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Investigation of selenium compounds as targets for ^{76,77}Br production using protons of energies up to 34 MeV

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Abstract: Selenium compounds of Zn, Sn and Cu were prepared using a conventional sintering method and the phase composition of each compound was investigated using X-ray diffraction. The compounds prepared were tested under variable irradiation and separation conditions for ^{76,77}Br production. The activity of ^{77}Br was measured as a function of proton beam current within the range 2–15 μA and the thermal stability of the irradiated compound was investigated. The results showed that the compounds ZnSe and Cu_2Se are thermally more stable in comparison to the SnSe. The effects of several factors, such as temperature, gas flow rate and separation time, were studied to obtain the maximum separation yield of radiobromine by the dry distillation method. The data showed that the compound Cu_2Se is the most suitable target for proton irradiation to produce ^{76,77}Br at energies up to 20 MeV. A simplified method was used to prepare also CuSe, which was tested in irradiations with intermediate energy protons of beam currents up to 10 μA. The data of a typical production run using 17 MeV protons and the Cu_2Se target are reported.

Keywords: ^{76,77}Br Radioisotopes, distillation method, selenium compounds, radionuclide production, nuclear reactions.

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1 Introduction

The radionuclides of bromine, such as ^{75}Br ($T_{1/2}$ = 1.6 h), ^{76}Br ($T_{1/2}$ = 16.0 h), ^{77}Br ($T_{1/2}$ = 57 h) and ^{80m}Br ($T_{1/2}$ = 4.4 h), have excellent physical and chemical characteristics to be used either in imaging via Positron emission tomography (PET) or single photon emission tomography (SPECT), or for internal radiotherapy [1–8]. Charged particle accelerators are the most suitable tools for their production through different nuclear reactions using a wide variety of projectiles and targets [9–34]. The (p,xn) reactions on selenium were found to be very suitable in the low and intermediate energy regions (5–40 MeV). Small sized cyclotrons can be used [9–13], but relatively high-intensity particle beams (>10 μA) and highly enriched target isotopes are needed to obtain sufficient production yields. Suggestions have been made to use binary compounds of the element Se as a target to achieve good stability during irradiation, which in turn decreases the processing cost [12, 17, 21, 22, 34]. However, suitable compounds of the stable enriched Se isotopes are not available. Therefore, it is mandatory to prepare these compounds in the local laboratories, taking into account that the available amounts of the expensive materials are small. Thermodynamic data and phase transformation diagrams have to be taken into consideration while attempting to prepare a pure phase of the desired compound. The stability of the prepared target is generally tested via irradiation followed by separation of radiobromine by dry distillation or thermochromotography [cf. 17, 18, 22, 34]. The radionuclide activity increases with the increasing incident beam current till a saturation level is reached beyond which further increase in the beam intensity does not affect the production yield [cf. 35]. This stagnation in yield may be due to material damage caused by the thermal instability or due to loss of radioactivity by evaporation, or both. For practical purposes, an estimation of the target activity as a function of the beam intensity was considered to reflect the performance of a target material.

The compound Cu_2Se has been used in several laboratories for radiobromine production through the proton induced nuclear reactions on enriched Se composites [21, 22]. Similar experiments were done on compounds of

Table 1: Composition and melting points of the ZnSe, SnSe, CuSe and Cu_2Se compounds [39].

Compound	ZnSe	SnSe	Cu_2Se	CuSe
Se-content (%)	54.7	39.95	38.32	55.4
Melting point (°C)	1100	861	1113	550

^{78}Se ($Na_2SeO_{3.88} \cdot 0.38Na_2O$) as a target for production of ^{77}Br via the reaction ^{78}Se(p,2n)^{77}Br [12]. Irradiation currents of up to 6 μA were used. The separation was done by heating the irradiated target in a flow of oxygen gas at a temperature of 1025 °C for 30–70 min. The target loss was 0.08 % per min. A number of metal selenides were tested as target material for the production of ^{75}Br via the ^{76}Se(p,2n)^{75}Br reaction [17] using 1–4 μA beam of 28 MeV protons. A ^{76}Se-metal target on Al-backing was employed for the production of ^{75}Br via the ^{76}Se(p,2n)-reaction using 15 μA of a 24 MeV proton beam on a rotating target [18]. The separation of radiobromine was achieved through thermochromotography. In a very recent work [26], a NiSe target was tested which could withstand up to 16 μA of a 17 MeV proton beam, and radiobromine was efficiently separated by distillation at 940 °C. The advantage of using NiSe is that radiobromine is completely removed from the distillation apparatus and collected in a water trap.

The phase formation diagrams allow preparation of a binary compound of selenium by a conventional sintering method [36]. Synthesis of Se(II–VI) compounds is done by mixing stoichiometric percentages of two elements in a sealed quartz tube and sintering the mixture in a high temperature oven (800–1200 °C) [37]. It is preferred to apply a low pressure of the inert gas instead of vacuum atmosphere in the sealed quartz tube to avoid oxidation or reaction with some impurities in the inner environment [38].

In this study, we performed experiments to investigate the formation and separation of the isotopes ^{76,77}Br from the selenides ZnSe, SnSe, CuSe and Cu_2Se. The emphasis was on the determination of activity-beam-current relations and separation efficiency of the dry distillation method. The selection of the investigated compounds was based on the properties listed in Table 1. The highest selenium content was found to be in ZnSe which was expected to produce more yield of radiobromine than the Sn and Cu selenides.

2 Experimental

2.1 Preparation of ZnSe, SnSe, CuSe and Cu_2Se

All the used elements were of scientific grade (purity >99.99, Sigma Aldrich) and in powder form, except for Sn which was available as pellets (0.5–1 mm). Preparation of the compounds ZnSe, SnSe, CuSe and Cu_2Se was done by a conventional sintering method. The quantity of each element Se, Zn, Sn and Cu was taken as one tenth of its respective atomic mass number in grams. The element Zn, Sn or Cu was added to Se individually in a quartz vial and then evacuated to 1.3×10^{-5} bar. Ar gas of pressure 500 mbar was then introduced in the tube before sealing its nozzle. Each vial was placed separately in an oven and the temperature was raised gradually to 1000–1200 °C according to the melting point of the expected compound for a period of 4 h. Thereafter, the quartz ampoule was taken out of the oven and suddenly quenched in water. The formed compounds were pulverized manually to fine powders using an agate mortar. Parts of the prepared compounds were subjected to XRD analysis using PHILIPS analytical system with wavelength 1.54 Å (K-Alpha). The obtained XRD spectra were compared with the standard cards for the expected compounds to estimate the formed phases.

The preparation of Cu(I)Se was done by mixing Cu and Se in an equal molar ratio (1:1). The mixture powder was placed into a Ti-disc cavity (∅ = 16 mm; depth = 1 mm) to be used directly as a target holder after preparation. Then the target was carefully transferred to the oven and the temperature was raised gradually to 570 °C and kept for 2 h; thereafter the target was cooled gradually to room temperature.

2.2 Proton irradiations

The target holders used for irradiations of the Se compounds at the compact cyclotron CV 28 of the Forschungszentrum Jülich, Germany, are shown in Figure 1a–c. The first was at a perpendicular position relative to the beam direction with cooling water flowing through the target base (Figure 1a). The powders were pressed in the form of thin disks of 13 mm diameter. The disks of the Se compounds were fixed by a threaded open cap on the top of the holder [15]. The second holder design was inclined with an angle of 20° relative to the beam (Figure 1b) [40]. The Se compound was pressed in a slab of copper with a circular groove of 7 mm diameter and 0.6 mm depth. This slab was soldered to the holder using Sn soldering wire. The proton beam was again directly incident on the Se compound, as in Figure 1a. After irradiation, this slab was removed from the holder by heating and counted by the HPGe detector; thereafter further processing was done. The same irradiation conditions as for normal configuration were used. In the third target arrangement the cooling was done by water on the backside of the sample

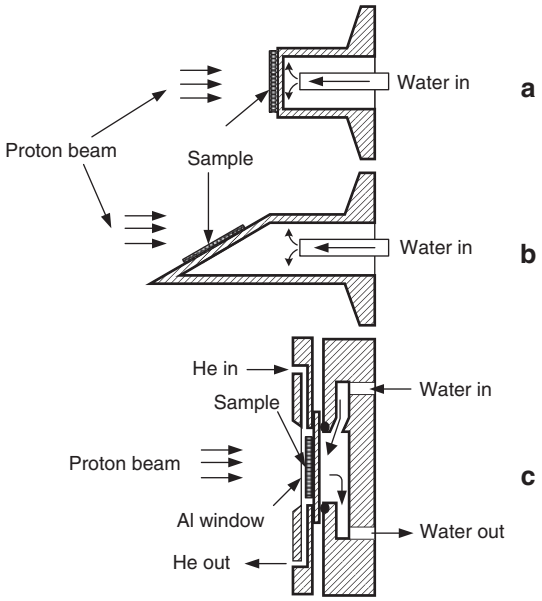

Figure 1: Target holders used in irradiation of selenium compound samples at the CV 28 cyclotron: (a) Normal target cooled by water at the back [cf. 15], (b) inclined water cooled target [cf. 40] and (c) target cooled in front by He and at the back by water [cf. 41].

and a stream of He gas on its front side, as shown in Figure 1c [41]. The sample was fixed with silver paste on a copper base coupled to the holder. A closed cycle heat exchanger was used to cool circulating He gas flowing through the target surface. Different samples of the ZnSe, SnSe and Cu_2Se compounds were irradiated with 19 MeV protons for 10 min with beam currents of 2, 4, 6, 8, 10 and 12 μA. The irradiated samples were counted on a HPGe detector coupled to ORTEC electronics modules. A suitable cooling time after irradiation was chosen to avoid high values of dead time of the detection system. The ^{77}Br activity was determined using the area under the 520 keV γ-ray photopeak. All the determined activities were extrapolated to the end of bombardment (EOB) and normalized to 1 h irradiation time.

Irradiation of the CuSe samples was carried out with 40 MeV protons at the AVF 930 cyclotron of the National Institute of Radiological Sciences, Chiba, Japan. Seven Al-foils, each of thickness 300 μm, were used to decrease the primary proton energy to ~34 MeV at which the maximum cross section for ^{76}Br production from ^{nat}Se occurs [cf. 26]. The absorbed proton energy in about 160 μm thick CuSe target amounted to 1.3 MeV. The irradiation beam currents used were 3, 5, 7 and 10 μA for a fixed time of 60 min. Furthermore, the produced activity was estimated for different irradiation times of 60, 110 and 170 min at a fixed beam current of 8 μA.

2.3 Dry distillation experiments

The radiobromine produced could be isolated from the irradiated targets by evaporation at high temperature. For optimization studies, a number of ZnSe, SnSe and Cu_2Se target samples were irradiated with 19 MeV protons for 30 min at a beam current of 3 μA and then left for cooling for 3–5 days to allow short-lived impurities to decay out. Each irradiated sample was inserted inside a specially designed quartz tube consisting of four parts that are tightly connected and placed inside a high temperature oven as shown in Figure 2. The sample surface was exposed to a stream of Ar gas introduced from the inlet of the tube, which carried the evaporated radiobromine towards the tube outlet immersed inside cold water. The activity of radiobromine was determined for each sample before and after distillation to estimate the efficiency of separation for various oven temperatures (500–1100 °C) and separation times (15–90 min). At the end of the distillation process, the activity of radiobromine dissolved in

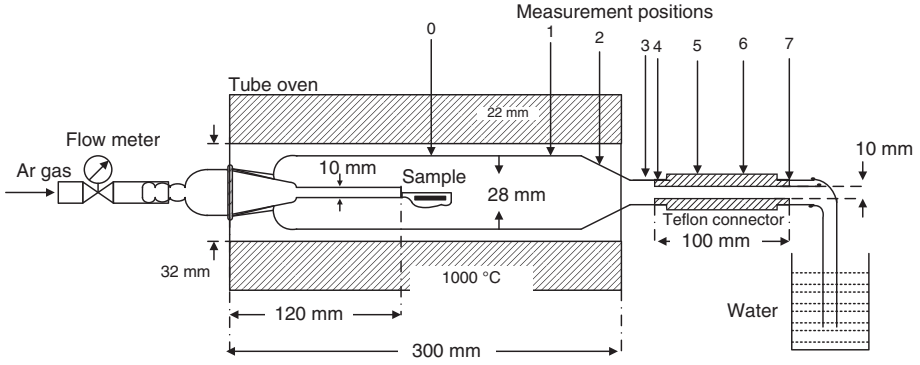

Figure 2: Apparatus used for dry distillation experiments for the separation of radiobromine from irradiated selenium compounds. The positions where the radioactivity was measured are given.

the water trap as well as that deposited on all the various parts of the quartz tube was measured using the HPGe γ-ray spectroscopic system. The tube was taken out of the oven and put on a narrow slit (width = 5 mm) formed by two parallel lead bricks placed above the detector head to monitor distant regions along the tube. All the determined activities were normalized to EOB. The effect of several separation parameters (temperature, gas flow, time, etc.) on the removal efficiency and the total yield of radiobromine was studied.

3 Results and discussion

3.1 Structure confirmation of the prepared Se compounds

The X-ray diffraction spectra of the prepared ZnSe, SnSe and Cu_2Se are shown in Figures 3–5, respectively. The intense peaks at several diffraction angles indicate the high degree of crystallinity of the formed compounds. The spectrum of ZnSe (Figure 3) contains four significant peaks at the diffraction angles 27.28°, 45.23°, 53.58° and 66° which are in agreement with those in the card Number JCPDS-37-1463 of cubic zinc blend ZnSe [42]. Some additional peaks of low intensities were found at 23.5° and 30° which may be due to formation of some oxides with very low percentages. The SnSe spectrum (see Figure 4) indicates that there are two formed phases, namely SnSe and $SnSe_2$, which could be assigned using the two XRD cards JCPDS-89-0236 and JCPDS-892939 [43]. The result does not affect the nuclear reaction with

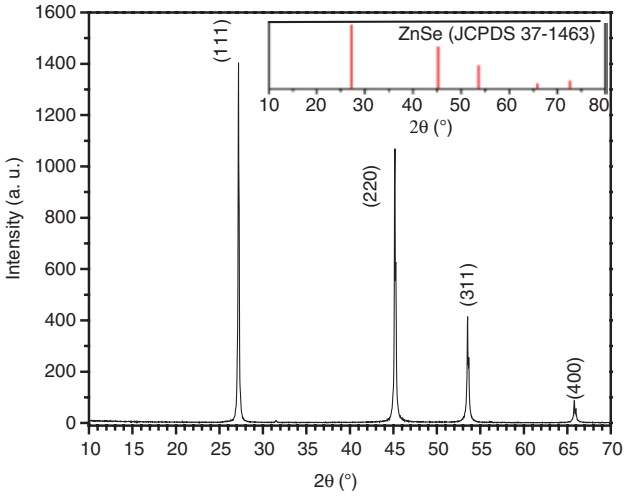

Figure 3: The XRD spectrum of the prepared ZnSe compound.

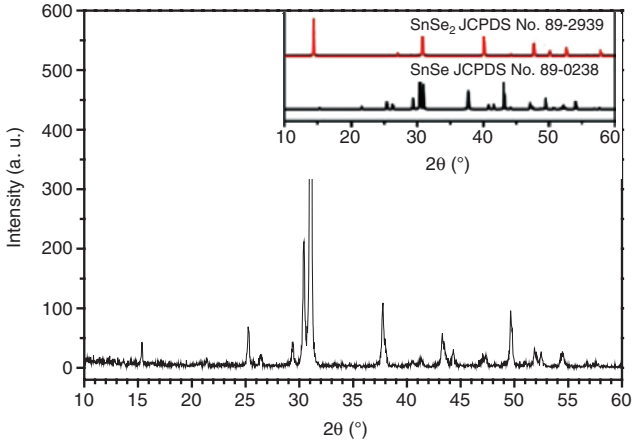

Figure 4: The XRD spectrum of the prepared SnSe compound.

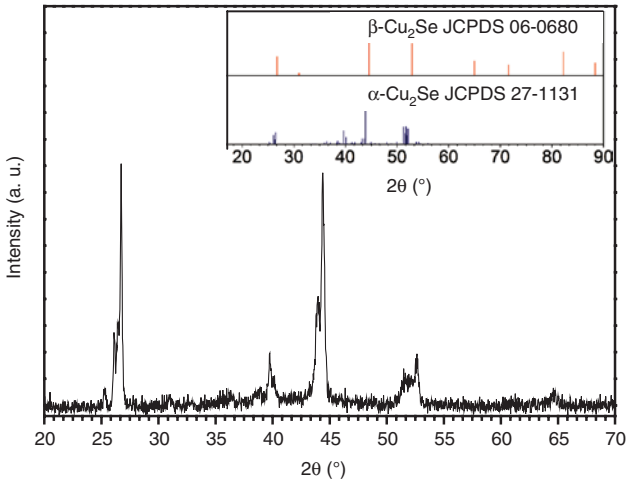

Figure 5: The XRD spectrum of the prepared Cu_2Se compound.

the incident proton beam since the Se content remains constant for the total amount of the compound. Similarly, the Cu_2Se showed two phases, α-Cu_2Se (JCPDS 27-1131) and β-Cu_2Se (JCPDS 06-0680) as depicted in Figure 5 [44]. Similarly, the structure of the CuSe was confirmed by the using JCPDS cards No. 020-1020 and 65-3562 [45, 46].

3.2 Target stability tests

3.2.1 ZnSe, SnSe and Cu_2Se targets

The radioactivity of ^{77}Br was measured as a function of irradiation current to test the stability of the three selenide compounds ZnSe, SnSe and Cu_2Se. It needs to be pointed out that in this type of investigation one

observes the cumulative effect of target deterioration and radiobromine loss, both of which are expected to increase with the increasing projectile beam current. In our judgment, this cumulative effect is a good index of target performance. The three target materials were irradiated using the three target holders given in Figure 1. The ^{77}Br activity obtained through the compound ZnSe was higher than that from SnSe and Cu_2Se due to higher Se content (cf. Table 1). Use of the normal target position (Figure 1a) did not show high performance for any target material and the ^{77}Br yield stagnation reached already at 8–10 μA beam currents. For the inclined target (Figure 1b) the activity showed a linear increase with the increasing beam current, presumably due to the good performance of the target cooling with low power density dissipated by the beam inside the target. On the other hand, the level of the obtained activity was found to be lower than that for the normal target which was attributed to the positioning of the proton beam and the slight difference in the energy thickness in the two target configurations. The incident proton energy on the target with front He cooling (Figure 1c) loses part of its energy in the Al window and in the He gas. The incident energy on the sample was verified using a Cu foil as monitor [47] and was found to be 16.5 ± 0.2 MeV. This energy is not enough for producing a large amount of ^{77}Br activity due to low cross section for protons on ^{nat}Se [24]. The results are shown in Figure 6. The theoretical yield of ^{77}Br from ^{nat}Se for this arrangement ($E_p = 16.5 \rightarrow 10$ MeV) was estimated to be 11.6 MBq/μAh. The yield of ^{77}Br obtained from ZnSe using this type of target was approximately 70 % of this value at 12 μA considering the selenium content (see Table 1). For SnSe and Cu_2Se, the yields were lower due to lower Se content and due to dissipation of the target surface, which was observed as reddish brown traces on the He cooling pipe lines, particularly at currents above 6 μA in the case of SnSe. That material was therefore rejected for use as target. The data obtained revealed that ZnSe is the most thermally stable target at proton current values of about 12 μA, followed by Cu_2Se.

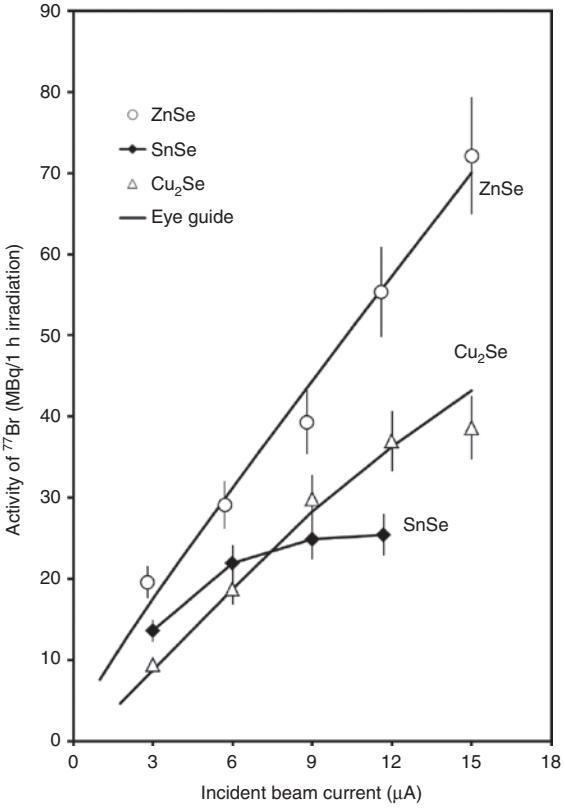

Figure 6: Activity of ^{77}Br produced in irradiation of selenium compounds with 17 MeV protons using double window water–helium cooled target holder (shown in Figure 1c).

3.2.2 CuSe target

For this target material the determined ^{76}Br activity was plotted as a function of the incident beam current and the result is shown in Figure 7. The short-lived isotopes ^{75}Br ($T_{1/2} = 1.6$ h) and ^{80m}Br ($T_{1/2} = 4.42$ h), also formed during the irradiation, had decayed out prior to measurements. The activity of ^{76}Br increased from 25 to about 45 MBq by increasing the beam current from 5 to 10 μA, and was lower than the calculated yield by 30–45 % at all points. Since the target was rather thin, the heat dissipation problem was not serious. The ^{76}Br activity was found to increase almost linearly with the irradiation time up to 170 min. The loss in the target mass was found to be <0.5 % at 10 μA during a 60 min irradiation. While increasing the time of irradiation from 60 to 170 min at 8 μA beam current, the loss of target material amounted to about 2.5 %. The target CuSe is thus stable against short irradiations of up to 10 μA. However, the loss of the target material in longer irradiations appears to increase substantially which is considered as a significant drawback.

3.3 Loss in mass of samples during distillation

The loss in the mass of the target compounds ZnSe and Cu_2Se during the distillation process was investigated in a tube oven with variable temperature at a constant Ar gas flow rate (30–100 mL/min of gas). The sample was

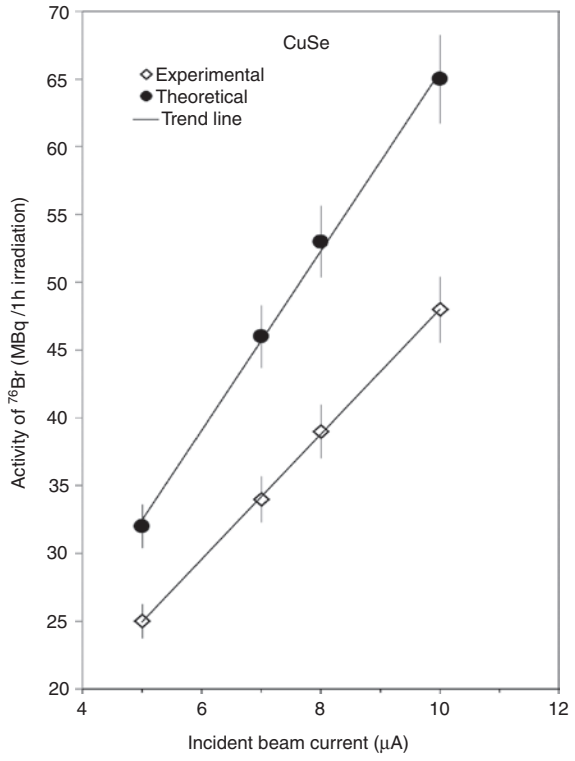

Figure 7: Activity of ^{76}Br produced by irradiation of CuSe compound with 34 MeV protons shown as a function of the incident beam current.

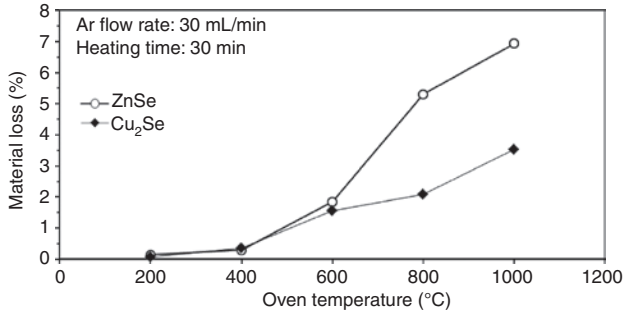

Figure 8: Variation in the relative mass loss (%) in the unirradiated ZnSe and Cu_2Se samples with the increasing oven temperature.

weighed before and after heating and there from the loss was determined. Figure 8 shows the mass loss as a function of the applied temperature. For both ZnSe and Cu_2Se, considerable loss was observed at temperatures above 600 °C. The surface of the SnSe sample was highly influenced by the high temperature of the oven and therefore it was excluded from the comparison with other compounds. Similar experiments were carried out also on the CuSe target that was fixed inside a Ti-cavity. The average mass loss was found to be about 20 %, presumably due to formation of $Cu_{2-x}Se$ in the top layer.

3.4 Radiobromine separation parameters

3.4.1 Radioactivity distribution

Based on the radiation stability and mass loss tests described above, we concentrated further only on the target materials Cu_2Se and ZnSe. The ^{77}Br radioactivity mapping over the quartz tube and its Teflon connector was done by determining the activity at the positions shown in Figure 2. The results are summarized in Table 2. It was found that the temperature gradient through the distillation tube affects the deposition of the released radiobromine on the inner surface of the tube. The major part of the activity (~78 %) was found in the outer tube. It should be mentioned that some of the evaporated radioactive ^{75}Se was deposited on the tube inner surface as a transparent red film close to the oven outlet, while the isotope ^{77}Br was carried by the Ar gas further up to the Teflon tube. By rinsing it with 5 mL of hot water, the ^{77}Br activity could be easily collected.

3.4.2 Separation efficiency

To estimate the separation efficiency and the amounts of ^{77}Br obtained at different operating temperatures and times, several samples of ZnSe and Cu_2Se were irradiated for 30 min with 19 MeV protons at a beam current of 3 μA. The separation was started 72 h after EOB. Figures 9–12 show the separation results for the two targets. It was found that the efficiency of separation did not exceed 75 % for both the compounds. It has low values within the temperature range 500–800 °C and starts increasing above 800 °C (Figures 9 and 10). This indicates that ^{77}Br is strongly bound in the target and needs a high temperature

Table 2: Distribution of radiobromine in the distillation apparatus after release from an irradiated Cu_2Se or ZnSe target at an oven temperature of 1000 °C, Ar gas rate of 30–100 mL/min and distillation time of 60 min.

Measurement point	Distance from sample (mm)	^{77}Br activity	
		Absolute (kBq)	Percentage (%)
0	0	4.2	0.1
1	120	306.3	10
2	140	350.2	11
3	160	965.7	31
4	170	604.9	19
5	200	496.2	16
6	230	363.2	12
7	270	12.6	0.4

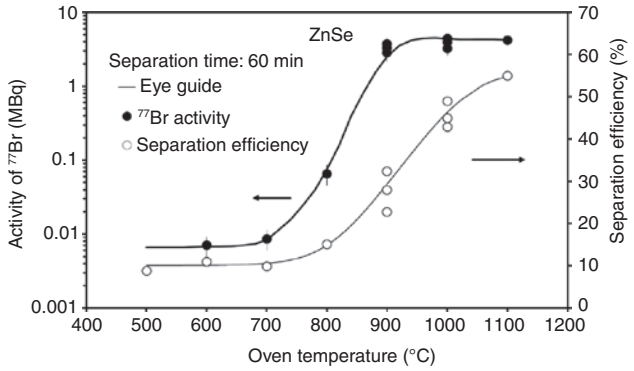

Figure 9: Temperature dependence of the separation efficiency and ^{77}Br-yield from the ZnSe target irradiated with 19 MeV protons at 3 μA for 30 min.

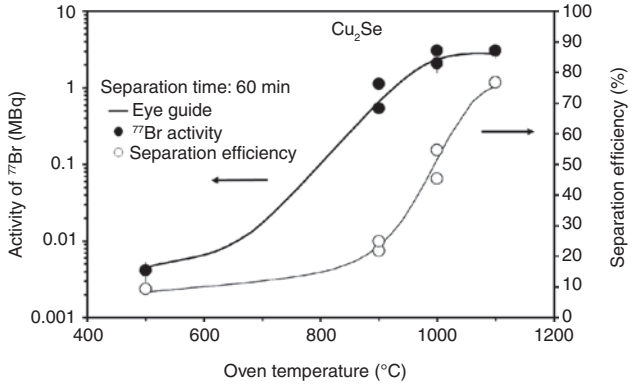

Figure 10: Temperature dependence of the separation efficiency and ^{77}Br-yield from the Cu_2Se target irradiated with 19 MeV protons at 3 μA for 30 min.

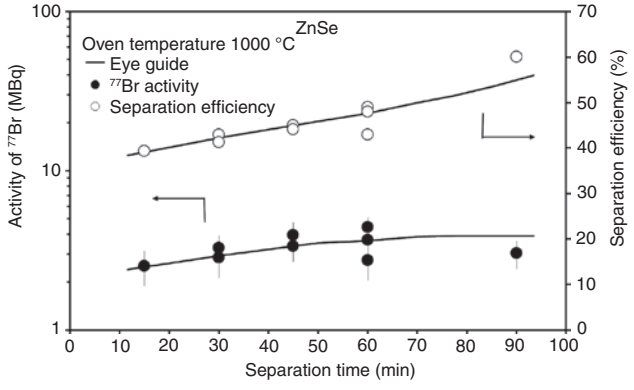

Figure 11: Separation efficiency and ^{77}Br-yield from the ZnSe compound irradiated with 19 MeV protons at 3 μA for 30 min as a function of separation time at a constant oven temperature.

to be released. At temperatures above 1000 °C both the efficiency and total ^{77}Br activity reach a saturation level, possibly due to the difficulty of radiobromine exhalation from deeper positions inside the irradiated sample. The

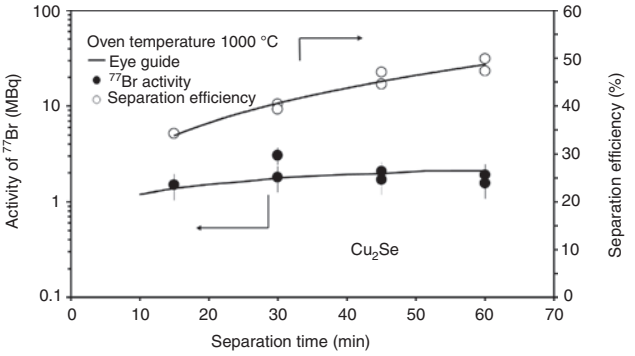

Figure 12: Separation efficiency and ^{77}Br-yield from the Cu_2Se compound irradiated with 19 MeV protons at 3 μA for 30 min as a function of separation time at a constant oven temperature.

total yield curves show almost the same trends as efficiency. While increasing the temperature to 1100 °C, the sample surface exhibited corrosion damage.

The separation time has only small effect on the efficiency of ^{77}Br separation from the two compounds (Figures 11 and 12). The efficiency increases by about 20 % by increasing the separation time from 15 to 90 min. The total yield was found to be nearly constant after about 40 min separation time.

From all the experiments described above it was concluded that the optimum conditions of separation of ^{77}Br from both the compounds ZnSe and Cu_2Se are: 1000 °C oven temperature, 30–40 min separation time and 30–120 mL/min Ar gas flow. The thermal and mechanical stability of Cu_2Se was found to be higher than that of ZnSe.

3.5 Typical production run using a Cu_2Se target

The Cu_2Se sample of 10 mm diameter was irradiated for 5 h with 17 MeV protons at a beam current of 3 μA. The target holder with front He cooling was used (see Figure 1c). The calculated actual beam energy on the sample surface was approximately 16.5 MeV and the target thickness was 470 mg/cm^2 which corresponds to an absorbed energy of 10 MeV. The ^{77}Br was separated using a small distillation system at a temperature of 1000 °C, Ar flow rate of 30–100 mL/min and the separation time of 40 min. The target was counted before and after separation to determine the amount of ^{77}Br removed from the target. The outer tube was rinsed with 5 mL of hot water and the solution containing ^{77}Br was investigated by HPGe γ-ray spectroscopy for determination of the impurities. Table 3 presents the experimental values of the ^{77}Br yield in comparison to that theoretically expected. Regarding the

Table 3: Results of radiobromine separation from the Cu_2Se target of natural selenium content.

Parameter	Value
^{77}Br activity in the target before separation	18.4 ± 3 MBq
Separated ^{77}Br activity	11.2 ± 1 MBq
Separation efficiency	60 %
Expected thick target ^{77}Br activity (for 38 % Se content) at EOB	85 ± 4 MBq
Expected ^{77}Br activity (for 38 % Se content) at the time of separation	35 ± 2 MBq
Overall experimental yield as percentage of theoretical value	50 %

radionuclidic purity, about 99 % of the activity consisted of radiobromines. The major non-isotopic radionuclidic impurities were: ^{74}As, ^{76}As and ^{77}As, formed via ^{nat}Se(p,α or αn)-processes. Traces of ^{75}Se were also observed. It is expected that the use of highly enriched ^{76}Se or ^{77}Se would decrease the level of radioarsenic impurity. Nonetheless, if medical application is the aim, a second purifying step for radiobromine, would be necessary, also in view of the toxicity of selenium.

The obtained results presented in Table 3 are considered to some extent as optimum for proton reactions on ^{nat}Se targets but, on the other hand, improvement is needed for large scale production of ^{77}Br. The Cu_2Se target described here can withstand proton beam currents of up to about 12 μA and if irradiation is done for about 6 h, the separated ^{77}Br activity would amount to about 50 MBq. Use of highly enriched ^{77}Se target [cf. 48] could lead up to about 600 MBq of ^{77}Br. The radionuclidic purity and total amount produced would then be comparable to ^{77}Br produced via the ^{75}As(α,2n)^{77}Br reaction using high-current Cu_3As target [15]. The method could also be adapted to production of ^{76}Br by using a highly enriched ^{76}Se target [cf. 22].

3.6 Concluding remarks

The three compounds of natural selenium, namely ZnSe, SnSe and Cu_2Se, were prepared by a conventional alloying method and their structures were confirmed using X-ray diffraction. An irradiation system with He cooling in front and water cooling at the back was found to be optimum for radiobromine production. The ZnSe and Cu_2Se targets showed high thermal stability in proton irradiations of beam currents up to 15 μA. Examination of separation conditions for radiobromine showed that the highest yield is achieved at an oven temperature of 1000 °C. The radiobromine is deposited on the inner wall of the outer tube and recovered by rinsing with about 5 mL of hot water. The method is thus similar to that of Tolmachev et al. [22] for a Cu_2Se target, but the various optimization studies presented here are much more extensive. Furthermore, we prepared the two compounds ZnSe and Cu_2Se by a relatively simple technique and confirmed their structures by X-ray diffraction studies. Our radiobromine separation technique is not as elegant as in the case of a NiSe target [34] where the separated radiobromine is directly collected in a water trap. It is known that collection of radioactivity in a trap generally leads to a somewhat more pure product [cf. 40] than thermochromatography where a subsequent purification step may be necessary [cf. 49]. Nonetheless, it has yet to be demonstrated whether NiSe can be as easily produced and characterized as we have shown in the case of ZnSe and Cu_2Se. It is also understood that further extensive work on the preparation of binary compounds incorporating enriched selenium isotopes is absolutely necessary to obtain ^{76}Br or ^{77}Br in higher yields and with high radionuclidic purity.

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