achieving As recovery rates of about 100% after evaporation.

To achieve complete precipitation of an arsenic sample of 80 μg, several experiments were done to determine the optimal Ag:As ratio. The selected low quantity of stable As represents the upper level of stable arsenic carrier which is in alignment with the chemical toxicity limit set by the Occupational Safety and Health Administration (OSHA) for the given space settings in the accelerator vault, and was therefore used throughout the method optimization. For a quantitative formation of silver arsenate, a 1.3-fold ratio of Ag resulted in a precipitation yield of around (94.2 ± 4.1)%. However, complete precipitation of (100.0 ± 4.2)% at 5.7- and 12.7-times excess amounts of Ag was obtained. The error includes the propagated error from the ICP-OES analysis and the respective dilution factors. Based on these results, the 5.7-fold surplus of Ag was selected to achieve optimized precipitation yields of silver arsenate, while minimizing the amount of silver in the sample. Notably, the ICP-OES analysis of the supernatant indicated a depletion of silver, corresponding to the expected quantity when a three-fold molar excess of Ag to As is trapped in the precipitate. This finding supports that the formed precipitate is silver arsenate, which is characterized by a 3-to-1 stoichiometric ratio of Ag and As.

3.2. ^{73}As source sample preparation

After the optimized method was determined by the experiments with stable arsenic, it was then employed for the formation of a silver arsenate precipitate with the radioactive ^{73}As material. Most arsenic compounds are, however, characterized by a relatively high volatility (Beard, 1965). Utilizing such compounds for source samples in BMIS would deplete them quickly, and only limited ion rates could be extracted towards the end of a several-day-long beam experiment. Silver arsenate decomposes at temperatures of around 830 °C, which is within the operating temperature range of BMIS, and was therefore considered as a suitable material to supply adequate beam rates over prolonged periods (Rumble, 2023).

Throughout the formation of the radio-silver arsenate precipitate and the preparation of the source sample, the activity was regularly checked through gamma-ray spectroscopic measurements. The silver arsenate formation was highly quantitative, with only (13.1 ± 0.4) μCi ^{73}As left in the supernatant, indicating a precipitation yield of (99.4 ± 4.5)%, which is comparable to the stable arsenic sample preparation that had achieved a 100% yield. However, during the transfer of the precipitate onto the tantalum foil (697.7 ± 18.3) μCi ^{73}As adhered to the pipette tip and the surface of the Eppendorf tube. In repeated rinse cycles with hexane, only μCi-quantities of ^{73}As could be removed. After transferring (1.556 ± 0.10) mCi ^{73}As, which corresponds to $(5.76 \pm 0.37)*10^{14}$ atoms, onto the tantalum foil, the so-prepared source sample was introduced into the BMIS oven. The most notable ^{73}As activity loss of (511.7 ± 17.2) μCi is due to adsorption to the surface of the Eppendorf tube, while the rest remained on the pipette tip. However, in retrospect it was observed that rinsing with 2 mL of 3% nitric acid effectively removed any remaining ^{73}As, leaving only (18.3 ± 0.6) μCi ^{73}As in the tube after this step. These findings can be useful for future source sample preparation efforts, however, the effect of nitric acid on the final sample composition needs to be still determined.

3.3. Sample characterization

The analytical instruments were not approved for radioactive materials, therefore the characterization was performed with stable source samples, as they are expected to exhibit comparable chemical behavior to the radioactive sample. Following the outlined procedure, it was predicted that the arsenic sample would form silver arsenate with arsenic in the +5 oxidation state.

3.3.1. SEM-EDS analysis

Scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM-EDS) yielded the morphology of the stable silver arsenate precipitate as well as the identification of the present elements. Fig. 1a shows a recorded SEM image of the sample surface. The prepared source sample displayed an uneven morphology, with regions completely covered with precipitate alternating with areas of visible tantalum substrate (the darker regions in Fig. 1a). Variations in the drying rates can cause an uneven distribution of the precipitate on the foil. However, the irregular distribution did not affect the application of the prepared source sample in the ion source.

An EDS spectrum taken from a central point on the image is shown in Fig. 1b (indicated as Spectrum 1 in Table 1). The presence of the most abundant species, encompassing silver, arsenic, and oxygen, was expected for the prepared samples. To characterize the precipitate, spectra were taken from three different spots on the precipitate. The data obtained from recording these spectra (Spectra 1–3) are shown in Table 1. Spectra 1 and 2 were taken from spots in the central region, while

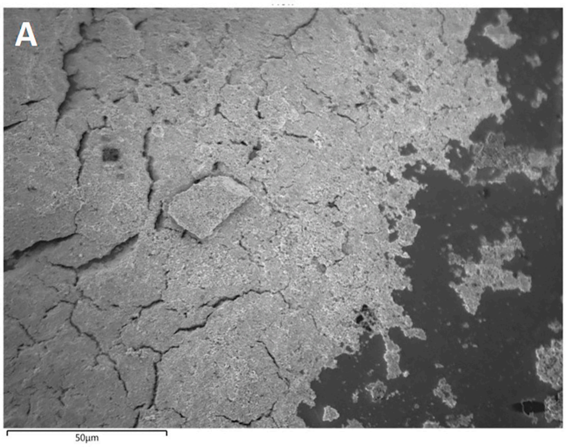

Fig. 1a. SEM image of stable arsenic precipitate.

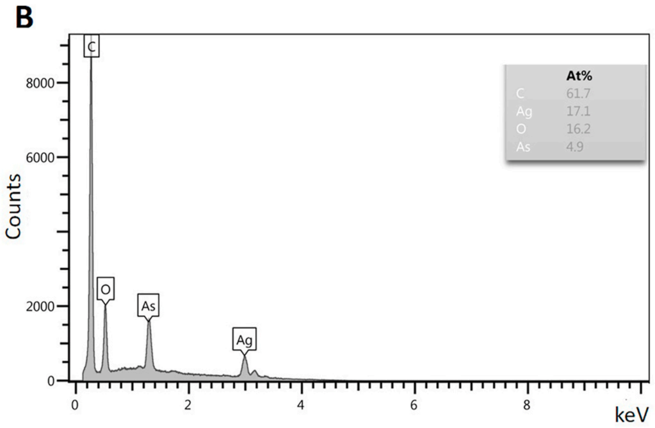

Fig. 1b. EDS spectrum of the stable arsenic precipitate, taken from a central point (Spectrum 1) in the shown SEM image.

Spectrum 3 was recorded from an edge region of a section in Fig. 1a. The EDS analysis suggested the presence of carbon, which possibly originated from the hexane rinses used to transfer the precipitate onto the tantalum substrate. The atomic percentages of silver, arsenic, and oxygen were used to estimate the stoichiometric ratios of each element within the precipitate. The ratios of Ag, As, and O in Spectra 1 and 2 suggest the presence of either silver arsenate (Ag_3AsO_4) or silver arsenite (Ag_3AsO_3), both having an Ag-to-As ratio of 3-to-1. This finding is corroborated by the ICP-OES analysis of the supernatant, where the depletion of Ag points towards an approximate 3:1 stoichiometric ratio of Ag:As in the formed precipitate. However, the analysis of light elements through EDS is challenging due to their low photon energies (Goldstein et al., 2003), therefore the oxygen content alone cannot be used to identify the specific silver-arsenic compound. Spectrum 3, however, suggests a significantly higher Ag:As ratio, with nitrogen also detected in that area. This spectrum was taken from an edge region, while the first two (Spectra 1 and 2) were taken from the center. During the source sample preparation, excess silver nitrate from the supernatant could have been entrained in the precipitate. In the evaporation step, the silver nitrate could have migrated towards the edges, leading to higher silver content and additional presence of nitrogen at the precipitate edges (Deegan et al., 1997; Suárez-Domínguez and Betancourt-Mar 2005). Therefore, Spectra 1 and 2 provide a better representation of the majority of the precipitate.

3.3.2. *XPS analysis*

The XPS analysis of the stable silver arsenate source sample, shown in Table 2, indicated the presence of the same elements as the SEM-EDS measurement. The quantities of Ag, As, and O are largely comparable and corroborate the SEM-EDS results. Furthermore, the presence of carbon on the precipitate was also determined via XPS. Additionally, tantalum was detected, likely because the larger selected area for the XPS analysis included some Ta surface area that was not covered by precipitate. Similar to the SEM-EDS results, a small amount of nitrogen was found, which may be attributed to some silver nitrate being entrained at the edges of the precipitate.

The enlarged part of the XPS spectrum shown in Fig. 2 can be ascribed to the peak from the As-O bond. The spectrum has been fitted to show the contributions of the As-O bonds in the As(III) and As(V) compounds to the As $3d_{5/2}$ peak. In literature, the As $3d_{5/2}$ position for oxygen-containing compounds of As(III) is indicated for the range of 44.7–45.1eV, while the range for the As(V) counterparts is slightly higher, between 45.8 and 46.2eV (Moulder et al., 1992). The fitted spectrum suggests that the arsenic-based precipitate consists of a combination of As(III) and As(V), with proportions of 78.3% and 21.7% respectively. During the first step of the sample preparation, arsenic was fully converted from the +3 to +5 oxidation state, and the majority of As in the precipitate was expected to be present as As(V). However, with arsenic in particular, the literature suggests X-ray-induced photo-reduction of arsenic oxides; in our case, there can be a reduction of arsenic(V) species down to arsenic(III). This reduction is dependent on the X-ray intensity and is magnified by the presence of carbon. The X-ray irradiation of hydrocarbons produces highly energetic radicals that can scavenge oxygen from the surface, further inducing the reduction to arsenic(III) (Viltres et al., 2020). It is possible that the hexane rinses introduced a surplus of carbon to the source sample, which would promote the probability of arsenic reduction. Therefore, using XPS to determine the oxidation state of As, with the intent of corroborating the specific silver-arsenic compound, proved to be of limited validity in this sample.

Based on the composition of the precipitate suggested by XPS and

Table 2
Data table of the percent composition of each element in the precipitate.

ID	Composition (atomic %)
Ag	18.0
As	8.0
O	32.3
C	33.8
Ta	5.4
N	2.5

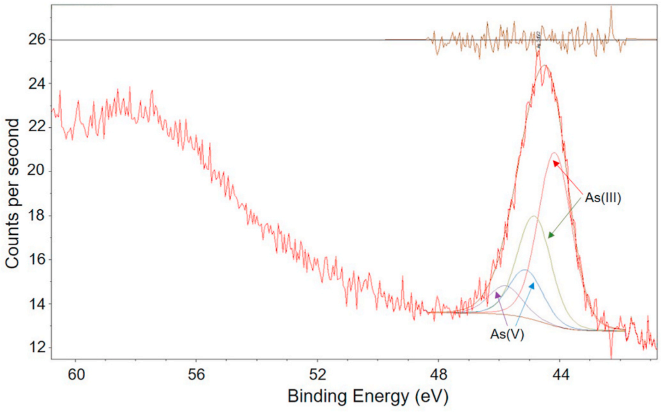

Fig. 2. XPS spectrum of the prepared stable silver arsenate source sample. This part of the spectrum has been enlarged and fitted to show the contributions of the As-O bonds in the As(III) and As(V) compounds to the As $3d_{5/2}$ peak.

Table 1
The atomic percentages of silver, arsenic, oxygen, and nitrogen from all recorded spectra. For Spectra 1 and 2 the estimated stoichiometric ratio between Ag:As:O is given, while the estimation for spectrum 3 additionally considers the present nitrogen.

Spectrum	Ag (atomic %)	As (atomic %)	O (atomic %)	C (atomic %)	N (atomic %)	Estimated stoichiometric ratio of Ag:As:O
1	17.1	4.9	16.2	61.7	–	3.5:1:3.3
2	15.8	4.9	12.6	66.7	–	3.2:1:2.6
3	29.7	3.1	46.6	1.7	18.9	Estimation for Ag:As:O:N = 9.6:1.0:15.0:6.1

SEM-EDS, as well as the ICP-OES analysis data from the supernatant, it can be concluded that a compound mainly comprising Ag, As, and O was formed at a stoichiometric ratio that points towards silver arsenate or silver arsenite. To provide a more detailed analysis of the chemical species, an additional characterization method would be necessary, with scanning transmission electron microscopy (STEM) in annular dark field (ADF) mode appearing as a promising option. This method is described as being less prone to induce beam-related artifacts (Johnston-Peck et al., 2016). This could make it a valuable option for future source sample characterization, however, its applicability needs to be determined on a case-by-case basis.

Furthermore, it is possible that small amounts of silver nitrate were trapped in the edge regions of the precipitate. In addition, results from both SEM-EDS and XPS indicate carbon contamination, thus future source sample preparation efforts should avoid the use of hexane rinses.

3.4. ^{73}As beam delivery

The manufactured ^{73}As source sample was inserted into the oven of BMIS and the ^{73}As extracted as a monovalent ion $^{73}As^{+}$ at mass 73. The ^{73}As beam was employed by scientific users to interact with a hydrogen gas cell to study the proton capture reaction ^{73}As(p,γ)^{74}Se (Simon, 2024; Tsantiri and Spyrou, 2024). This reaction is one of the most important reactions for the production of ^{74}Se in stellar environments (Kusakabe et al., 2011; Rauscher et al., 2016). Fig. 3 visualizes the mass scans of the relevant region obtained from a stable silver arsenate sample, showing the stable silver and arsenic species at masses 107, 109, and 75 respectively. This source sample was utilized to refine beam extraction and beam delivery processes. However, the mass scan for the radioactive ^{73}As source sample was very similar, where only the more abundant, stable species were present, while the low-level ^{73}As signal at mass 73 could not be discerned. Such behavior is expected for a low-mass sample; however, mass 73 was still selected by the magnetic mass analyzer, and the ion beam was accelerated and delivered at an average rate of $5*10^{5}$ particles per second to the ReAccelerator, achieving a beam purity close to 100%. During beam transport, losses occur due to transmission through various devices, including charge breeding, selection, and reacceleration. The transmission efficiencies of these devices are designed to range between 60% and 80%, while the mass-to-charge separator has a selection efficiency of 20% (Villari et al., 2016). Overall, about 7% of the extracted ions are delivered to the experiment.

To realize adequate beam rates, the oven temperature had to be raised to about 870 °C, before that the evaporation was at a minimal level. This observation is in line with the decomposition point of silver arsenate, which is reported at 830 °C. The two peaks at masses 107 and 109 arise from the two naturally occurring silver isotopes ^{107}Ag (51.839%) and ^{109}Ag (48.161%) (Singh and Chen, 2019). The observed strong signal can be ascribed to the higher stoichiometric ratio of Ag and different extraction behavior between Ag and As ions from the BMIS.

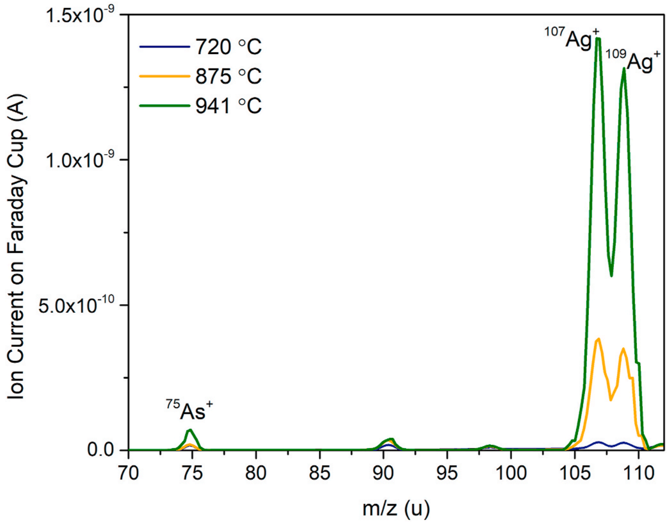

Fig. 3. Mass scans of the introduced stable silver arsenate source sample, showing peaks of the monoisotopic ^{75}As and the co-present stable silver isotopes ^{107}Ag and ^{109}Ag, at oven temperatures between 720 and 941 °C.

Following extraction from BMIS, the ^{73}As beam was accelerated in the ReAccelerator to meet the desired energy, as specified by the scientific users. The energy spectrum of the ^{73}As beam, measured on a silicon detector, showed a single peak consistent with the energy of the reaccelerated ^{73}As (Fig. 4). This confirms the identity of the beam. The absence of contaminants was investigated by directing the beam through an aluminum foil, which confirmed that no contaminants were present (Henriques et al., 2023). The adjacent peaks are likely attributed to a damaged area in the detector and low count rates.

4. Conclusions

This work demonstrates the preparation of a ^{73}As source sample, used in the offline ion source BMIS to successfully generate a ^{73}As beam, which was then provided for a science experiment at FRIB. Silver arsenate was selected as a suitable compound due to its favorable volatility in the operating temperature range of BMIS. A chemical methodology to synthesize a low-mass silver-arsenic-based precipitate was developed. High precipitation yields of (99.4 ± 4.5)% were achieved with the ^{73}As sample, which was used to prepare a source sample. The prepared ^{73}As source sample ((1.556 ± 0.10) mCi, (5.76 ± 0.37)$*10^{14}$ atoms ^{73}As) was utilized to deliver a pure ^{73}As beam at an adequate rate for an eight-day-long user experiment. Characterization via SEM-EDS and XPS suggested that the synthesized material encompassed a silver-arsenic compound with a Ag to As ratio of 3-to-1, however, the exact stoichiometry could not be determined. Several improvements could be inferred for the source sample manufacturing process, such as avoiding the use of hexane and improving the quantitative transfer of ^{73}As activity. The here-developed sample preparation method broadens the range of low-energy and stopped ion beams for the offline beam program at FRIB. The inclusion of the ^{73}As beam is particularly valuable, given its applicability in nuclear sciences (Rauscher et al., 2016).

CRediT authorship contribution statement

Andrew C. Candia: Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation. **Georg Bollen:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition. **Suvan Campbell:** Investigation, Formal analysis, Data curation. **Ana Henriques:**

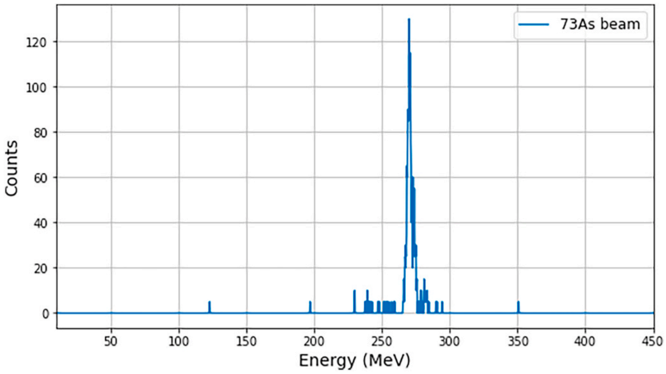

Fig. 4. Graph representing the total kinetic energy of the $^{73}As^{23+}$ beam after acceleration to 3.7 MeV/u in ReA, as measured on a silicon detector. The full-width half maximum (FWHM) of the beam peak is 5.6 MeV.

Visualization, Formal analysis, Data curation. **Alain Lapierre:** Visualization, Formal analysis, Data curation. **Samuel Nash:** Visualization, Formal analysis, Data curation. **Stefan Schwarz:** Writing – review & editing, Formal analysis, Data curation. **Chandana Sumithrarachchi:** Methodology, Formal analysis, Data curation, Conceptualization. **Antonio C.C. Villari:** Methodology, Data curation, Conceptualization. **Katharina A. Domnanich:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to thank Prof. Gregory Severin for providing the laboratory space to perform these experiments. The authors would also like to thank members of the Severin group (Chloe Kleinfeldt, Vladyslav Bodnar, Jose Blanco), Prof. Alyssa Gaiser, members of the Gaiser group, and Deepika Davuluri for their support in offering helpful insights into the development of the precipitation methodology and assisting with the practical execution. The authors are grateful to Dr. Stanley Flegler and Abigail Vanderberg for their services with SEM-EDS analysis, Dr. Per Askeland for his services with XPS analysis, and Prof. Artemis Spyrou for providing information on the science applications for the extracted ^{73}As beam. This material is based upon work supported by the National Science Foundation under grant PHY-65546 and the Department of Energy, Office of Science under award number DE-SC0000661. The isotopes used in this research were supplied by the U. S. Department of Energy Isotope Program, managed by the Office of Isotope R&D and Production.

Data availability

Data will be made available on request.

References

Beard, H.C., 1965. Radiochemistry of Arsenic 46.

Curtman, L.J., Daschavsky, P., 1916. A study of the silver arsenate test for arsenic. J. Am. Chem. Soc. 38, 1280–1282. https://doi.org/10.1021/ja02264a005.

Deegan, R.D., Bakajin, O., Dupont, T.F., Huber, G., Nagel, S.R., Witten, T.A., 1997. Capillary flow as the cause of ring stains from dried liquid drops. Nature 389, 827–829.

Domnanich, K.A., Satija, S., Bodnar, V.S., Bollen, G., Kleinfeldt, C.R., Liu, Y., Rogers, S., Schwarz, S., Severin, G.W., Sumithrarachchi, C., Villari, A.C.C., 2023. Preparation of stable and long-lived source samples for the stand-alone beam program at the Facility for Rare Isotope Beams. Appl. Radiat. Isot. 200, 110958. https://doi.org/10.1016/j.apradiso.2023.110958.

Glasmacher, T., Gade, A., Bollen, G., Wei, J., 2024. The facility for rare isotope beams: providing new Opportunities for science. Nucl. Phys. News 34, 5–12. https://doi.org/10.1080/10619127.2024.2375963.

Goldstein, J.I., Newbury, D.E., Michael, J.R., Ritchie, N.W.M., Scott, J.H.J., Joy, D.C., 2003. Scanning electron microscopy and X-ray Microanalysis, scanning electron microscopy and X-ray Microanalysis. https://doi.org/10.1007/978-1-4939-6676-9.

Henriques, A., Nash, S., Barofsky, D., Bollen, G., Lapierre, A., Schwarz, S., Sumithrarachchi, C., Zhao, Q., Villari, A.C.C., 2023. Quantification and purification of isotopic contamination at the ReAccelerator of the facility for rare isotope beams. Rev. Sci. Instrum. 94. https://doi.org/10.1063/5.0165850.

Johnston-Peck, A.C., Winterstein, J.P., Roberts, A.D., DuChene, J.S., Qian, K., Sweeny, B. C., Wei, W.D., Sharma, R., Stach, E.A., Herzing, A.A., 2016. Oxidation-state sensitive imaging of cerium dioxide by atomic-resolution low-angle annular dark field scanning transmission electron microscopy. Ultramicroscopy 162, 52–60. https://doi.org/10.1016/j.ultramic.2015.12.004.

Kusakabe, M., Iwamoto, N., Nomoto, K., 2011. Production of the p-process nuclei in the carbon-deflagration model for Type Ia supernovae. Astrophys. J. 726. https://doi.org/10.1088/0004-637X/726/1/25.

Minamisono, K., Mantica, P.F., Klose, A., Vinnikova, S., Schneider, A., Johnson, B., Barquest, B.R., 2013. Commissioning of the collinear laser spectroscopy system in the BECOLA facility at NSCL. Nucl. Instruments Methods Phys. Res. Sect. A 709, 85–94. https://doi.org/10.1016/j.nima.2013.01.038.

Molnár, L., Virčíkova, E., Lech, P., 1994. Experimental study of As(III) oxidation by hydrogen peroxide. Hydrometallurgy 35, 1–9. https://doi.org/10.1016/0304-386X(94)90013-2.

Moulder, J.F., Stickle, W.F., Sobol, P.E., Bomben, K.D., 1992. Handbook of X-Ray Photoelectron Spectroscopy.

Rauscher, T., Nishimura, N., Hirschi, R., Cescutti, G., Murphy, A.S.J., Heger, A., 2016. Uncertainties in the production of p nuclei in massive stars obtained from Monte Carlo variations. Mon. Not. Roy. Astron. Soc. 463, 4153–4166. https://doi.org/10.1093/mnras/stw2266.

Rumble, J.R., 2023. Handbook of Chemistry and Physics, 104th edit. CRC Press.

Satija, S., Domnanich, K.A., Sumithrarachchi, C., Liu, Y., Cingoranelli, S.J., Saini, S., Chaple, I., Lapi, S.E., Severin, G.W., 2024. Production and separation of 7Be for use in an ion source. Appl. Radiat. Isot. https://doi.org/10.1016/j.apradiso.2024.111382.

Sherrill, B.M., 2018. Future Opportunities at the facility for rare isotope beams. EPJ Web Conf. 178, 1–5. https://doi.org/10.1051/epjconf/201817801001.

Simon, A., 2024. p-process investigation. https://groups.frib.msu.edu/SuN/SuN_summing.php.

Singh, B., Chen, J., 2019. Nuclear data sheets for A=73. Nucl. Data Sheets 158, 1–257. https://doi.org/10.1016/j.nds.2019.02.006.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem. 17, 517–568. https://doi.org/10.1016/S0883-2927(02)00018-5.

Suárez-Domínguez, E.J., Betancourt-Mar, J.A., 2005. Mechanisms of bands and spirals formation during the drying of watery solutions of mercury (II) chloride with agar-agar. J. Phys. Conf. Ser. 23, 78–86. https://doi.org/10.1088/1742-6596/23/1/009.

Sumithrarachchi, C., Liu, Y., Rogers, S., Schwarz, S., Bollen, G., Gamage, N., Henriques, A., Lapierre, A., Ringle, R., Yandow, I., Villari, A.C.C., Domnanich, K.A., Satija, S., Severin, G.W., Au, M., Ballof, J., Vila Garcia, Y.N., Owen, M., Reis, E., Rothe, S., Stegemann, S., 2023. The new Batch mode ion source for stand-alone operation at the facility for rare isotope beams. Nucl. Instrum. Methods Phys. Res. B 541, 301–304.

Ten Brink, B.O., Van Nes, P., Hoetmer, C., Verheul, H., 1980. On the structure of 71As and 73As. Nucl. Phys. 338, 24–44.

Tsantiri, A., Spyrou, A., 2024. Constraining the astrophysical γ process: cross section measurements of (p,γ) reactions in inverse kinematics. In: 8th P-Process Workshop. Budapest.

Villari, A., Alt, D., Bollen, G., Crisp, D.B., Ikegami, M., Krause, S.W., Lapierre, A., Lidia, S. M., Morrissey, D.J., Nash, S., Rencsok, R.J., Ringle, R., Schwarz, S., Shane, R., Sumithrarachchi, C., Williams, S.J., Zhao, Q., 2016. Commissioning and first accelerated beams in the ReAccelerator (ReA3) of the national Superconducting Cyclotron laboratory. In: IPAC 2016 - Proceedings of the 7th International Particle Accelerator Conference, pp. 1287–1290.

Villari, A.C.C., Bollen, G., Henriques, A., Lapierre, A., Nash, S., Ringle, R., Schwarz, S., Sumithrarachchi, C.S., 2023. Gas stopping and reacceleration techniques at the facility for rare isotope beams (FRIB). Nucl. Instrum. Methods Phys. Res., Sect. B 541, 350–354. https://doi.org/10.1016/j.nimb.2023.05.037.

Viltres, H., Odio, O.F., Lartundo-Rojas, L., Reguera, E., 2020. Degradation study of arsenic oxides under XPS measurements. Appl. Surf. Sci. 511, 145606. https://doi.org/10.1016/j.apsusc.2020.145606.