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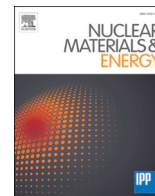
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## Tritium measurements by nuclear reaction analysis using $^3\text{He}$ beam in the energy range between 0.7 MeV and 5.1 MeV

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### ABSTRACT

A solid thick tritiated W sample was produced in order to probe the efficiency of detecting tritium via  $^3\text{He}$  ion beam using nuclear reactions analysis (NRA). Extensive literature search showed that there were only a few measurements done more than sixty years ago using the reaction with  $^3\text{He}$ . Their aim was mainly to measure the absolute cross section of the reaction. In order to use this reaction as an analysing tool for low level radioactive waste we need the differential cross section at certain angles. Using a thick tritiated W sample we measured the NRA signal in the  $^3\text{He}$  energy range from 0.7 MeV to 5.1 MeV and we have detected reaction products with energies between 6.5 MeV and 9.75 MeV that were not present on a deuterated W sample prepared in the same manner. This NRA signal proved to be due to deuterium and protons coming from the nuclear reaction between tritium and  $^3\text{He}$ . The detection signal increased with  $^3\text{He}$  energy up to 3.4 MeV and decreased with energy at the highest beam energies. At higher energies particles from W and target impurities start to disturb the measurement. Their origin might be due to other nuclear reactions, for example between  $^3\text{He}$  and W or  $^3\text{He}$  with  $^{13}\text{C}$  or  $^{14}\text{N}$ .

### Introduction

Among all the difficult-to-measure beta emitters, tritium (T) is an important radionuclide to measure in fusion and fission activities (for nuclear power plants (NPP) and facilities under dismantlement) since it can be released easily into the environment due to its high mobility. Moreover, the control of the retained fuel (D and T) in fusion materials is an especially important issue, due to safety limitations and high T expense in future fusion devices (ITER and DEMO).

Tritium is a radionuclide very difficult to analyze mainly because of its energy, type of decay ( $\beta^-$ ) and its chemical and physical behaviour. To investigate T in-situ directly on radioactive wastes coming from fusion or fission facilities, robust, sensitive and cost-effective analytical techniques are rather scarce [1], especially for low level waste management. An easy way to obtain spots of radioactivity in the field of dismantling is to use smears and proportional counters or liquid scintillation counting technique (LSC). Following advices from Organisation for Economic Co-operation and Development (OECD)/Nuclear Energy Agency (NEA)

working group, innovative procedures for T and other beta emitters are still required for decommissioning [2].

Most of the hydrogen isotope retention, transport and recycling studies in the plasma-facing material research are currently performed with deuterium (D) utilizing ion beam analysis (IBA) methods and thermal desorption spectroscopy (TDS) [3,4]. TDS gives information on the total inventory of hydrogen isotopes in the entire sample and IBA methods enable the measurement of hydrogen depth and lateral profiles. Both methods give complementary results on hydrogen retention. The results obtained with D are then extrapolated to predict T retention.

IBA methods are an important tool in the plasma-facing material analysis [4]. They are especially important in determination of hydrogen isotope retention since ion beam analysis [5], in particular nuclear reaction analysis (NRA) [6] and elastic recoil detection analysis methods (ERDA) [7], are the only methods that can detect low amounts of hydrogen isotopes on a quantitative level. There is yet no well-established IBA method, sensitive for detecting low levels of T. The ERDA method utilizing the  $^4\text{He}$  beam is a useful method as it enables

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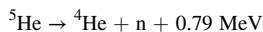
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simultaneous depth profiling of H, D and T [8,9] with a sensitivity for T detection of about  $10^{15}$  at./cm<sup>2</sup> [9] but its sensitivity to surface roughness and shallow depth information makes it not the ideal candidate to analyse rough samples typically coming from fusion devices or nuclear wastes. Bykov et al. [7] used the <sup>12</sup>C beam to detect tritium via ERDA and at the same time also NRA detection method using T(<sup>12</sup>C,p)<sup>14</sup>C reaction to overcome the possible problem of surface roughness of the samples. When samples contain small amounts of hydrogen, the NRA method is usually utilized for hydrogen isotope detection due to its insensitivity to surface roughness and contamination [10,7]. The most often used and most effective detection of protium by NRA is via the resonant <sup>1</sup>H(<sup>15</sup>N,αγ)<sup>12</sup>C nuclear reaction [11]. The detection of D by NRA is most efficient by the use of the <sup>3</sup>He ion beam [12–14]. For this purpose the <sup>2</sup>H(<sup>3</sup>He,p)<sup>4</sup>He nuclear reaction is very sensitive to D detection, due to the strong resonance like cross-section (detection limit < 10<sup>-3</sup> atomic %). By the <sup>3</sup>He-NRA, one is able to detect D to a depth of about 7 μm below the sample surface [15] in tungsten, using MV electrostatic accelerators. Lastly and most importantly, nuclear reactions like <sup>3</sup>H(p,n)<sup>3</sup>He [16,17] and <sup>3</sup>H(d,α)n [18,19] are typically used to detect and quantify tritium in a solid material. However, in the first case one needs to detect neutrons in time of flight [17] which is not trivial in common ion beam laboratories. The second NRA with deuterium probing beam produces high neutron yields and the detection of α particles makes it more surface sensitive [16]. Moreover, the deuterium ion beam is not allowed to be used in many laboratories due to generation of intense flux of high energy neutrons that consequently reach radiation safety limitations.

With regard to tritium detection there are also other methods such as the accelerator mass spectrometry (AMS) and full combustion method (FCM) that can deliver quantitative tritium profiles and were shown to have better detection sensitivity as compared to ion beam analysis methods e.g. [20]. Moreover, chemical etching and subsequent analysis of tritium in the etching solution using liquid scintillation counting can also provide quantitative tritium depth profiling e.g. [21,22]. All methods were successfully used to determine the very small amounts of tritium on samples exposed in fusion device JET [21,20] and gave very much valuable information on the tritium retention. However, one needs to stress that all these methods are destructive whereas ion beam methods are in most cases non-destructive. Still at present, no ion beam method could outperform the tritium sensitivity of the above listed methods.

After a thorough search through the literature one can find that <sup>3</sup>He also induces nuclear reactions with tritium, via three reaction channels [23–25].



The listed Q values are calculated from updated mass tables [26]. It was shown by Moak [23] that the dominant peak in the charged particle spectrum is due to the reaction channel (1) with a probability of 43 % for the <sup>3</sup>He impact energy range between 225 keV and 600 keV. The reaction channel (2) gives a continuous spectrum of protons due to three particles in the final state with a probability of 51 %, in the same <sup>3</sup>He energy range as stated above. The reaction (3) proceeds through the ground state of <sup>5</sup>He. In this case the proton spectrum will be discrete and the probability of such decay is 6 %. The total cross section for all three reactions was measured up to an energy of 800 keV and is exponentially increasing with energy reaching almost 0.2 barns at the maximum measured energy. There exist some measurement of cross section in reverse kinematics <sup>2</sup>H(<sup>4</sup>He,t)<sup>3</sup>He e.g. [27–29]. Schreider et al. [30] studied <sup>3</sup>H(<sup>3</sup>He, pα)n reaction in a kinematically complete experiment at

<sup>3</sup>He bombarding energies between 0.31 and 2.80 MeV in order to detect a possible resonant energy dependence of the spin singlet (T = 1) neutron-proton final state interaction. They have also discussed the strong isospin violations found in the two-body reaction <sup>3</sup>H(<sup>3</sup>He, d)<sup>4</sup>He at similar <sup>3</sup>He energies. According to Nocken et al. [25] there are broad maxima in the cross section at <sup>3</sup>He laboratory energies of 0.8 MeV and 2.4 MeV at angles of 10 and 90° in center-mass-system, respectively. Therefore, it is a question whether such a broad maximum exists also at scattering angle of 135° in laboratory system which is the typical angle for NRA analysis. Measuring the differential cross section for the nuclear reaction between <sup>3</sup>H and <sup>3</sup>He will enable us to detect both deuterium and tritium together with other impurities like carbon [31], oxygen [32], boron and beryllium [33] simultaneously by the use of <sup>3</sup>He ion beam. This is important for post-mortem analysis of samples and tiles exposed in fusion devices like JET and future fusion devices like ITER and DEMO.

For this purpose we want to develop a new NRA technique for tritium detection via the <sup>3</sup>H(<sup>3</sup>He,d)<sup>4</sup>He nuclear reaction. This is analogue to the detection of D via the <sup>2</sup>H(<sup>3</sup>He,p)<sup>4</sup>He reaction commonly used in plasma-facing material research. To this end we elaborate on the possibility to measure tritium with the <sup>3</sup>He probing beam simultaneously with D depth profiling, where proton energy spectra are typically measured with the <sup>3</sup>He beam energy range between 650 keV and 4.5 MeV. There is no differential cross section available for energies above 1.1 MeV <sup>3</sup>He energy. Kühn and Schlenk [24] measured the angular distribution of the differential cross section for both reaction channels up to a <sup>3</sup>He energy of 1087 keV. For the reaction (1) it was shown that the differential cross section has a maximum at 90° in the center-of-mass system. The cross section increases with impact energy and reaches a value of about 2.2 mb/sr at 1087 keV <sup>3</sup>He energy. Just for comparison the cross section for the reaction between <sup>3</sup>He and D has a maximum differential cross section of 60 mb/sr at the laboratory angle of 135°.

A stable tritiated sample with little outgassing has to be produced to allow the detection of reaction products and to make the evaluation of the cross section. For safety reasons, we limited the maximum T content in the sample to be below 1 GBq. This means that we can analyze samples with a maximum number of  $5 \times 10^{17}$  T atoms. Such tritiated sample was produced and the NRA signal was measured. Here we present the measured signal due to the nuclear reaction between <sup>3</sup>He ions and tritium in the energy range between 400 keV and 5.1 MeV at a scattering angle of 135°, an angle typically used for deuterium detection [14,34].

## Sample preparation

The samples for the method development were prepared at French Alternative Energies and Atomic Energy Commission (CEA), Saclay via hydrogen isotope gas loading at elevated temperatures. A test sample was first prepared by deuterium loading. Then, in order to confirm the success of the loading procedure, the sample was analyzed by the <sup>3</sup>He NRA method at Jožef Stefan Institute (JSI). Once successful, the sample was prepared on the same way as the deuterated sample only this time by pure tritium gas loading.

For the first test, we decided to choose tungsten (W) as the loading material. In the experiment we used two  $12 \times 15 \text{ mm}^2$  and 0.8 mm thick samples cut from a hot-rolled polycrystalline tungsten sheet with a purity of 99.997 wt%. Crystal grains were oriented parallel to the surface. Samples were mechanically and electrochemically polished to a mirror-like finish [35] and then heated for 2 min in ultra-high vacuum at 2000 K for re-crystallization. This procedure enlarges the grain size to 10 – 50 μm [36]. Then the samples were homogeneously irradiated by 20 MeV W ions to a fluence of  $7.8 \times 10^{17}$  atoms/m<sup>2</sup> at room temperature (300 K) [37], the so called self-damaging. Using a displacement energy of 90 eV and evaluating the “vacancy.txt” output of the “Ion Distribution and Quick Calculation of Damage” calculation option of the SRIM 2008.04 code [38] we calculated the creation of a displacement-damage zone

extending down to 2.3  $\mu\text{m}$  with a peak damage level of 0.23 displacements per atom (dpa) at a depth of 1.35  $\mu\text{m}$  [37]. In such a W matrix, hydrogen isotopes are strongly bound to defects created by high energy W ion irradiation [39] and little outgassing is expected. The exposure procedure was first benchmarked by 1 bar  $\text{D}_2$  gas loading of the sample at 723 K for 2 h, where the whole sample is exposed to gas but due to low solubility of tungsten the deuterium retention will be dominated by trapping in the irradiated layer. The same procedure was previously applied on similar samples [40] and showed homogeneous D depth profiles with a concentration of 0.33 at. % in the damaged area. The D depth profile on our  $\text{D}_2$  loaded W sample within 7  $\mu\text{m}$  depth (as a simulation for T) was measured by NRA and results will be presented in the results section. By analogy with deuterium experimental results, we considered that pre-irradiated W samples and gas loaded with  $\text{T}_2$  would strongly trap T down to 2.3  $\mu\text{m}$ . The sample for tritium exposure was first cut in half and then exposed to tritium gas at the same exposure conditions as deuterium: 723 K at 1 bar  $\text{T}_2$  for 2 h, with isotopic purity of 99 %. Then one half of the sample was analysed for its total activity using liquid scintillation technique at CEA. The second half of the sample was used for ion beam analysis.

For NRA background signal reference, we have used a polished polycrystalline tungsten sample prepared on the same way as the samples above only without W ion irradiation and not exposed to  $\text{D}_2$  or  $\text{T}_2$  gas at CEA, Saclay.

## Experiment

### Liquid scintillation assisted by electrochemical dissolution

Liquid scintillation counting technique is widely used to measure the total amount of T in a liquid. By mixing the active material with a liquid scintillator and counting the resultant photon emissions, the activity of the original material and so the T content can be determined with a very good efficiency and sensitivity (a value of 1 Bq/mL is easily achievable corresponding to  $\sim 5 \times 10^8$  T atoms per sample).

A different pathway had to be followed to evaluate the T inventory in a solid sample by LSC. First, full dissolution of the solid sample through an aggressive medium has to be undertaken. But this technique is time consuming and produces new radioactive wastes. However, LSC can also be used with a pyrolyzer coupled to the output of a bubbling system to evaluate the amount of tritiated species (HT and HTO) that can desorb from a solid sample when heated in a dedicated oven. This technique is similar to TDS except that in the LSC case, the experiment is not undertaken in vacuum. A controlled gas flow circulates in contact with the sample, from which HTO and HT desorb. The analysis of the desorption of HT and HTO from a tritiated solid sample can proceed by varying the type of gas flow and temperature. In any experiment, after reaching the highest available temperature, a full dissolution of the sample is undertaken in order to ensure that all T is released. The first test measurement showed a slow process of pyrolysis for the W sample. For this reason, a new procedure was applied where samples were electro-polished. The dedicated set-up is a derivative from the full dissolution technique using less aggressive media. The system is coupled to a bubbler as used for the pyrolyser. Thus, the total activity release during the dissolution is measured from the electrolyte solution and from the bubbler. The system will be described in detail in a separate paper. We need to take note that this technique is destructive and gives no information on the retention profiles which is an essential parameter for in situ tritium inventory. Values of T content of the investigated solid material are provided in Bq/g.

### Ion beam analysis set-up

After the exposure to the  $\text{D}_2$  gas the W sample was analysed by NRA utilizing a  $^3\text{He}$  ion beam and the  $\text{D}(^3\text{He},\text{p})^4\text{He}$  nuclear reaction [12] in the in situ ion beam analysis (INSIBA) chamber [4,41,42]. The

experimental set-up is schematically shown in Fig. 1. The ion beam impacts perpendicularly to the sample surface. Particles produced in the nuclear reaction are detected by a thick silicon detector (called NRA detector) with a depletion thickness of 1.5 mm. It is positioned at an angle of  $135^\circ$  with respect to the incoming probing beam. The detector has a circular aperture with a diameter of 19.54 mm and is positioned 104 mm from the target. The geometrical solid angle of the detector is 26.69 msr. In order to stop the backscattered  $^3\text{He}$  beam, a 24  $\mu\text{m}$  thick Al absorber foil was placed in front of the NRA detector. The size of the beam spot on the target was defined by two consecutive circular orifices of 2 mm in diameter, positioned in the beam line. We also employed a detector to detect backscattered particles, the so-called RBS detector. The depletion thickness of this detector is 300  $\mu\text{m}$ . It is located 135 mm from the target at an angle of  $165^\circ$  with respect to the incoming beam covering a geometrical solid angle of 0.7 msr. The backscattered signal from  $^3\text{He}$  ion beam on W in the RBS detector served us to measure the absolute dose of  $^3\text{He}$  particles impacting on the sample and to minimize possible errors of the beam current measurement. The beam current was measured by the ion mesh charge collector with 77.4% geometrical transmission [43] and a bias of 600 V.

To measure the protons and deuterons from the nuclear reactions on deuterated and tritiated samples, respectively, we used a sample holder which can hold 20 samples for ion beam analysis. To make the energy calibration of the NRA detector we employed two deuterium-containing targets. They consist of dense, plasma-deposited amorphous deuterated thin hydrocarbon (a-C:D) film of two different thicknesses grown on single crystalline silicon (100) substrates. The thickness of the film was measured with tactile profilometry to be 50 nm in one case and 275 nm in the other. The D/(C + D) ratio was assumed to be about 0.34 consistent with a-C:H films deposited under the same conditions [44]. In the NRA spectrum measured on the a-C:D sample the dominant signal is due to energetic protons from the  $\text{D}(^3\text{He},\text{p})^4\text{He}$ ,  $^{12}\text{C}(^3\text{He},\text{p}_{0,1,2})^{14}\text{N}$  and  $^{28}\text{Si}(^3\text{He},\text{p}_{0,1,2,3,4})^{30}\text{P}$  reactions that reach the detector. The energy calibration of the RBS spectra was performed by measuring multiple mono-elemental solid targets.

To obtain a D depth profile [15] on the deuterated W sample, the proton signal from the nuclear reaction  $\text{D}(^3\text{He},\text{p})^4\text{He}$  was measured at six  $^3\text{He}$  energies (730, 1040, 1550, 2570, 3390 and 4320 keV). For one D depth profile, the proton energy spectra are first checked for energy calibration by SIMNRA, version 7.02 [45] for all six measured energies. These six proton energy spectra are then all input into NRADC program [46] that outputs the most probable D depth profile.

To develop the NRA method via  $^3\text{He}$  beam that would enable the detection of T trapped in materials over depths of a few  $\mu\text{m}$ , the cross section of the nuclear reaction needs to be measured. The analysis

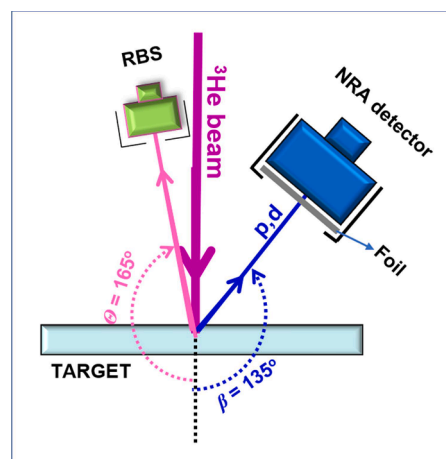


Fig. 1. A schematic picture of the setup for ion beam measurements with the NRA detector and the RBS detector in their positions.

method relies on the detection of products (d and p) from the nuclear reaction between  $^3\text{He}$  and T. For this purpose, we performed measurements with  $^3\text{He}$  beam with energies from 0.7 MeV to 5.1 MeV on self-damaged W sample loaded by  $\text{T}_2$  gas. At energies above 2.5 MeV doubly charged  $^3\text{He}$  ions were used to reach the higher energies. The applied analysing dose was  $34.2 \mu\text{C}$  for energies  $\leq 2500 \text{ keV}$  and  $17.1 \mu\text{C}$  for energies  $> 2500 \text{ keV}$ .

The rotary voltmeter that measures the accelerator terminal voltage and with that the beam energy was calibrated with two resonant nuclear reactions  $^{19}\text{F}(p, \alpha\gamma)$  and  $^{27}\text{Al}(p, \gamma)$ . With the  $\text{CaF}_2$  target three resonances at proton energies 340, 872 and 1371 keV were studied and with the Al target, the resonance at 992 keV proton energy was used for calibration [47,48]. The final error of the calibrated ion beam absolute energy is below 10 keV.

## Results

The deuterium depth profile as obtained on the self-damaged W sample exposed to  $\text{D}_2$  gas at 723 K is shown in Fig. 2. We can observe near the surface a D concentration of  $0.35 \pm 0.04 \text{ at. \%}$  which at a depth of 230 nm decreases to  $0.25 \pm 0.01 \text{ at. \%}$  and is then constant down to 2  $\mu\text{m}$ . Below this depth the D concentration decreases stepwise to  $2 \times 10^{-2} \text{ at. \%}$  and  $5 \times 10^{-4} \text{ at. \%}$  deeper in the W sample. The increased D retention down to 2  $\mu\text{m}$  is due to D trapping at the defects created by W ion irradiation (the self-damaged zone) whereas beyond this zone, D is trapped to intrinsic crystal defects existing before W ion irradiation [49,40]. The total deuterium amount as obtained by NRA on this sample measured down to 7  $\mu\text{m}$  was  $(35 \pm 3) \times 10^{15} \text{ D/cm}^2$ . The measured D concentration in self-damaged zone is in agreement with the measurements by Alimov et al. [40], where they obtained at similar exposure conditions a D concentration of 0.33 at. %. We have observed also small contamination on the surface by C and O obtaining about  $18 \times 10^{15} \text{ atoms/cm}^2$  and  $15 \times 10^{15} \text{ atoms/cm}^2$ , respectively. Since we have obtained a good agreement with the literature we proceeded with the exposure of W self-damaged sample to  $\text{T}_2$  gas at the same exposure conditions as for  $\text{D}_2$ .

For the tritiated W sample we measured the total activity on one half of the sample with dimensions  $7 \times 12 \text{ mm}^2$  after the  $\text{T}_2$  gas loading. After the complete dissolution of the sample the measured total activity of the sample was  $159 \pm 24 \text{ MBq}$ . If one transforms this activity into particles per  $\text{cm}^2$ , which is the quantity we get by NRA, we obtain  $(138 \pm 20) \times 10^{15} \text{ T/cm}^2$ , considering only the W irradiated area on half of the sample that is  $0.65 \text{ cm}^2$ . For this calculation we assumed that 1 g of tritium has the activity of

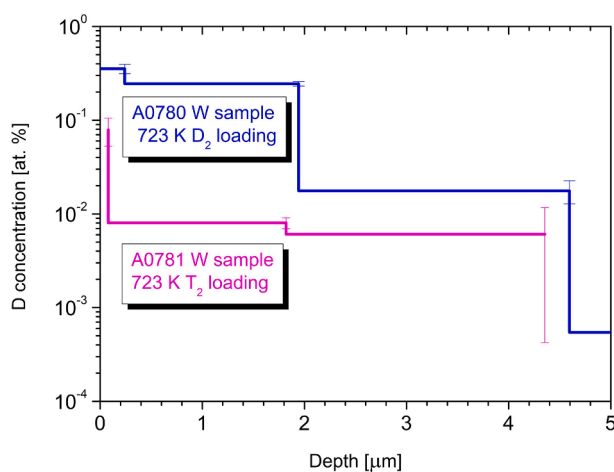


Fig. 2. The D depth profile as obtained on the W self-damaged samples exposed to  $\text{D}_2$  gas at 723 K, shown in blue line, and to  $\text{T}_2$  gas at 723 K, shown in magenta colour. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

355 TBq. We could not measure the total amount of tritium in the sample prepared for NRA measurement by any other non-destructive method, since the amount of tritium is too low and too deep in the sample to be detectable for instance by ERDA and unfortunately the deuterium NRA is not allowed in our laboratory. For this reason, we assumed that the activity of this sample is the same as for the sample analysed by liquid scintillation technique and that the depth profile should be similar to the one measured on the deuterated sample, since both were self-damaged by 20 MeV W ions. However, when we compare the total amount of tritium as measured by liquid scintillation technique to the total amount of deuterium measured by NRA in the deuterated sample we get  $3.9 \pm 1$  times more tritium in the  $\text{T}_2$  exposed sample than we would expect from the NRA measurement on the sample exposed to  $\text{D}_2$ . Here we have to consider that the back side of the sample was not analysed by NRA and that there is a nonzero D concentration of the order of  $1 \times 10^{-3} \text{ at. \%}$  in the bulk of the sample. This bulk retention adds additional  $(50 \pm 20) \times 10^{15} \text{ T/cm}^2$  considering that the sample is 0.8 cm thick. This all-together sums up to  $(85 \pm 23) \times 10^{15} \text{ T/cm}^2$ , which means we are missing  $53 \times 10^{15} \text{ T/cm}^2$  compared to the LSC activity. With the added deep bulk retention to the total T amount based on the deuterated sample measured by NRA we obtain the ratio between total T amount as measured by LSC and T amount based on deuterium NRA measurements to be  $1.6 \pm 0.7$  times. Moreover, as can be seen in Fig. 3 there is some carbon and oxygen contamination on the surface which can accumulate tritium on the back side and adds to the total tritium amount.

A spectrum obtained on the tritiated self-damaged W sample at 2.5 MeV  $^3\text{He}$  energy is shown in Fig. 3. There we can observe a broad peak at the energy of about 13 MeV which is caused by the deuterium present in the sample. The peaks at lower energies are due to carbon and oxygen contamination, as marked in the figure. The amount of C and O contamination is about  $10 \times 10^{15} \text{ atoms/cm}^2$  and  $50 \times 10^{15} \text{ atoms/cm}^2$ , respectively, which is similar to the contamination of deuterated samples. The next highest broad peak at 7 MeV is from the nuclear reaction between  $^3\text{He}$  and  $^3\text{H}$ . When the spectra were recorded on the deuterated sample, there were very few counts at 7 MeV energy and the integral of the peak due to deuterium in the sample was 14 times higher as compared to the one measured in the tritium case. The D depth profile obtained on the tritiated sample after the deconvolution procedure of the signal at several  $^3\text{He}$  energies by NRADC [46] is shown in Fig. 2. One can see that we obtained more than an order of magnitude lower D concentration on the  $\text{T}_2$  loaded W sample compared to the  $\text{D}_2$  loaded sample. This contamination of the sample by deuterium could take place during the tritium loading. It could be also a leftover of previous history of this sample. Namely, before  $\text{T}_2$  loading the sample was exposed to D atoms at 450 K where shallow penetration of D was observed [50]. This

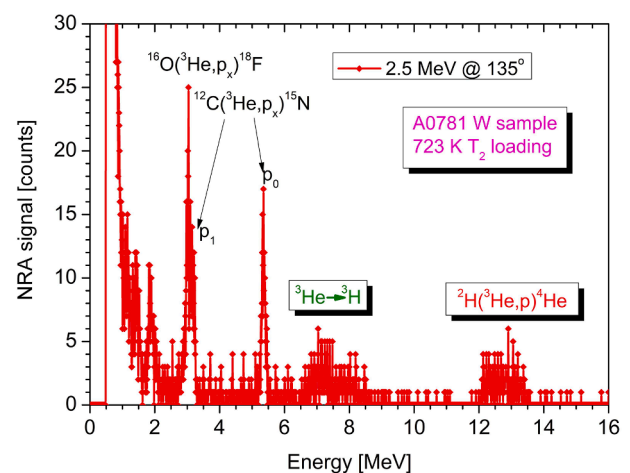


Fig. 3. Signal measured by the NRA detector at 2.5 MeV  $^3\text{He}$  energy. One can recognize peaks from protons due to the  $^2\text{H}(^3\text{He}, p)^4\text{He}$ ,  $^{12}\text{C}(^3\text{He}, p)^{15}\text{N}$  and  $^{16}\text{O}(^3\text{He}, p)^{18}\text{F}$  reactions and from deuterium due to the  $^3\text{H}(^3\text{He}, d)^4\text{He}$  reaction.

pre-exposure should not affect the experiments with tritium except for this little deuterium amount in the bulk. Naturally there is no D inside such samples.

The numbers of counts divided by the beam charge due to nuclear reactions between  $^3\text{He}$  and  $^3\text{H}$  (presumably from channels (1) and (3)) as measured on the tritiated W sample in the energy range between 6.50 MeV and 9.75 MeV are shown in Fig. 4 as a function of the  $^3\text{He}$  beam energy. At  $^3\text{He}$  beam energies above 3.4 MeV we observed a strong background signal appearing in this energy range and for this reason we measured the background signal on a W background reference sample without T, which is also shown in Fig. 4. The surface contamination of the reference sample by C and O was  $10 \times 10^{15}$  atoms/cm<sup>2</sup> and  $20 \times 10^{15}$  atoms/cm<sup>2</sup>, respectively. The origin of this background might be due to other nuclear reactions between  $^3\text{He}$  and W or  $^3\text{He}$  with  $^{13}\text{C}$  or  $^{14}\text{N}$ . We can observe that the signal attributed to nuclear reaction between T and  $^3\text{He}$  subtracted by the background signal is steadily increasing with the impact energy and is showing a small peak at 3.4 MeV. Above this energy it stays almost constant at a level of 50 % of the maximum peak signal. We need to note that at  $^3\text{He}$  energies above 5.1 MeV the protons from the carbon contamination move into the tritium signal region and for this purpose tritium identification gets complicated at these energies except in cases when there is no carbon contamination.

To obtain the shape of the differential cross-section we first need to

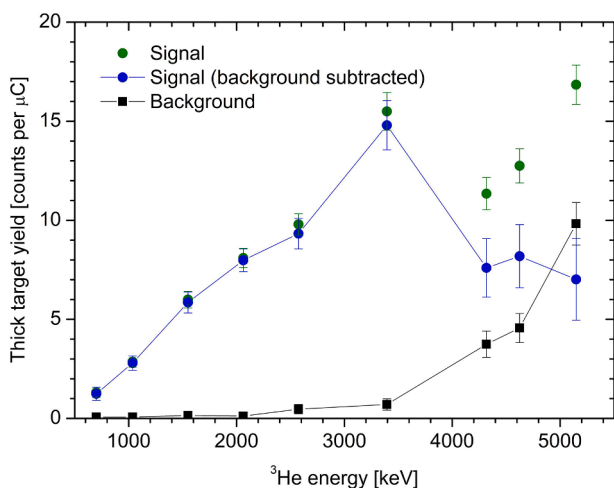


Fig. 4. Numbers of counts divided by beam charge in microcoulomb ( $\mu\text{C}$ ) in the energy range between 6.5 MeV and 9.75 MeV on the tritiated W sample (signal-green dots), on the empty W sample marked as background (black squares) and signal subtracted by the background signal (blue dots). Connecting lines are only to guide the eye. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

assume the distribution of tritium in the sample. As our tritium target is considered as a thick sample the transformation from the measured signal to the cross-section is not straight forward since stopping of the  $^3\text{He}$  beam and the product particles in the target layer needs to be considered. Our initial assumption was that the distribution of tritium is the same as was measured in the W sample loaded with  $\text{D}_2$ . In order to calculate the cross section from the measured data we could apply the method for thick targets as described in [31]. In Fig. 5 the spectra are shown for three different  $^3\text{He}$  beam energies of 1.5 MeV, 2.5 MeV and 3.4 MeV where high integral signal was measured. For  $^3\text{He}$  energies below 3.4 MeV we see a clear single peak whereas for 3.4 MeV energy there seem to be two peaks or one could say also homogeneous signal in the whole energy range. From the kinematics the peak measured around 7 MeV at the  $^3\text{He}$  impact energies of 1.5 and 2.5 MeV is presumably due to deuterons from channel (1). However, there could be in the spectra a non-negligible contribution from the protons from channel (3) which could be the signal around 8 MeV. One cannot straight forwardly resolve the signal due to deuterons and protons, coming from channels 1 or 3, respectively. For this reason, we think that the second part of the signal at 3.4 MeV  $^3\text{He}$  impact energy is no longer due to channel (1) but could be from channel (3) as indicated in the figure. Moreover, there is background signal that starts to increase at 3.4 MeV. Due to all these ambiguities and the very small measured signal at individual measured particle energies (Fig. 5) the quantification of the cross section was not possible. In order to make proper quantification more pronounced and well separated peaks should be obtained, which could be done with a thinner target with high tritium amount e.g. [23].

Since we cannot obtain the cross section from our measurements we have extracted the cross section from Kühn and Schlenk [24] and Nocken et al. [25], as shown in Fig. 6. The cross-section data are available only in the low energy region up to 1.1 MeV where our NRA signal is rather small. Nocken et al. [25] provided angular distribution measurements only in arbitrary units for several impact  $^3\text{He}$  energies (Fig. 2 in [25]) and scaled his data to the literature data for scattering angles of 10 and 90° (Fig. 3 in [25]). To obtain the cross-section data at other angles we have, based on the cross-section data for 90° angle, scaled the angular distribution data for each impact  $^3\text{He}$  energy. The obtained scaling factors for energies 291, 369, 600 and 800 keV  $^3\text{He}$  energies were 0.44, 0.66, 1.29 and 1.83, respectively. With these numbers we have multiplied the angular distribution data for each energy and obtained the cross-section values also at other angles. In Fig. 6 the cross-section data for angles between 133° and 142° are shown, which are close to our 135°. One can see that the agreement between Kühn and Nocken is rather good.

Moreover, based on Nocken et al. [25] there should be broad maxima in the cross section at energies of 0.8 MeV and 2.4 MeV in laboratory system at angles of 10° and 90° in center-of-mass system (CMS), respectively. From the present measurements at the angle of 135°, Fig. 4,

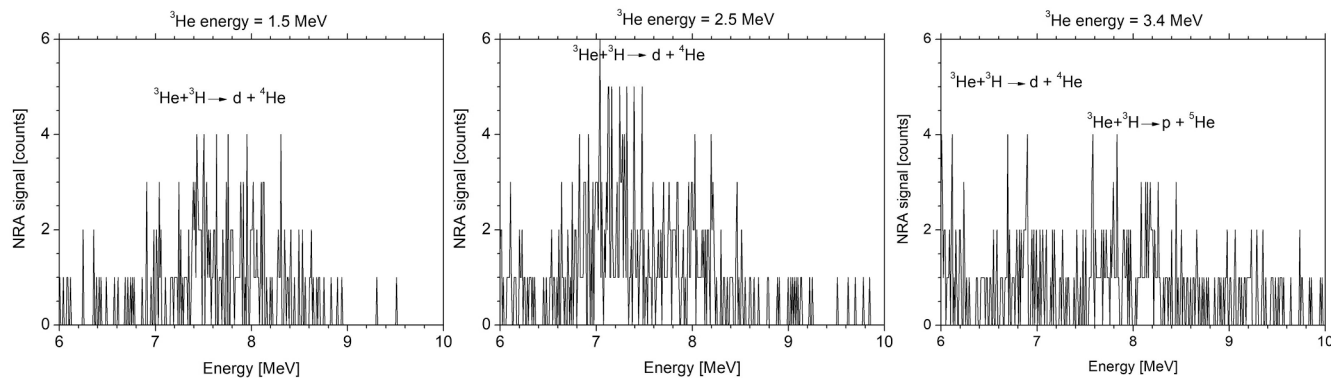


Fig. 5. Experimental spectra measured at different primary  $^3\text{He}$  ion energy. Left figure shows the spectrum measured at 1.5 MeV, middle at 2.5 MeV and the right one at 3.4 MeV  $^3\text{He}$  beam energy.

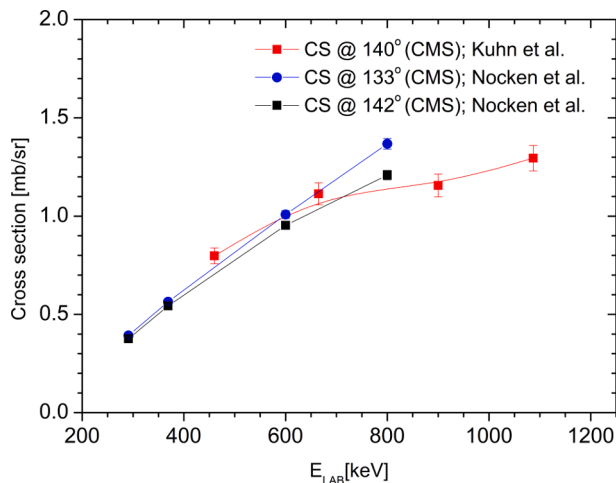


Fig. 6. Differential cross sections measured by Kühn and Schlenk [24] at 140° in the center-of-mass system (CMS) and Nocken et al. [25] at 133° and 142° in the CMS are shown. The angle of 140° in the center-of-mass system equals 135° in the laboratory system at 1 MeV  $^3\text{He}$  energy.

one could say that there is an increase in signal for energies above 1 MeV. This could indicate that there is a maximum but it is very weak in intensity.

## Discussion and conclusion

W samples that were irradiated by MeV W ions to create traps for hydrogen isotopes were exposed to  $\text{D}_2$  and  $\text{T}_2$  gas. With this we have created stable deuterium and tritium samples for nuclear reaction analysis using  $^3\text{He}$  beams. When measuring the NRA spectra on the tritiated sample we observed a signal which we attributed to nuclear reaction products due to the  $^3\text{He}$  and T nuclear reaction. The NRA signal increased with the  $^3\text{He}$  beam energy. From the measured spectra we tried to obtain a differential cross section, however, the procedure is not straightforward since the target is thick and the probing beam loses all its energy in the target. Moreover, one can speculate that the measured signal has contributions from deuterium and protons coming from channels (1) and (3), respectively. In the case of protons, we would expect the peak at 8 MeV to move with  $^3\text{He}$  beam energy. This was not the case in our spectra and for this reason we believe that the majority of the signal is coming from channel (1). Moreover, the ground state of  $^5\text{He}$  has a width of 0.6 MeV [51] and this should be reflected in the width of the proton peak in the spectrum. Indications for this could be seen in the spectrum measured at 3.4 MeV (Fig. 5) and higher beam energies (not shown). To prove or disprove this we would need to make a sample with a thin tritiated layer where clear peaks coming from one or the other channel should be observed. This is however out of the scope of the present work. The main aim of this work is to show that there is measurable signal due to nuclear reaction between tritium and  $^3\text{He}$  beam and this could be a new detection method for tritium. At this point we need to stress that the  $^3\text{He}$  probing beam is one of the most often used analyzing beams in plasma-facing material community. It is typically used to determine deuterium depth profile in solid targets and other important analyzed elements in fusion like C, B, Be and O. However, based on these results and the obtained counting statistics of the signal we can already now say that the ion beam method based on nuclear reaction with  $^3\text{He}$  will not outperform the very sensitive methods like AMS, FCM and LSC with chemical etching that can detect tritium amount of the order of  $10^{12}$  atoms/cm $^2$  [21]. We still believe that this method could be useful as a non-destructive analysis method on solid samples. One of the goals of this work was also to review the existing literature on the reaction between tritium and  $^3\text{He}$  and we have shown that work was already done on this subject in the 50's, 60's and 70's and

now it is time that it comes to its renaissance.

## CRediT authorship contribution statement

**S. Markelj:** Conceptualization, Methodology, Writing - original draft, Investigation, Writing - review & editing. **M. Payet:** Investigation, Writing - review & editing. **E. Bernard:** Investigation, Writing - review & editing. **M. Lipoglavšek:** Conceptualization, Investigation, Writing - review & editing. **M. Kelemen:** Investigation, Writing - review & editing. **A. Cvetinović:** Investigation, Writing - review & editing. **C. Grisolia:** Resources, Conceptualization, Writing - review & editing. **P. Pelicon:** Resources.

## 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.

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