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Review of the different techniques to analyse tritium

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Summary

The document describes a review of the different techniques available to analyze tritium, commercially developed and/or published. Tritium is a radionuclide being very difficult to analyze and therefore lots of different techniques can be encountered in the literature. R&D is still required to improve methods to analyze tritium. This document corresponds to the deliverable D2.1 of the TRANSAT project. Autoradiography, Ion beam technology and LIBS will be developed during the TRANSAT project.

Approval

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Abbreviations

WP	Work package
TRL	Technology Readiness Level
LSC	Liquid Scintillation Counting
LIBS	Laser Induced Breakdown Spectroscopy
AMS	Accelerated Mass Spectrometry
NRA	Nuclear Reaction Analysis
ERDA	Elastic Recoil Detection Analysis
CRDS	Cavity Ring Down Spectroscopy
D	Deuterium
T	Tritium
PFC	Plasma Facing Components
TRAMPEL	Tritium Activity Measurements with Photomultiplier in Liquids
BIXS	Beta Induced X-ray Spectroscopy
TRL	Technology Readiness Level
CANDU	CANada Deuterium Uranium
LIBS	Laser Induced Breakdown Spectroscopy
AMS	Accelerator Mass Spectrometry

Summary

The following document describes a review of the different techniques available to analyze tritium, commercially developed and/or published. It is very difficult to analyze Tritium and thus there are lots of different techniques can be encountered in the literature. R&D is still required to improve methods to analyze tritium. This document corresponds to the deliverable D2.1 of the TRANSAT project.



1 Introduction

This deliverable concerns the WP2 “Tritium Inventory management and modelling” and particularly the Task 2.1 entitled “Online and in material tritium inventory measurement development”.

Tritium (also noted below T or H-3) is a radionuclide very difficult to analyse mainly because of its energy, type of emission (β^-) and its chemical and physical behaviour. In all kinds of developments concerning the tritium (dismantling processes, fusion development, environmental control), it is essential to characterize the radionuclide with high accuracy and minimum of uncertainty. In the different Work Packages of the TRANSAT project namely WP1 (Assessment and proposal for developments of barriers against tritium permeation and the treatment of the operational tritiated gases), WP2 (Tritium inventory management and modelling), WP3 (Impact of tritiated products on environment and human health) and WP4 (Tritium issues in waste processing and decommissioning), it will be important to characterize tritium. As it will be described in the document, there exists several characterisation techniques to measure tritium, but different ways for sample preparation before measurement must be considered. The methods for sample preparation can deeply differ if tritium is the single radionuclide present in a matrix or if tritium must be investigated in a mix of radionuclides. In different applications, tritium must be measured at trace amounts (Bq or less) or at important levels of activity (GBq or more).

For physical techniques, in principle, any methods, used for hydrogen measurements, can be used for tritium measurements. In addition, T can also be readily detected by its disintegration (β decay emitting an electron) or a radiation measurement.

In the following chapters, different techniques will be described to analyze tritium, some of them are commercial but others possess a low TRL and can only be found in research laboratories.

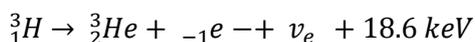
The report begins by presenting a brief description of tritium. The following chapter presents all the available detection techniques for tritium, present in a liquid, with their characteristics. The next two chapters will focus respectively on techniques to analyze tritium contained in gas and solids. Then, the last chapter completes the report with techniques with low TRL as described in different published papers.

2 Generalities about tritium

2.1 Tritium radionuclide

In the short time, since the radioactivity of tritium was discovered by Rutherford (1934) and identified by Alvarez and Carnog (1939), this radionuclide has become important in many scientific and industrial fields [NCRP, 1976].

In order to discuss the possible ways to detect tritium, one has to be familiar with the characteristics and nature of tritium. Tritium is a radioactive isotope of hydrogen with a nucleus made up of a proton and two neutrons. As a general characteristic, Tritium is a beta emitter that undergoes radioactive decay to form stable helium-3 atom, a beta particle and a neutrino.



Tritium produces an electron of average energy 5.7 keV. Beta particle from Tritium has one of the lowest energy beta particles with a maximum energy of emitted beta particle at 18.6 keV [Tanabe, 2017]. Due to this low energy, the beta particles quickly lose their energy and cannot travel far from their origin. Thus, tritium radiation has low penetration capability with maximal range of tritium beta particle in air at around 6 mm [Tanabe, 2017]. Maximal range is defined as the maximum distance reachable by the particle as it progressively loses energy travelling through matter till the particle kinetic energy is zero. With such a low maximal range, it will be very difficult to remotely characterized tritium.

Tritium with a half-life of 12.312 (25) years [LNHB] is considered as short lived radionuclide. However, tritium is still a key concern for decommissioning and monitoring because it is generally volatile and environmental release can easily occur.



Tritium can be produced naturally or in a man-made nuclear process. Naturally, tritium is produced when cosmic rays interact with atmospheric nitrogen. Fast moving neutron with energy more than 4 MeV reacts with nitrogen to produce carbon-12 and tritium.

Anthropogenic tritium is mainly from nuclear reactors especially CANDU NPP (nuclear fission reactors cooled with heavy water). The experimental reactors like JET, JT60 and TFTR currently use the tritium produced in CANDUs as fuel. Tritium is produced from nuclear reactions such as fusion, fission or activation process.

Tritium specific activity is $358 \text{ TBq}\cdot\text{g}^{-1}$ [French authority, 2010] or $3.58 \cdot 10^{14} \text{ Bq/g}$.

Chemically, Tritium behaves like hydrogen and will readily form tritium gas or replace hydrogen in part of an organic molecule. HTO, T₂O or tritium organic molecule may be formed which can be easily absorbed into the human body. Thus, tritium is a highly hazardous material due to its permeability in the human body. However with its low penetration capability tritium is not harmful unless ingested.

With low range, quite long half-life and chemical property similar to hydrogen, tritium will be hard to detect while being able to permeate through many materials. Tritium has a high coefficient of diffusion. It readily diffuses through porous substances such as rubber and can also diffuse through metals. [DOE, 2008]

One of the main radionuclide produced in large quantities in fusion reactor is tritium. Tritium has not been a major topic in the past fission reactor (except CANDU) as it is produced in small quantities and is difficult to detect. However in fusion reactors [ITER fusion reactor, 2017], an estimated 300 g of tritium is required for production of 800 MW of electricity per day. As such, there will be a plethora of tritium materials and wastes produced from the operation of fusion reactor. It will be crucial to develop proper tritium characterization and monitoring tools for future decommissioning and waste management of the fusion reactors. Hence, characterization or monitoring tools, specifically for tritium detection, techniques will be reviewed in this report.

2.2 Main approaches for characterizations

Tritium beta particle has much lower range (6 mm in air) than other radionuclides. This results in difficulty of detection by “conventional” radioactivity detector. Hence alternative detection methods that overcome the problem of short range of tritium beta particle prove to be very interesting but are rather scarce.

Moreover, detection of tritium is complicated by the fact that detection method differs greatly depending on the phase of the tritium and there is no single detector that could accomplish universal detection of tritium regardless of phase. Tritium can exist either as a gas, liquid or trapped within a solid. Different techniques that will be described below are only applicable to certain phases.

For environmental measurement of tritium, there exists another well-known classification. But for tritium inventory this type of classification goes far beyond the goal of this document. As a brief explanation [Baglan, 2010], the measurement of tritium in its various forms (mainly gas (HT), water (HTO) or solid (hydrides)), is an important key step for evaluating health and environmental risks and finally, dosimetry assessment. In vegetable or animal samples, tritium is often associated with the free water fraction, but may be included in the organic form as organically bound tritium (OBT). In this case, two forms exist: (i) a fraction called exchangeable or labile (E-OBT), bound to oxygen and nitrogen atoms, and (ii) a so-called non-exchangeable fraction (NE-OBT) bound to carbon atoms. The notion of labile and non-labile for tritium analysis is very important for solid measurements.

Liquid Scintillation Counting (LSC) is the well-known and accurate technique to measure tritium in a liquid form but being ineffective for tritium in solid materials except with specific sample preparation (such as pyrolysis). Currently, there is no established non-destructive detection technique for tritium in solid materials but new techniques are currently developed.

Key characteristics such as objective, detection limit when available, destructive, phase, in situ measurement and accuracy will be taken into consideration when reviewing the tritium detection techniques. Different techniques will be described and some of them detect tritium with physical properties (mass spectrometry for example) and others with its radioactivity (example: LSC).

The problem to find an efficient characterization process is not new. As an example, in US, a document was already published in the mid-seventies describing different techniques to measure tritiated material [NCRP, 1976].

2.3 Different international regulations and patents

It is very difficult to quote all national and international regulations dedicated to the analysis of tritium. However most of regulations deal with the tritium analysis at very low level or for survey of tritium release in Nuclear Power Plants.

Lots of regulations concern the use of LSC (Liquid Scintillation Counting) to control the water quality (tritium in a liquid form) [ISO 13168, 2015]. When potential interferences can be encountered for tritium analysis a distillation procedure is applied [ISO 9698, 2015]. For analysis of labile tritium on a solid surface, the wipe technique followed by LSC is used [ISO 7503-2, 2017]. The wipe test depends strongly to the matrix and a conservative yield of 10% is generally used. But the removal factor is affected by varying the pressure applied during smearing, by the type of surface or smear, and by the form of the contamination [IAEA, 1970]. This value of 10% is also indicated in reference [JR Johnson, 1991]. Tritium is given in Bq/100 cm² (typical surface rubbed).

The analysis of different chemical forms of tritium was very recently published (national regulation in France) for environmental investigation [XP M60-824, 2016]. The pyrolysis technique to extract tritium and the measurement of He-3 coming from tritium by mass spectrometry are described in this document. He-3 measurement by mass spectrometry was also published to evaluate the degassing of a whole drum [NF M60-321, 2005]. This degassing technique is a non-destructive technique requiring no sampling preparation process and this could be of great interest for nuclear wastes management. The degassing technique can also be equipped by an ionisation chamber [NF M60-309, 2001] or equipped with container filled with water, where tritium can be trapped [NF M 60-327, 2008]. The measurement is obtained in this second system by liquid scintillation counting.

Tritium as a gas form can be trapped into bubbling system containing water [NF M60-312, 1999]. This system is of particular importance not for environmental measurement but for nuclear plant survey. All the calculations of potential release of tritium are well described in the regulations [NF M60-822-0, 2014; NF M60-822-1, 2011; NF M60-822-2, 2013]. As it will be highlighted in the following chapter the sampling process of tritium is very problematic. Because C-14 can also be found as gaseous form, the measurement of both radionuclides can be done at the same time. Figure 1 provides a scheme of a typical trapping system generally described in such regulations.

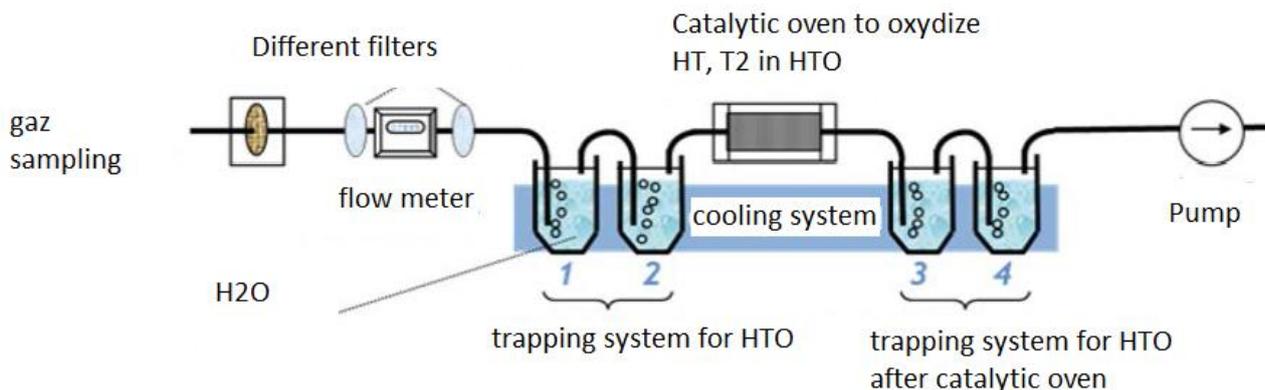


Figure 1: Trapping system for tritium in a gaseous form

Another regulation proposed different systems to extract tritium from aqueous liquids (by distillation) from organic liquids (oxygen bomb) and solids (pyrolyzer) that can be found in nuclear wastes [NF M60-325, 2005].

It appears clearly that the most common technique to measure tritium is by LSC but methods to collect tritium in solid, liquid and gas can dramatically vary. The problem to find efficient ways to sample radionuclides is one of the most important difficulty for the dismantlement of nuclear power plants. Non-destructive technique to extract tritium from concrete was proposed in a patent [JP



patent, 1991]. A concrete area is heated by a device and the extracted water that can potentially contain tritium is measured by LSC.

With the advent of decommissioning fission facilities and the developments of fusion devices (JET (UK), ITER (France), CFETR (China)), it is of great importance to develop relevant and new techniques to measure tritium inventory. As it will be shown below, the different characterization tools depend strongly on the chemical form of tritium. These tools are essential for determination of the inventory and ensuring safety in the operation.

3 Direct analysis of liquids containing tritium

This section describes in details the well-known and accurate method to measure tritium when this radionuclide is trapped in a liquid.

3.1 LSC Technique

The LSC (sometimes referenced as LSA: Liquid Scintillation Analyser) technique can be applicable for tritium contained in a liquid or coming from the use of smear survey. Smears can be dissolved in a liquid and after digestion the measurement is possible by LSC.

Due to the need to measure the removable tritium on surfaces and in the body water of workers, almost all tritium facilities are equipped with or have access to a liquid scintillation counter.

In order to utilize scintillation technique, the sample will have to be mixed or placed with a scintillator. Radioactive decay within the sample will produce ionizing radiation that interacts with the scintillator. Then, the most commonly used scintillation technique in tritium detection is Liquid Scintillation Counting (LSC) analysis [Leo, 1994].

In liquid scintillation counting (LSC) analysis, a liquid scintillator is added into liquid sample [Pujol, 1999]. The liquid scintillator usually comprises of solvent and phosphor. The Solvent is responsible for absorption of energy from the radioactive particles (the electron emitted by tritium) and transmission of energy to phosphor. The phosphor will convert the energy to photons. The released photons will be recorded by a light sensor (generally a photomultiplier tube). The quantity of tritium is measured by counting the light flashes that occur in the scintillation cocktail as the tritium decays. Liquid scintillation analysis is mostly used for samples that contain only a single isotope, in our case - tritium, and the technique is not considered a spectroscopic but a counting method.

Liquid scintillation counting analysis is widely used in many areas and has been commonly used in tritium detection. More generally, this technique has been developed to test even gas or solid sample. These could be done through proper treatment of the tritium in these phases. For gas sample especially those in the environment, tritium can be condensed or bubbled into liquid water. This liquid sample can then be added with scintillator for liquid scintillator counting analysis.

For solid measurement, a known weight of a material (example of smear) is dissolved to produce a liquid and then the liquid is sampled and measured in the scintillation counter. This latest technique is generally difficult because solid cannot be dissolved (see pyrolyser part below).

For liquid measurement, a sample of the liquid to be measured is placed in the liquid scintillation cocktail and measured. The tritium concentration of the liquid is calculated in Bq/mL or Bq/L generally.

3.2 Different LSC commercial systems

The aim of this section is not to promote a particular commercial system but to provide an overview of the different providers of LSC counters. All the paragraphs will not be constructed as a complete description of all the LSC models but as a global information of all the different systems.

3.2.1 Perkin Elmer system

There exist different types of Perkin Elmer systems and these systems are very common in lots of laboratories that need to analyse beta emitters in particularly tritium. One of the most common

systems that can be provided by Perkin Elmer is the Tricarb (see Figure below). This system possesses generally an internal source to evaluate the quenching correction in order to improve the measurement accuracy.

Quenching is always present in water samples and the degree of quenching can vary from one sample to another even within the same batch. This means that quench correction should be carried out for each sample in order to determine the activity so that comparisons can be made between samples and other batches. There are mainly four different types of quenching that may occur in the mixture: absorption or physical quenching, chemical quenching, photon or color quenching and solvent dilution quenching [Varlam, 2001].



Figure 2: Liquid Scintillation Counter Tri-Carb A 4910.

This system is generally sufficient for nuclear waste investigation (detection limit around 0.1 Bq/L). For very low level of tritium and thus for environmental measurement another system Quantulus GCT 6220 with a very low background can be used.

3.2.2 *Hidex system*

This Finnish manufacturer produces two models of counters: 300 SL and 600 SL. These two counters work with the technique known as TDCR (Triple to Double Coincidence Ratio) which is an absolute counting method for obtaining counting efficiency of the samples without external or internal standard sources. Unlike external standard methods, TDCR is a universal method applicable for both chemical and color quenching, for aqueous and organic samples and for different cocktails and range of isotopes.



Figure 3: Hidex 300 SL

Hidex proposes also a transportable LSC system (Triathler) which is a very efficient in situ system but containing a single photomultiplier tube.

3.2.3 SDEC system

Another transportable LSC system is proposed by SDEC Company. Two photomultiplier tubes equip this system which can be an advantage to improve coincidence.



Figure 4: Portable system DPM 7001 SDCE

3.2.4 Hitachi system

A similar system as the Perkin Elmer Tricarb is proposed by Hitachi. As for the Perkin Elmer systems, it exists different models for low (around 0.1 Bq/mL) and ultra-low (0.4 Bq/L) measurement of tritium. Quenching standardization is applied with a Ba-133 internal source.



Figure 5: AccuFlex LSC-8000 (model for low level tritium)

4 Direct analysis of gas containing tritium

Generally, this type of device is used as a survey. Tritium in a gas is generally in the form of HT, HTO and CH₃T [Connan, 2017]. But the following systems are not able to separate all these kinds of tritium forms.

The term generally used for this measurement is “outgassing”. Tritium outgassing can be expected from any material that has been exposed to tritium gas. However these techniques are important for tritium in a gas form survey but problematic if tritium is for example fixed in a metal as a tritides [DOE, 2008].

4.1 Ionization chambers

Among various radiation measurements, gas ionization detectors such as an ionization chamber and a proportional counter are particularly beneficial to detect and to quantify tritium in gas phase. This

system cannot be used to measure tritium in solid or liquid phase. Ionization chambers are also not specific for tritium analysis. They can be used also for gamma, X rays. The ionization chamber detects charge (electrons and ions) induced by an ionizing radiation.

The ionization chamber is one of the simplest devices for radioactivity measurements. A typical ionization chamber consists of a detection chamber and electrodes in it. The following Figure gives a scheme of this chamber [Tetsuo Tanabe, 2017].

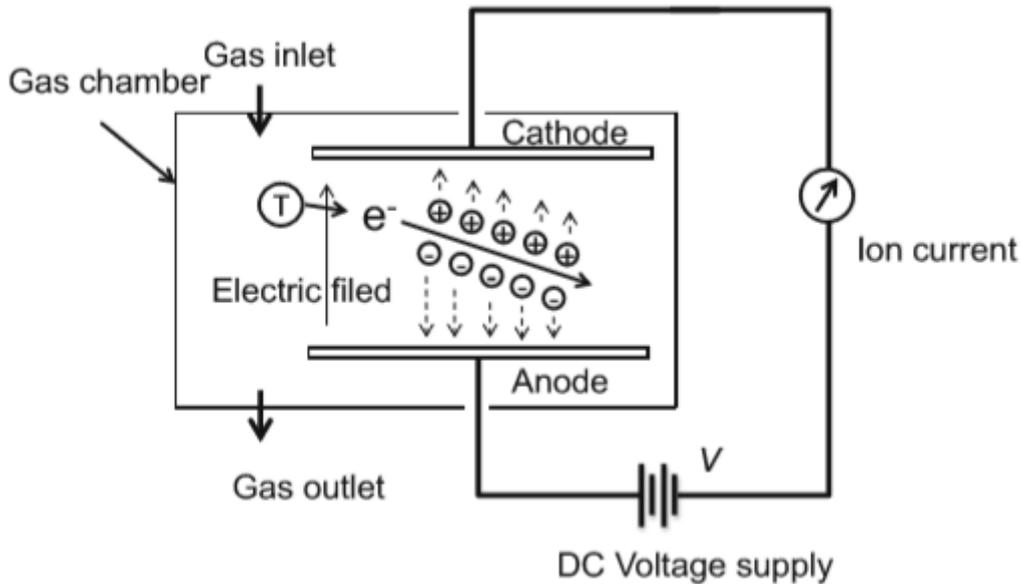


Figure 6: Scheme of an ionisation chamber

As an example, commercial systems exist (see Figure below) with detection limit of 2.5 kBq/m³ and a maximum activity measurement of 1,6 10¹⁵ Bq/m³.



Figure 7: Example of commercial system (premium analyse (left), TAM100D/DSI High Sensitivity(Right))

Tritium decays to He-3 by the ejection of a beta particle. The beta particle generated by the decay of tritium ionizes the surrounding gas found in the ionization chamber. The number of ions produced



due to the loss of energy of the beta particle is a function of the type of gas. A sample of gas is collected in the ionization chamber and the ionization current is measured. The resulting chamber ionization current is proportional to the quantity of tritium in the gas. The larger the measuring chamber volume, the higher the output current and the easier it is to measure. However, as the volume of the chamber increases, the longer it will take to get an accurate measurement. Modern electronic systems have solved most of the problems associated with measuring small ionization currents in small volumes and as a result, the volume of the ionization chambers has been reduced over the years from 50 L down to 1 or 2 L.

An ionization chamber can be employed as a process monitor in any gaseous tritium handling system. The gaseous T can be directly or partly introduced into the chamber, and the exhausted gases return to the system. It should be mentioned that ionization chambers do not work under vacuum conditions.

4.2 Proportional counters

Proportional Counters — Gas proportional counters are also used to measure the amount of tritium contained in a gas. A sample of the gas to be monitored is mixed with a counting gas and passed through a proportional counter tube where the pulses caused by the decay of tritium are counted. Proportional counter monitors can be used for most gas monitoring applications and are also available to measure surface contamination in special case.

Although the proportional counter has higher sensitivity compared with the ionization chamber, the addition of the proportional gas is unsuitable for an in-line monitor [Tetsuo Tanabe, 2017].

4.3 Scintillation crystal detectors

Scintillation detector systems are used to measure the total mole percent of tritium in a sample of gas independent of the chemical composition of the tritium in the gas (HT, DT, T₂, and CH_xT_y). A sample of the gas is introduced into a measurement chamber at low pressure, generally less than a few torr. The chamber contains a scintillation crystal, which is exposed to the tritium as it decays. The light pulse produced in the scintillation crystal is either counted or is used to produce a current, which is proportional to the mole percent tritium contained in the gas sample. Crystal scintillation detection is generally used to measure the mole percent of tritium in gases containing high concentrations of tritium [DOE, 2008].

The use of scintillation solid material has been extensively described recently by Tarancon (2017). The interest of this type of material is the reusability of the scintillator to avoid production of nuclear waste. However this technique is less sensitive to tritium compared with LSC measurement.

4.4 He³ measurement, mass spectrometry

Magnetic sector, quadrupole, and drift tube mass spectrometers are used as analytical tools to measure the individual components that make up the gas being measured. Mass spectrometers are generally used for the purposes of assay and accountability or for scientific purposes. A sample of the gas to be measured is introduced at low pressure into a chamber and ionized. The ions produced are then measured by a means that discriminates on mass. The number of ions produced at each mass is measured and is proportional to the partial pressure of the component in the gas sample. Owing to radioactivity of Tritium, particular care is required to use mass spectrometry for the analysis of T-containing gas.

This technique is always very expensive and requires knowledgeable well-trained personnel. High mass resolution is generally necessary. The individual detection of all isotopes of hydrogen and helium requires high resolution over 1000 in mass spectrometry, because the molecular masses of HT, D₂, and 4He are quite close with each other (4.0239, 4.0282, and 4.0026, respectively) [Tetsuo Tanabe, 2017].

4.5 Gravimetric and volumetric analysis

T as a gas form can be evaluated in a particular volume by the ideal gas law $PV = nRT$ [Tetsuo Tanabe, 2017]. The volumetric method is readily applied for the measurement of T in the gas

reservoir. However volumetric measurement cannot provide the gas composition and therefore a structural technique must be used to assess the effective presence of H-3 if there is any doubt.

In case of a T stored bed (for fusion developments as an example), the gravimetric method can be used. Mass difference of the stored bed before and after storage directly gives the mass of stored hydrogen isotopes.

These two types of measurements are not specific and thus must be used with other techniques to be sure that physical measurements correspond to tritium and not another gas.

4.6 RAMAN Spectroscopy

This technique can provide the quantitative analysis of gas that contains tritium. This method has the huge advantage to be non-destructive because the probe is a laser and photons are observed. Of course, this technique must be optimized but it can be used as in line control method. The Raman spectroscopy is used as an in-line T monitor in Tritium Laboratory in Karlsruhe, Germany, [Tetsuo Tanabe, 2017] and an example of spectrum of flowing gas sample containing T₂, DT, HT, and tritiated methane is shown in the following Figure.

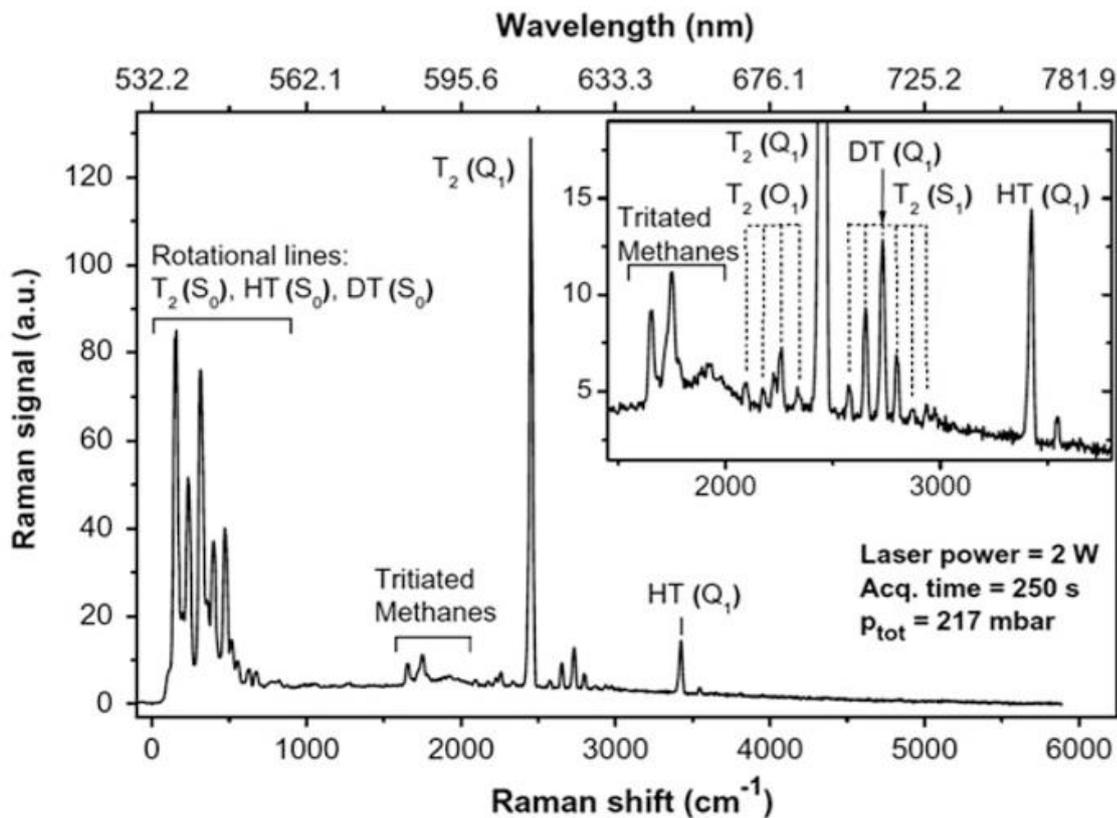


Figure 8: Example of Raman spectrum obtained with a tritiated gas [Tetsuo Tanabe, 2017]

4.7 Gas chromatography

This technique is a well-known quantitative technique to measure different gas and can be also used for tritium measurement in different chemical form.

It is not easy to separate tritium forms in a gas and with special gas chromatography columns cooled at cryogenic temperature different molecules can be separated and observed [Tetsuo Tanabe, 2017].

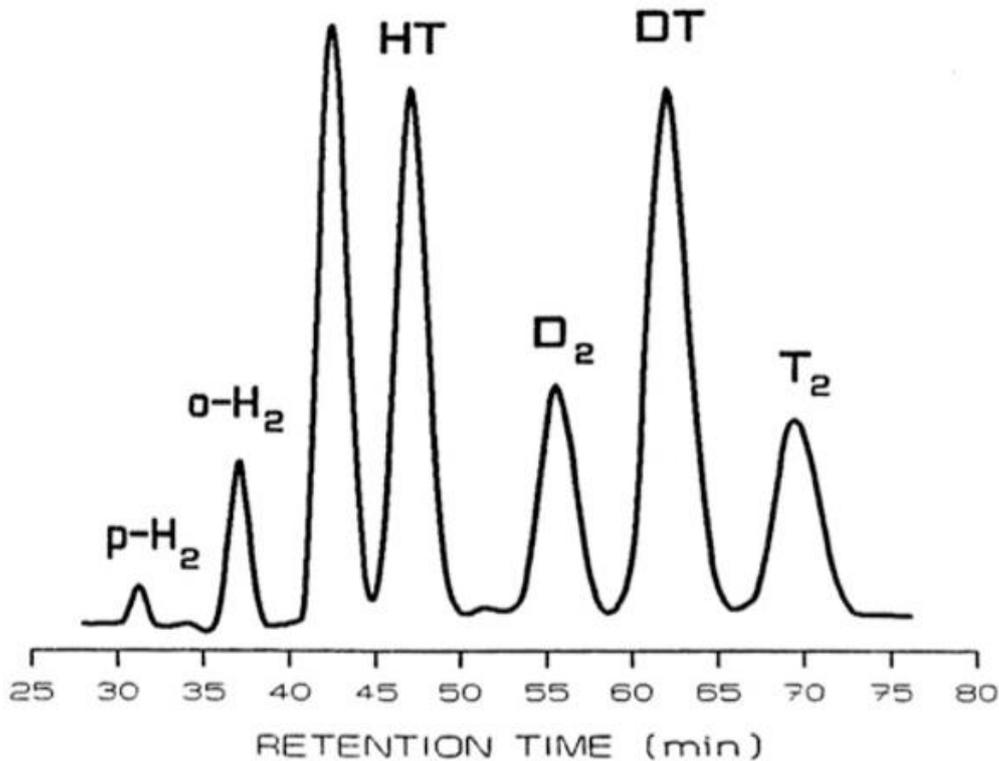


Figure 9: Example of a gas chromatogram obtained with a gas containing tritium

This technique has a detection limit for tritium of the order of 10 ppm but tritium pressures must be kept low for safety reason [Bachelet, 2016].

5 Direct analysis of tritium in solids

The measurement of tritium that is trapped inside a solid is very difficult but of course very important for quantitative estimation of total tritium inventory. The following techniques try to tackle this very problematic measurement.

5.1 Calorimetry technique

Calorimetry technique is a very important technique for the analysis of tritium contained in solids (generally nuclear wastes) because it is a non-destructive technique. More generally, calorimetry can be used for tritium measurements in solid, liquid, gas or mix. This technique is industrial with a high TRL and is often used for tritium inventory. It is one of the only techniques that can be used for high activity of tritium and has quite high detection limits. However the calorimetry is not a selective technique for tritium measurement and thus must be considered with care.

Deposited energy of the β -electrons in a material is turned to be decay heat and raises the material temperature. Although the decay heat of tritium (0.91 pW Bq^{-1} or 324 mW g^{-1}) is not large but it is not matrix dependant. The energy is fully deposited into the material retaining tritium owing to the very short range of the β -electron. Therefore, measurement of the decay heat of T retained in a sample using a calorimeter gives the absolute amount of tritium.

Calorimeters are commercial systems. As an example, KEP nuclear (<http://www.kep-nuclear.fr/>) proposes many different types of systems (see the following Table). The lowest detection limit that can be obtained is $5.6 \cdot 10^{10} \text{ Bq}$ with μLVC which is huge for environmental purpose. This type of result can also be obtained with long exposure time (several days).

Antech (www.antech-inc.com) is another company that can provide calorimeters of different sizes.



	LVC 3013	LVC 270-3W	LVC 270-15W	LVC 580	LVC 300	LVC 390	LVC 680	LVC 1380	μLVC Sous vide	μLVC Sous air
Range of power (mW)	2 – 20000	1.5 – 3000	3 – 15000	10 – 25000	1.5 – 3000	10 – 13000	15 – 26000	10 – 3000	50 μW 100 mW	1 - 500
Volume (liters)	3.3	15	15	20	25	60	90	380	40	
Accuracy (%)	0.15	0.2	0.3	0.15	0.3	0.5	0.5	1	25-0,5	10-0,5
Detection limit (μW)	300	250	500	1 500	250	1 500	2 500	5 000	50	1000
Tritium detection limit (mg)	95	80	150	465	80	465	775	1500	0,15	310
Measurement time (hours) with prediction calculation	3	3 – 4	3 – 4	3 – 4	4 – 5	5 – 6	5 – 6	10	3 – 4	2 – 3

Table 1: Different models of calorimeter (KEP nuclear providers)

In reference [Bükki-Deme, 2013], a new device has been tested to improve the detection limit of the calorimetry method. The IGC-V0.5 [Bükki-Deme, 2013] was the most accurate device in their laboratory able to measure tritium samples with activity from 10^9 Bq to 10^{16} Bq (1 μW to 1 W). The system proposes measurement under vacuum.

5.2 Pyrolyser technique

As it was mentioned in the paragraph describing the LSC technique, a proper sample preparation is required for solids containing tritium. This technique is known as pyrolysis. Different pyrolysers exist commercially and the following examples describe some devices that can extract tritium from the solid as gas form.

The gas stream is passed through a heated catalytic reactor where tritium in the form of HT, DT, T₂, and CH_xT_y, is cracked and oxidized to form tritiated water. The gas is trapped in tubes and a scintillation cocktail is added before a LSC measurement. Most of these devices have 100% yield but to ensure a high accuracy this must be checked for all matrices.

5.2.1 Perkin Elmer pyrolyser

The commercial name of Perkin Elmer pyrolyser is the “oxydiser”. This system is mainly used for environmental samples and a detection limit of around 280 Bq/L is generally announced by the manufacturer. Only one sampling tube is proposed. H-3 and C-14 can be extracted at the same time.



Figure 10: Perkin Elmer Oxydiser.

5.2.2 RADDEC pyrolyser

Raddec company (www.raddec.com) offers a pyrolyser with six independent tubes for six different pyrolysis at the same time. This device was developed for analysis of tritium in urines [Oh, 2014] but also in radioactive wastes [Warwick, 2010].



Figure 11: The Raddec pyrolyser

5.2.3 Eraly pyrolyser

The manufacturer (www.eraly.com) has adapted a pyrolyser that can be installed totally in a fume cupboard. For safety purpose of the user, this possibility represents a high advantage.



Figure 12: Eraly pyrolyser with multi tube (here two) to analyse two different samples (the main cover was taken off for the picture)

The pyrolyser is composed of two parts. One heating system for holding the temperature at 900 °C to allow oxidation and transfer of HTO up to the bubbling system and another one that can be automatically and rapidly changed from room temperature up to 900°C. At room temperature it is very convenient to move in a new sample with no risk to extract tritium immediately.

For nuclear wastes and considering a sample of 1 g, detection limit of 0.1 Bq/g was determined with this type of device. Matrices such as plastics, concrete, oil can be studied with this type of pyrolyser. Other matrix such as metals can also be analysed but extraction yield must be checked.

5.2.4 Fives pyrolyser

The main drawbacks of some pyrolysers is the maximum temperature that can be reached (around 1000°C. To reach higher temperatures required to extract tritium from steel samples (as an example), some manufacturer (<http://induction.fivesgroup.com/fr.html>) proposes induction systems that can melt solids with high fusion temperature (around 1600°C).

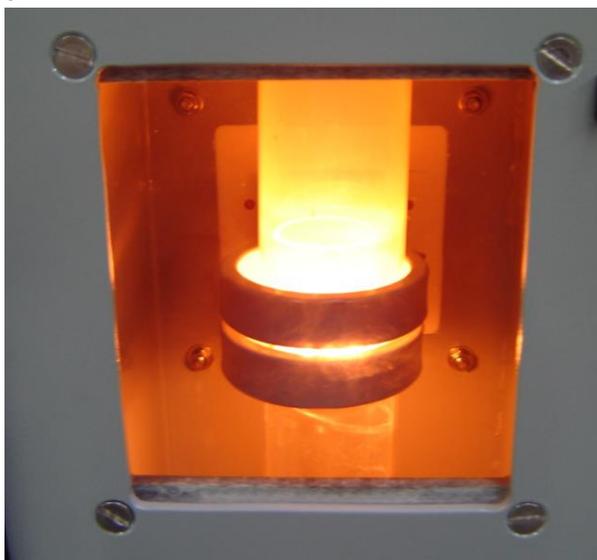


Figure 13: pyrolyser with induction heating. Tritium is trapped in bubblers (not shown in the picture).

6 Techniques with low TRL for tritium analysis

Following all the different techniques described above, there are many other types of specialized techniques and devices to detect tritium. Many of them are described below.

We have made a classification of the different techniques according to their basic use. A difference is systematically indicated between radioactivity measurement and physical measurement. In general, the direct physical methods and the radioactivity measurements can be applied for higher activity levels of T and for lower activity levels of T, respectively.

6.1 Digital Autoradiography system

This technique corresponds to a radioactivity measurement.

Autoradiography was in the past developed with photographic plates or X-ray plates to investigate alpha or beta emitters [IAEA, 1970]. But recent developments have highly improved the interests of the technique.

Autoradiography technique involves the imaging of decay emissions coming from tritium with a screen (Figure below). The autoradiography technique came from biology research and has spread to different new applications such as nuclear dismantling [Fichet, 2012; Leskinen, 2013; Haudebourg, 2016]. The autoradiography technique is a non-destructive measurement that can be used easily in situ.

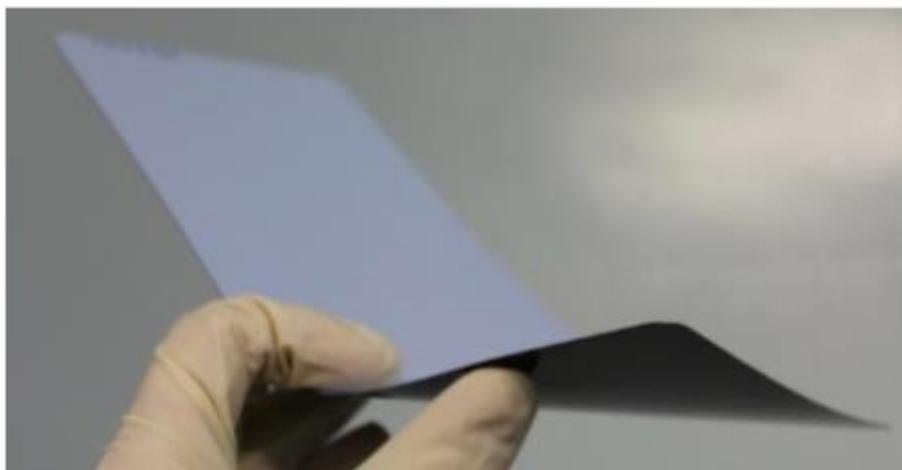


Figure 14: A typical screen (imaging plate) used as a sensor for autoradiography

Autoradiography is a technique that produces an image from the decay emissions such as alpha, beta and gamma radiation even for low energy emitter like tritium. Tritium distribution on material surface can be measured.

The technique has several advantages because it detects both fixed and removable contamination, it is non-destructive, and the detection area is 2D and rather large (as an example size of the screen shown in Figure above) is 12cm * 25cm. To analyse larger areas, batch of several screens can be used.

The flexible screens used contain photostimulable crystals, for example BaFBr:Eu²⁺, which accumulate and store radiation information when placed in close contact with a radiation source. The mechanism in accumulation of data is based on the ionization of Eu²⁺ to Eu³⁺ by the radiation (and particularly tritium radiation). These phosphor crystals which contain bromine vacancies serve as electron trap.

The photostimulable crystals are deposited on a support layer and they can be covered by a protecting layer (not for tritium). Perkin Elmer and GE Healthcare, as an example, have developed so-called TR films which are particularly sensitive to ³H and ¹⁴C, since the TR films do not have protecting layers which attenuate low energy betas before they reach the photostimulable crystals. That can be a real drawback because potential contamination of the screen is possible.

To obtain a result by autoradiography the screen must be deposited on a surface flat (example of a floor) or not (example of a tube). Autoradiography begins with exposure of the screen to the ionizing radiation. The required exposure time varies depending on the radionuclide and its activity and therefore the exposure time must be optimized experimentally. The accumulated signal can be

scanned by a He-Ne laser (with a spatial resolution of around 100 μm) installed in a Typhoon system (GE Healthcare).



Figure 15: Autoradiography scanner Typhoon FLA 7000 (GE Healthcare)

The laser transfers energy to the electrons in the bromine vacancies and liberates it from the electron trap. The freed electron will recombine with the Europium ions and europium will return to the ground state. A blue photon with mean energy of 390 nm will be emitted in this process. The blue photons will be recorded by the photon detector (a photomultiplier) in the scanner machine. The scanner machine will repeat this process regularly across the screen. The scanner converts the accumulated signal into digital form which is presented as a 2-dimensional image. The radiation information can be shown as shades of gray. The increase in the intensity of the gray to black corresponds to increasing radioactivity of the source. The unit of these intensity values is Digital Light Unit (DLU) which is a numerical value connected to the color scale.

A very important property of the previous screen is its reusability. The phosphor screen can be reused by erasing with exposure to intense white light. This possibility induces a requirement for the use of screen. The screen must be protected from light during exposure time of a surface to be investigated.

An example of a typical image that can be obtained with autoradiography, is presented in the following Figure. It was obtained with very small tritium fixed sources (size of each 5 mm *7 mm). 13 sources with activity between 7390 nCi/g and 2 nCi/g are fixed on a glass rectangle (manufactured by American Radiolabeled Chemicals). These sources are put on an autoradiography screen during one day to obtain the autoradiography image. The technique is linear with the activity with a dynamic range of 10^5 . For each sources, the images appearing as rectangles are homogeneous, which is generally not the case in real in situ application. Detection limit of 30 Bq/cm² was determined with the screen method for an exposure time of one day.

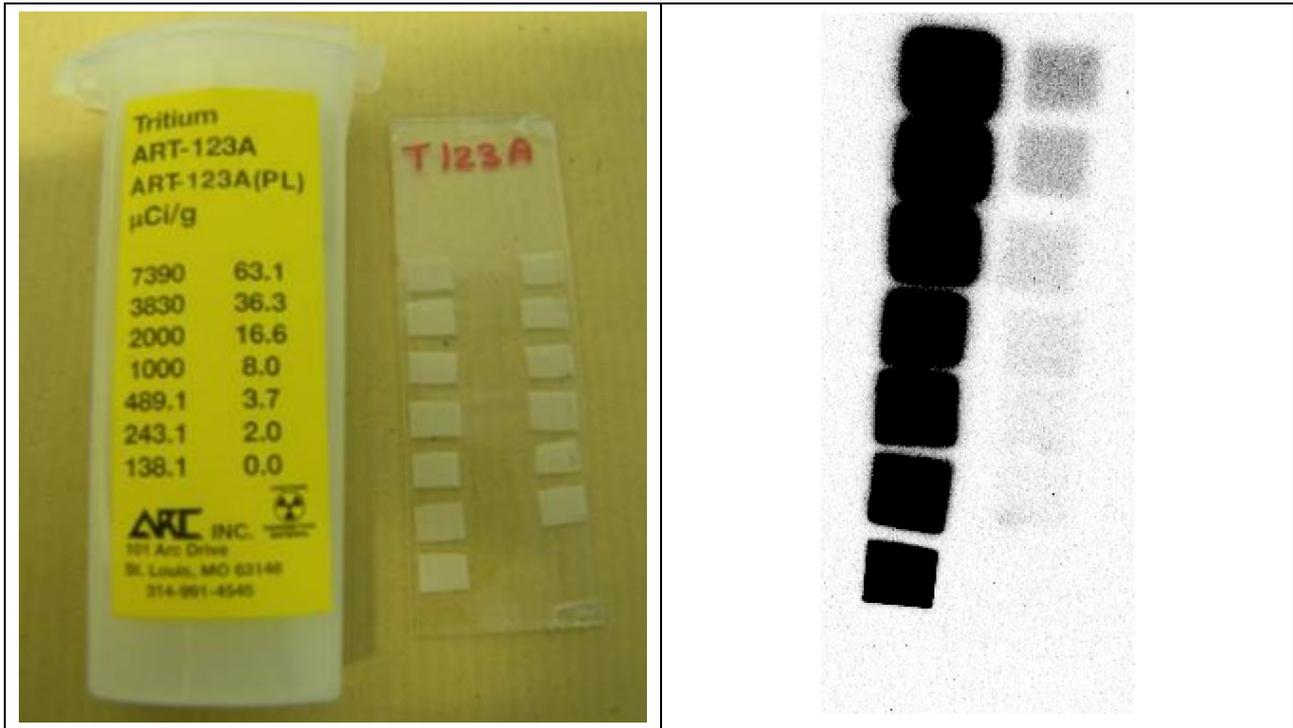


Figure 16: Tritium sources and image obtained by autoradiography

For measurements on decommissioning facility, areas of contamination can be identified with this technique. The following example shows a result obtained after several months of investigation with a batch of 20 screens. Different zones of a potential contaminated floor made of concrete was investigated, representing an area of 250 m². With regards the different researches made in the facility, historical documents proved that the only radionuclide present is tritium. Considering 20 % of the surface really investigated with the screen and a geostatistic calculation [Leskinen, 2013] different large spots of tritium were localised on the surface by autoradiography.

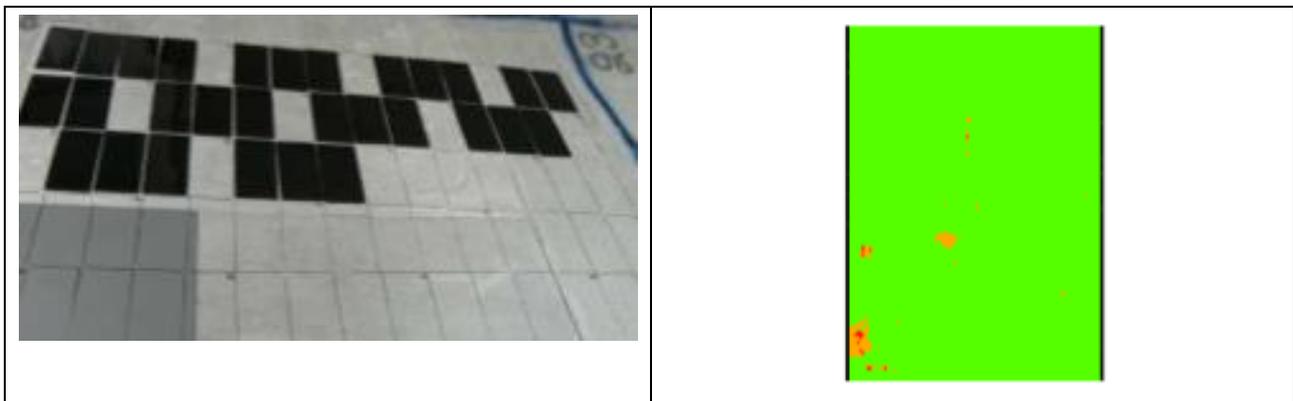


Figure 17: Typical use of batch of screen on a concrete surface (left) Spots of tritium (in orange and red) found on a concrete surface (250 m²) by autoradiography method (right)

Other information can be obtained with autoradiography. Considering the image of a contamination, improvement of waste sampling can be obtained easily. Moreover considering once again the image obtained, contamination in depth, for example on cores, can be obtained. For tritium the extraction of a core can be a problem because of potential outgassing of the radionuclide. The coring process must be done very slowly without any cooling fluid.

Another example of the use of autoradiography is described in Tetsuo Tanabe book [2017]. Because it is a non-destructive technique, an image of the profile of tritium on floor tiles of JET Mark II-A divertor can be obtained. Colors (Figure below) correspond to different amount of tritium on the surface.

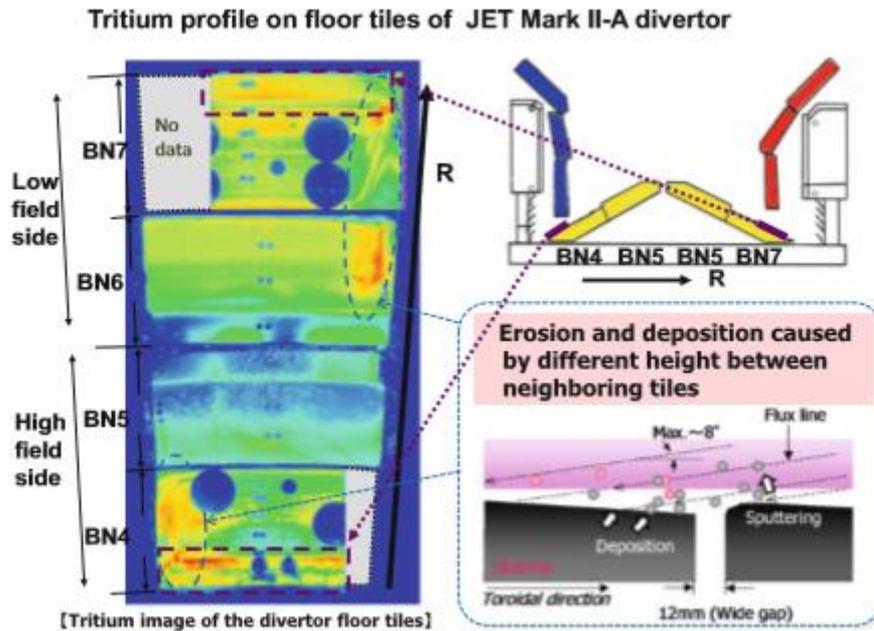


Figure 18: Example of Autoradiography technique [Testsuo Tanabe, 2017]

Other recent researches are still going on to improve the use of this technique for tritium investigation. The Autoradiography technique will be further developed in the course of TRANSAT project.

6.2 BIXS (Beta Induced X-ray Spectroscopy)

This technique corresponds to a radioactivity measurement.

Beta particles emitted during tritium decay may indirectly result in an external radiation hazard through the production of a continuous spectrum of low energy X rays, called Bremsstrahlung. The amount of X rays produced depends on the material and the quantity of tritium [JR Johnson, 1991]. Beta Induced X-ray spectrometry (BIXS) is a method which involves the detection of bremsstrahlung and characteristic X-rays induced by Beta particle from tritium decay. BIXS is based on the interaction between the beta particle and atom in the medium. This is done by exposing beta particles from tritium to a medium with sufficient atomic mass. The interactions between beta particle and the medium produce bremsstrahlung and characteristic X-rays. They are radiative interaction and collision with inner shell electron. Induced X-rays will then be recorded and information obtained from the spectrum [Matsuyama, 1998].

Bremsstrahlung X-rays are produced when radiative interactions occur. Radiative interaction occurs when travelling electrons decelerate due to deflection by a charged particle. The electron loses kinetic energy which induces the emission of X-rays due to the law of energy conservation. These X-rays have an energy range from zero to the maximal energy of the electron (18.6 keV for tritium). Electron with excess energy after undergoing one deceleration can experience another deceleration with other charged particle. This results in the emission of more low energy X-rays. However, low energy X-rays are easily absorbed and will be less likely being able to reach the detector. This results in the bremsstrahlung spectrum which has a continuous spectrum with a cut-off frequency corresponding to the maximal kinetic energy of the electron, shown in Figure 19.



Figure 19: Image of a typical continuous X-Ray spectrum obtained from Bremsstrahlung

In a BIXS setup (Figure below), a medium is exposed to the beta particle. This medium should preferably have distinct characteristic X-ray with energy that is near the average energy of Tritium beta particle. Since beta particle have extremely low range (around 6 mm in air), the medium has to be in close contact with the source.

The beta particles will interact with the medium to produce characteristic and bremsstrahlung X-ray. Usually the medium is argon gas or beryllium coated with gold. As beta particles are emitted in all directions, there may be interactions with the material in the sample which result in additional X-ray contribution from them.

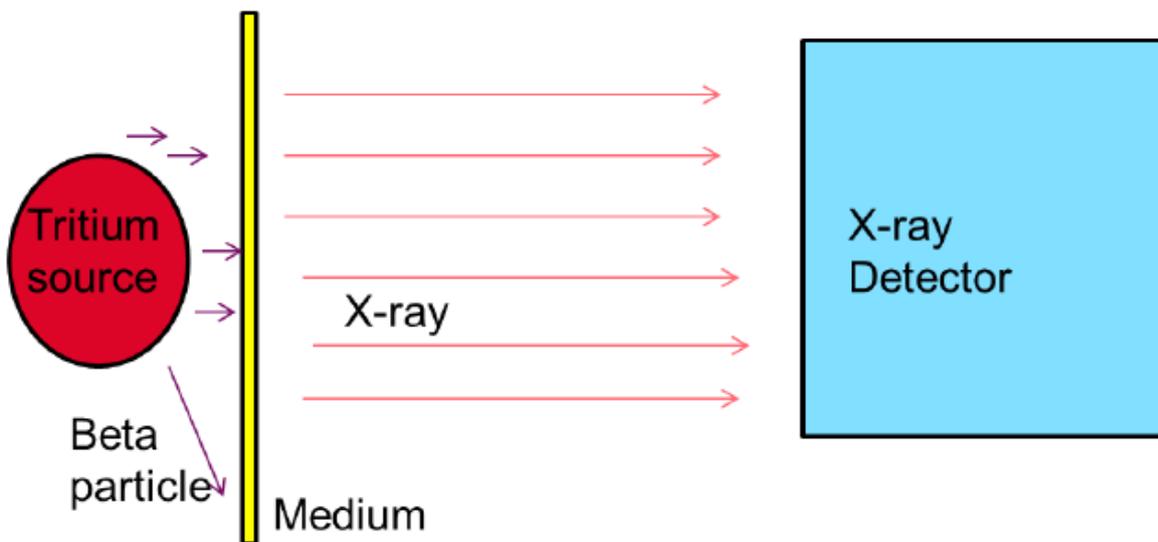


Figure 20: a simple BIXS set-up

The produced X-rays will be detected by an X-ray detector and an X-ray spectrum is produced (Figure below). The detected X-rays are sorted by their energies which gives us a spectrum with varying intensity of X-rays [Matsuyama, 2001]. The radiation can be detected with X-ray detectors such as a NaI scintillation detector and a Ge detector.

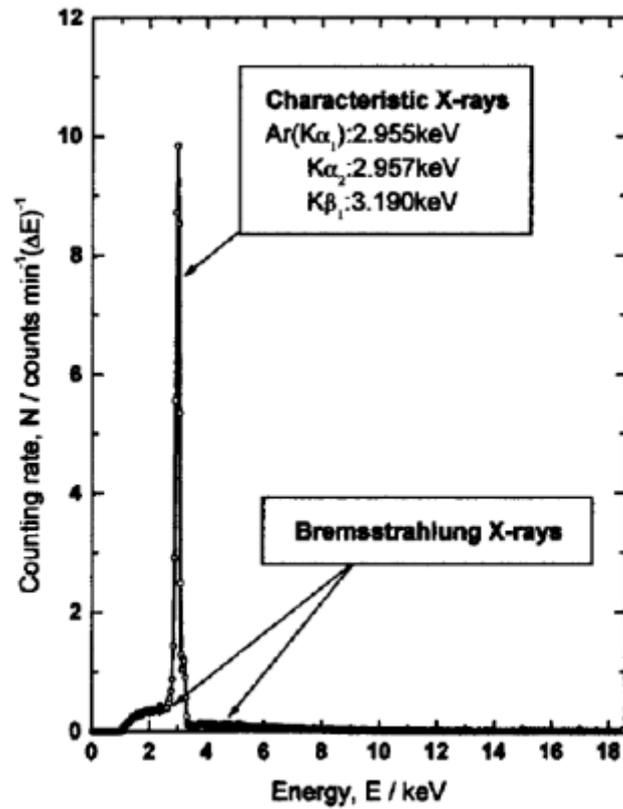


Figure 21: Typical spectrum obtained from BIXS. The characteristic spectrum of Argon used as a medium is well defined.

From BIXS setup, an X-ray spectrum is obtained. Much information can be derived from this spectrum (Figure below extracted from [Matsuyama, 2011]). Tritium surface amount, tritium depth profile, materials in sample, tritium retention rate and possible radionuclide in sample can be obtained from the spectrum.

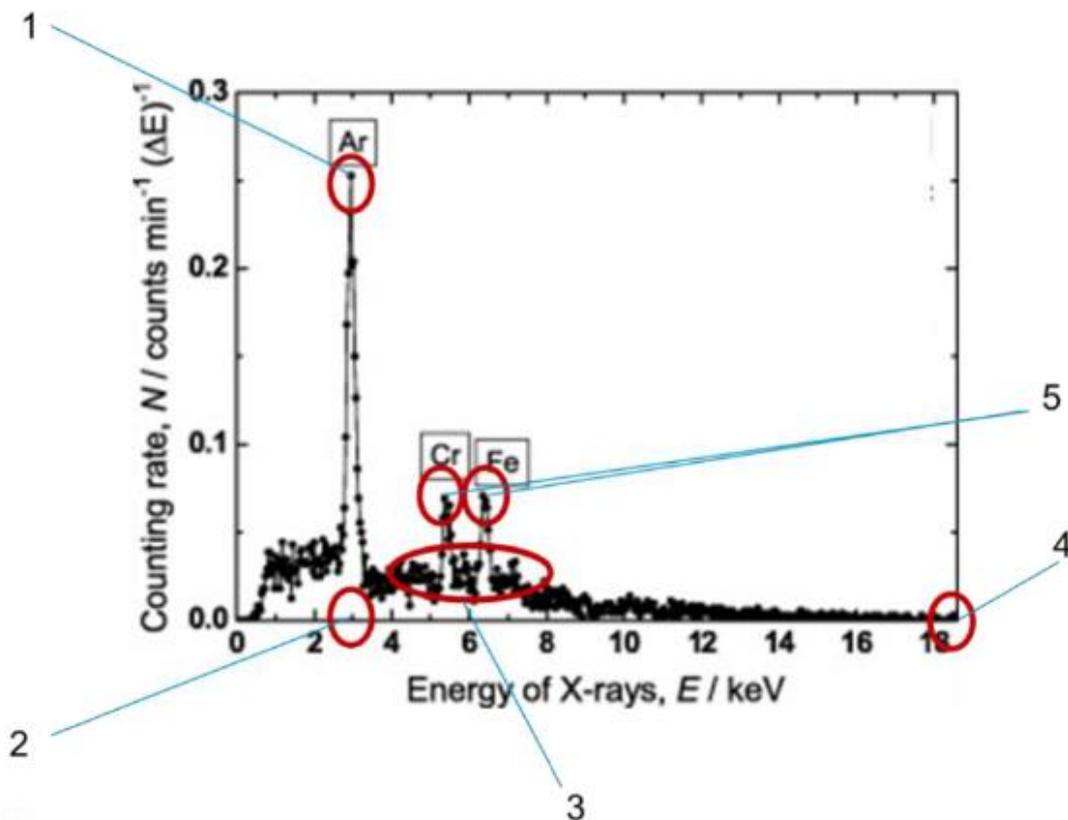


Figure 22: BIXS spectrum observed for a steel sample containing H-3

From the above Figure, the numbered points show important information offered by the BIXS results (here a steel sample containing tritium in the bulk and on the surface). Point one represents Characteristic X-ray intensity which are proportional to the amount of tritium on the surface layer of sample. Point two represents the energy of the peak intensity X-ray (here Ar). Point three refers to the bremsstrahlung spectrum which can be used to evaluate tritium surface content, tritium depth profile and tritium content in deeper area of sample. This information could come from bremsstrahlung effect from the medium and deeper regions of the sample. Depth Profiling can be performed by modelling the BIXS spectrum with computer simulation of the process of tritium diffusion. Point four represents the cut-off energy of the spectrum. This corresponds to the maximum energy of emitted radioactive particle and could be useful in partial determination of the radionuclide. Lastly, point five refers to characteristic X-ray of other material that may be part of the sample or detector.

BIXS technique is not a commercial system but is still in development [Matsuyama, 2016; Rölig, 2013] particularly to investigate high quantity of tritium that can be encountered in fusion system.

6.3 TRAMPEL (Tritium Activity Measurements with a Photomultiplier in Liquids) technique

This technique corresponds to a radioactivity measurement.

Priester [2016] designed a set up very compact for measuring tritiated water samples. It was developed with the aims at measuring in-line the activity of high tritiated water without sampling procedure. In the first tests described in Priester paper, the system was set up for static measurement.

TRAMPEL is an acronym for TRitium Activity Measurements with a Photomultiplier in Liquids. It is proposed as an alternative method of the standard LSC with application for in line process and no

waste production. This technique has been proposed for future in line fusion plants and tritium values of typically 10^8 Bq/mL.

Conversion of β - radiation in visible light is done by solid optical fibers (with a square section 2 mm*2mm) purchased in Saint Gobain company. The detector is a photo multiplier tube (see Figure below). In Priester paper tritiated water from 0.0215 MBq/mL to 24 MBq/mL was measured with the TRAMPEL system.

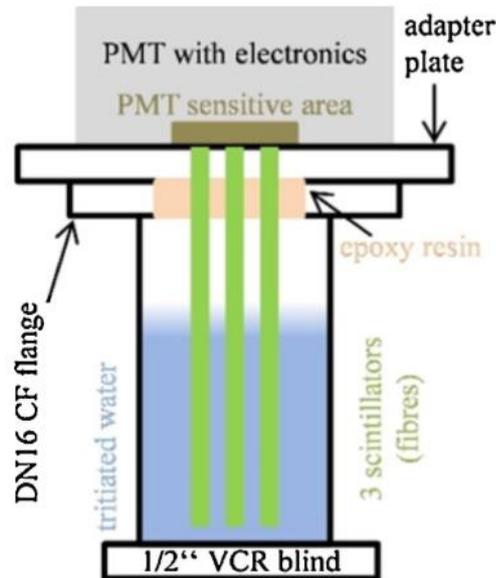


Figure 23: Scheme of the TRAMPEL system to analyse tritiated water

6.4 LIBS (*Laser-induced breakdown spectroscopy*)

This technique corresponds to a physical measurement. Only feasibility of the technique has already been published particularly concerning the two isotopes H and D. Tritium investigation with LIBS is an actual challenge which will be further developed within the TRANSAT project to be able to prove that it can be also applied for tritium detection.

The LIBS measurement of the components concentration within a material is based on the spectroscopic analysis of the plasma produced during or just after the interaction between a laser pulse and the material to be characterized (Figure). Delivering an energy higher than the material depending threshold, leads to a local heating enabling the solid to plasma transition over timescales of the order of the nanosecond. The resulting pressure increase leads to the sudden ejection of matter, therefore to a decrease of the plasma density allowing the emission of spectral lines depending on the components of the plasma, therefore of the sample. The plasma lifetime usually corresponds to $\sim 10 \mu\text{s}$ and the crater formed on the sample usually has a diameter of the order of several hundreds of μm . In most of the studies reported in the literature, the used laser pulses are of the nanosecond type.

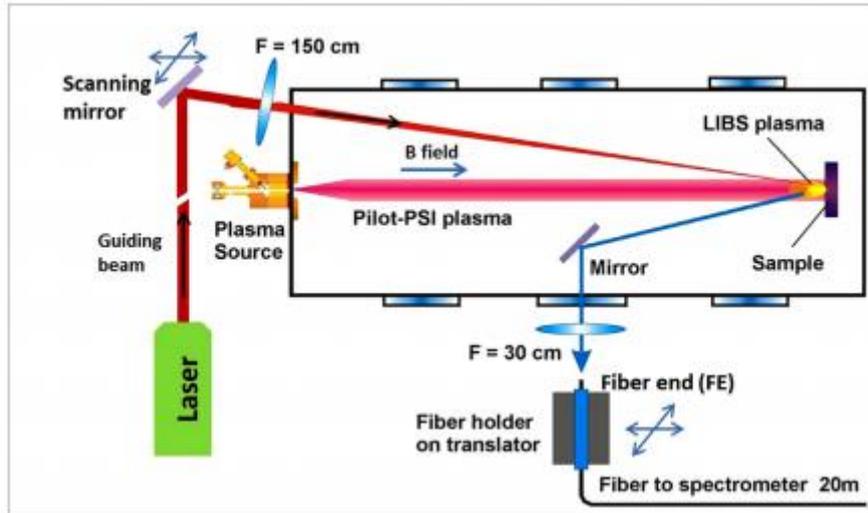


Figure 24: Example of a LIBS set-up [Piip, 2017]

The measurement of the hydrogen isotopes concentration in materials using LIBS faces the following four main difficulties (1) the activation of at least α -type emission, (2) the isotopic discrimination, (3) the specific features of spectra in case of experiments performed on W and, (4) the depth profiling capacity according to the laser pulse duration. We propose to discuss each of these points in the light of the more relevant papers.

(1) Activation of α -type emission

Tritium, deuterium and hydrogen present relatively high Einstein coefficients as illustrated by Table 2.

Type / transition	α ($n = 3 \rightarrow n = 2$)			β ($n = 4 \rightarrow n = 2$)			γ ($n = 5 \rightarrow n = 2$)		
Line	H α	D α	T α	H β	D β	T β	H γ	D γ	T γ
Wavelength / nm (in air)	656.283	656.093	656.039	486.134	485.995	485.954	434.047	433.924	433.887
Transition upper state energy / eV	12.088	12.091	12.092	12.749	12.752	12.753	13.055	13.058	13.059
Ionization limit / eV	13.598	13.602	13.603	13.598	13.602	13.603	13.598	13.602	13.603
Einstein coefficient / s ⁻¹	4.41 × 10 ⁷			8.42 × 10 ⁶			2.53 × 10 ⁶		

Table 2: Characteristics of the main transitions observable in spectra for the three hydrogen isotopes

Despite these high values, the excitation of the most common observable transitions is rather difficult. Indeed, the upper state of these transitions corresponds to an energy of at least 12 eV. The plasma produced during a laser shot on the material whose composition is expected has therefore to be sufficiently hot. A high plasma temperature is therefore required. In case the temperature is not high enough, too small power density in the sample therefore in the plasma may seriously limit the detection capability of the technique. This explains why the literature reports measurements based on the α -type transition. Indeed, the β -type transition seems to have not yet observed. This is due to the concomitancy of the higher energy for the upper state of the transition and the lower Einstein coefficient. A rapid calculation gives that the ratio between signals observed at 486 nm and at 656 nm is of the order of 0.1 for a plasma temperature of the order of 10 000 K. Nevertheless some authors report spectroscopic analysis also performed using γ -type lines [Semerok, 2013].



The literature does not report studies devoted to the observation of the $T\alpha$ line for LIBS measurements. This is basically due to the radioactivity of this element. Until now, tests have been performed on materials containing H and/or D to simulate tritiated samples.

(2) Isotopic discrimination

Since tokamak operations can induce the penetration of deuterium and tritium within the Plasma Facing Components (PFC) materials, teams involved in the LIBS diagnostics have focused their attention on the capacity of the technique to separate spectroscopically the contribution of these two isotopes by working on samples charged simultaneously with H and D. Ishibashi [2014] performed experiments on mixed H_2O and D_2O water ice samples under classical LIBS conditions (Nd:YAG, 1064 nm, 100 mJ, nanosecond type). Since their work is dedicated to the measurement of H/D ratios within the framework of planetary sciences, the samples are treated at a pressure level of 0.15 Pa in water vapor. They obtain a correct discrimination of the H and D α -type lines if the densities are of the same order of magnitude, by implementing a deconvolution procedure. The upper states of the concerned transitions are sufficiently populated, and, in these low-pressure conditions, the low electron density value enables a low broadening of the lines compatible with a satisfactory spectral resolution. They clearly indicate that the overlapping of the α -type lines prevents their correct spectroscopic observation if the pressure is higher than 1 kPa.

Tests have also been performed on more realistic samples for tokamak purposes [Paris, 2017-Piips, 2017]. These samples can contain tungsten. These experiments confirm that measuring the presence of H and D in the sample requires a low-pressure background gas (argon in the present case). By using relevant coloured filters, the authors put in evidence the spatial segregation of the emission by the α -type lines. Indeed, at a pressure of 400 Pa, the emission is observed at 0.5 mm further from the sample surface as compared to the emission of argon (spatial emission was described). This is mainly due the low mass of hydrogen isotopes that reach a higher mean velocity at low pressure. Another important result is that using a low-pressure background gas avoids perturbative scattering that leads to lower noisy signals.

The H/D ratio can be also obtained for complex multilayers samples containing Mo, C and W atoms [Mercadier, 2011]. In this case, the well-known C II lines at 657.805 and 658.288 nm do not perturb the spectroscopic analysis. Similar analyses have been also performed on co-deposited layers containing C, B, Si, Fe and H [Grisolia, 2007].

(3) Specific features of spectra in case of experiments performed on W

In studies [Paris, 2017- Piip, 2017], H and/or D atoms are deposited near the sample surface. Therefore, the α -type lines are observed for a small number of shots. When the penetration within the sample is higher, the perturbation of the W I line at 656.320 nm (with the Einstein coefficient $2.04 \times 10^5 \text{ s}^{-1}$) becomes significant. Despite its relatively low Einstein coefficient, the related line can be easily observed in spectra since the upper state energy is 4.276 eV. In such cases, a deconvolution procedure must be performed including H, D and W lines.

Developing such a deconvolution procedure is not required in the case of the work of Semerok et al [2013] performed on JET, for which the spectroscopic analysis also covers the range 425-440 nm. Indeed, the $H\gamma$ line is observed without any perturbation of W I lines.

(4) Depth profiling capacity

In the papers previously discussed, the H and D signals are studied as a function of the shot number, without information about the depth at which the last laser pulse penetrates. This is also the case for the work reported by Malaquias et al. [2013]. In the work reported by Suchonova et al. [2017], the measurement of the ablation rate is performed in similar conditions to the LIBS experiments. This enables the depth profiling characterization of the studied samples. This ablation rate is rather small

(of the order of 100 nm per pulse). This weak value is due to the screening of the nanosecond laser pulse resulting from the plasma formation. Indeed, the plasma rapidly becomes optically thick during its formation (at ~ some ns), which avoids any additional ablation in the crater and leads to an increased plasma temperature. Using nanosecond laser pulses nevertheless modify the H or D profiles within the sample by coupled heat-species diffusion. As a result, ultrashort pulses can be preferred.

Such a study is reported in the paper due to Suyanto et al. [2012]. A picosecond laser pulse is used to reduce the ablation rate. The resulting plasma expands in a He flow maintained close to the sample using a simple pipe. The laser pulse energy is too low to enable the emission of lines having a sufficiently high spectral radiance. The plasma is therefore reheated using a second laser pulse of the nanosecond type. In these conditions, the authors found experimental conditions allowing a detection limit of 20 µg of D per gram of sample (zircaloy), which corresponds to a mole fraction of 10⁻³.

6.5 CRDS (Cavity Ring-Down Spectroscopy)

This technique corresponds to a physical measurement.

First result concerning HTO measurement was very recently published [Bray, 2015]. In this paper the developments concerned the outgassing control of the nuclear wastes contained in drums located in a repository site.

The CRDS is a laser absorption method and the measurement is based on vibrational molecular spectroscopy to quantify tritium in its oxidized form HTO. CRDS method is isotopically selective and does not need any calibration. This technique is not sensitive to HT and more generally to molecules that do not have a strong rotation-vibration dipole. In Bray et al (2015) study, detection limit of 3 kBq for tritium is announced.

The CRDS method has the advantage to be non-destructive (Figure below) but the developments remain at low TRL. This technique could be interesting for in situ measurements but a sampling process must be developed.

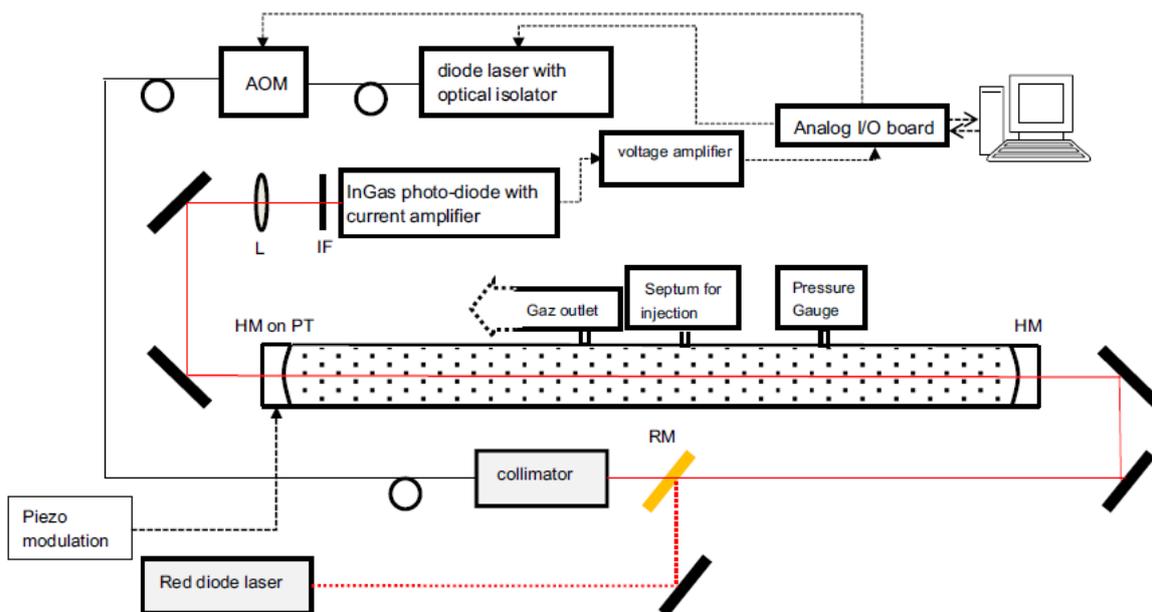


Figure 25: HTO measurement with CRDS method [Bray, 2015]

6.6 Ion Beam Analysis or beam probing methods

This type of technique corresponds to a physical measurement. These techniques will be developed for the TRANSAT project.

Ion beam Analysis involves the use of high energy ions (0.5-3 MeV) [Ion beam analysis, 2018] to impact upon the surface of a sample and probe its composition. The resulting collision will produce a myriad of products that gives information of the sample.

Various ion beam analyses that are usually used for H analysis in the near surface region can be also used for tritium analysis. They are SIMS (Secondary Ion Mass Spectrometry), Rutherford backscattering spectrometry (RBS) or Enhanced Backscattering Spectrometry (EBS) when cross section is not Rutherford, an Elastic Recoil Detection Analysis (ERDA), a Nuclear Reaction Analysis (NRA), and AMS (Accelerated Mass Spectrometry). As an example, SIMS may appear problematic to investigate tritium because it is a destructive technique that can spread tritium out of the sample. Ion beam analysis relies on the interaction between the high energy ions and the atoms in the sample. Firstly, a high energy ion beam is projected onto the sample in a vacuum environment. There are many possible interactions between the ions and the sample as schematically shown in Figure below. These interactions will produce protons, ions or electromagnetic radiation. These products could be detected and will give information of the sample based on their energy and intensity. The main interest of these methods is to investigate Tritium on surface and in depth of a solid material non-destructively. Each of the ion beam methods to detect Tritium has its benefits; this analysis is an attempt to extract the more significant results for hydrogen and tritium detection.

ERDA and NRA are the most efficient methods to detect and quantify hydrogen isotopes in the material; being developed in eighties and nineties they do not have a major impact on the sample properties. These methods also preserve the majority of the hydrogen content in the sample, as long as the ion beam flux and the dose are kept low. In ERDA, one detects elastically recoiled particles by the probing beam enabling the detection of light elements in the material like H, D, T when using a He, Li ion beam or heavier ions. However, in the case of heavier ions the method is not so much non-destructive anymore due to damage production. The ERDA method is applicable to the near surface regions.

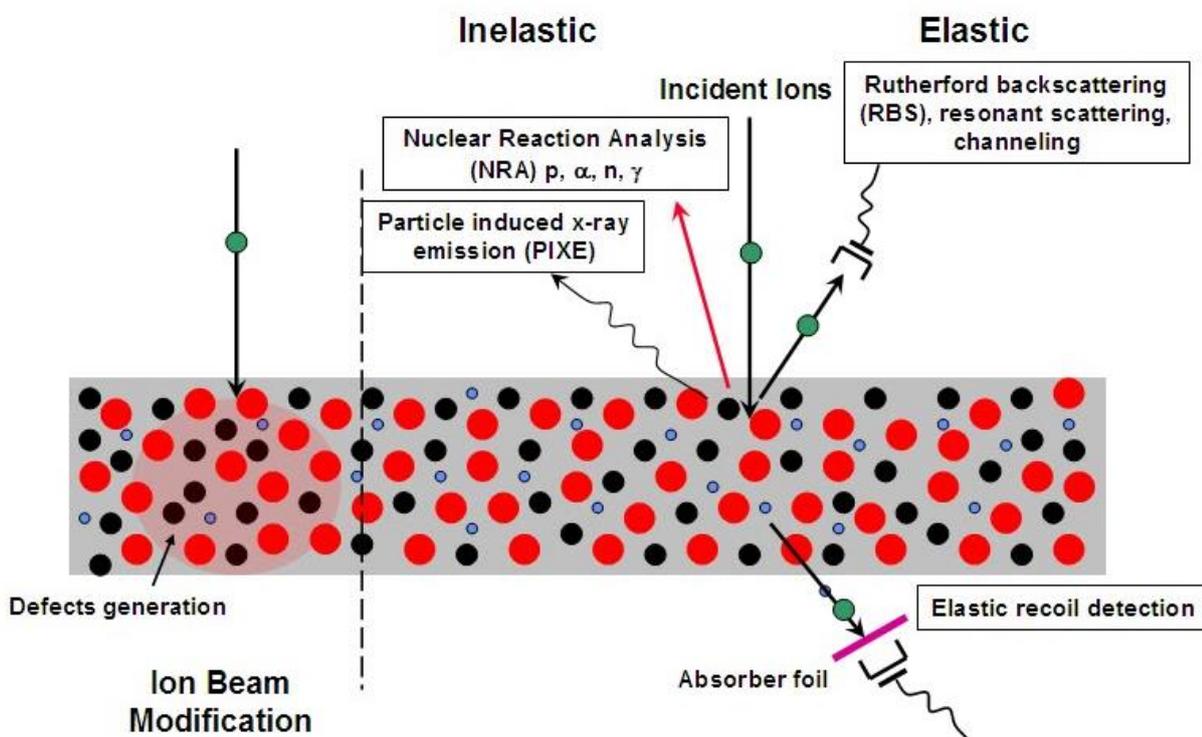


Figure 26: Different Ion beam analysis

Kreissig (1994) used the elastic recoil detection with heavy ions (HIERD technique using ^{35}Cl at 5 MeV) to investigate H, D and T in depth. The technique showed that H is more sensitive than D which is also more sensitive than T. In a Bragg chamber, the experiment showed a difference between hydrogen isotopes observed on a titanium surface and authors obtained a depth profile.

When samples contain small amounts of hydrogen isotopes (10^{-3} - 10^{-5} atomic fraction) the NRA method is usually utilized for hydrogen isotope detection due to its better sensitivity. Rudolph [1984] described the investigation of total content of Hydrogen on solid surfaces by resonant nuclear reaction. For ^1H detection in materials one applies a nuclear reaction available with ^{15}N ion beam $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ with high resonance-like cross section, which is very useful for ^1H concentration measurement and depth profiling in the bulk (i.e. steels, titanium alloys, etc.). Detection of Deuterium by NRA is enabled by the use of ^3He ion beam. The nuclear reaction $\text{D}(^3\text{He},\text{p})^4\text{He}$ is used due to the big resonance like cross-section enabling very sensitive deuterium detection (detection limit 10^{-3} atomic %). By ^3He -NRA one is able to detect deuterium down to about $7\ \mu\text{m}$ below the sample surface made of tungsten. Recently, The NRA and ERDA have been used to investigate Hydrogen and Deuterium in depth [Založnik, 2016]. Authors mentioned again that these techniques are nondestructive if compared to others (see LIBS technique for example). With ERDA the investigation in depth is very small (up to $0.5\ \mu\text{m}$) but the resolution is impressive (from 20 to 60 nm). On the contrary, NRA can provide result with depth up to few tens of μm but with a maximum resolution of $0.5\ \mu\text{m}$.

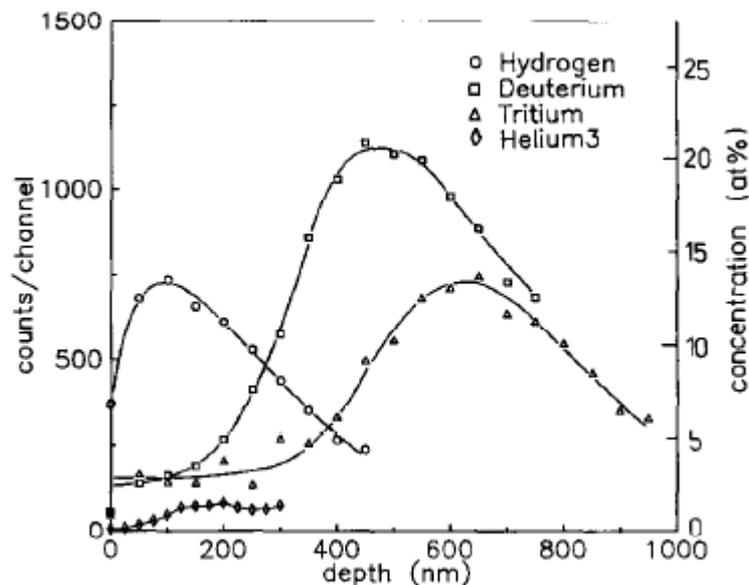


Figure 27: H, D, T depth profile on titanium surface [Kreissig, 1994]

For Tritium detection by NRA the nuclear reactions $\text{T}(p,n)^3\text{He}$ [Harmon, 1990] or $\text{T}(d,\alpha)n$ are typically used. Detection of tritium can be performed few μm deep but with worse depth resolution as compared to ERDA [Xia, 2008]. An example of Tritium detection utilizing $\text{T}(d,\alpha)n$ nuclear reaction can be found [Ochiai, 2004]. However, it seems hard to observe tritium easily, (see Figure below). For the authors “peak h” around 1200 keV could be due to tritium and the shoulders are not well resolved.

Proton backscattering is the third ion beam method proven to be a good technique to detect Tritium in materials due to enhanced elastic cross section, two orders of magnitude with respect to Rutherford cross section [Xia NIM B 266 (2008) 705]. However, the sensitivity depends on the host material whether Tritium signal can be separated from background signals and is therefore not applicable for heavy element matrix. The current developments are particularly focused on materials used for fusion experiments.

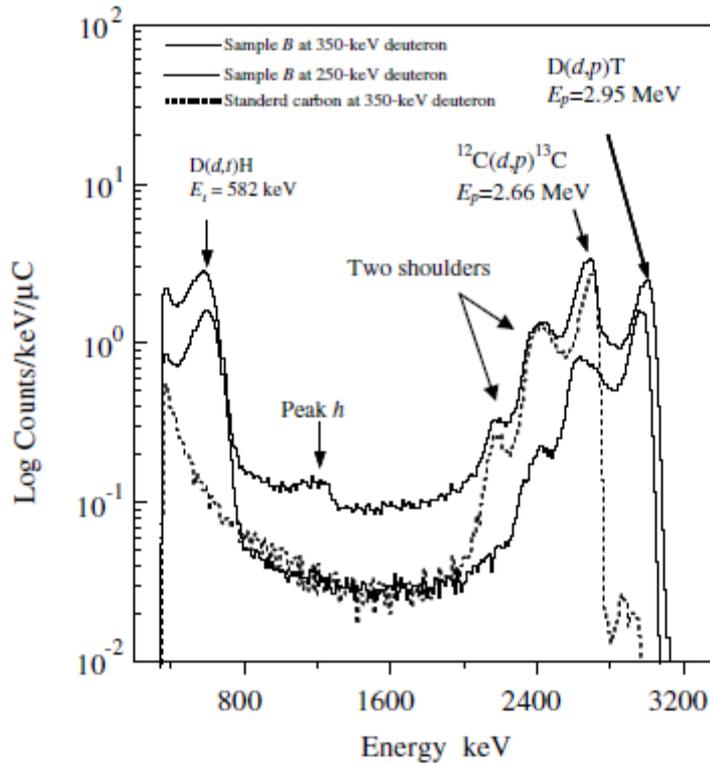


Figure 28: NRA example showing tritium signal [Ochiai, 2004]

The AMS (Accelerator Mass Spectrometry) [Friedrich, 2001] has also been used for the detection of low level of T in materials. Accelerator mass spectrometry is an ion beam analysis technique where a sample is impacted by ion beam and the resulting product undergoes mass analysis. Ions produced from the sample are accelerated in order to be separated by mass spectrometry. Friedrich et al presented results for Deuterium and Tritium analysis in depth on a carbon matrix (from 0 to 25 μm).

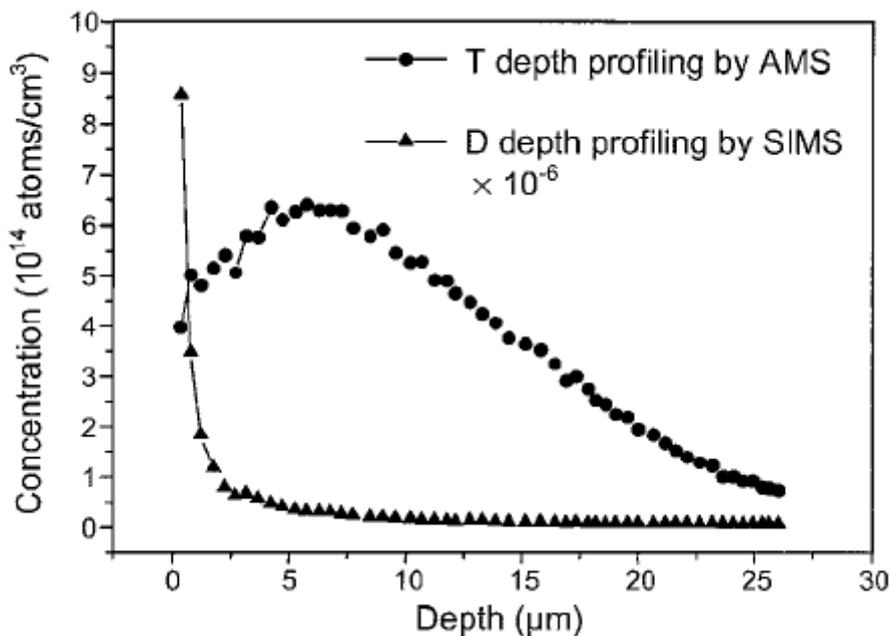


Figure 29: Tritium and Deuterium in Depth measured by AMS [Friedrich, 2001]

Tritium contamination is highly possible with the AMS system, therefore, great care must be taken and only small amount of tritium can be investigated safely.



6.7 Tritium analysis in ITER plasma

In a fusion reactor, Tritium accountancy is quite important both for safety and for T self-sufficiency. The largest T retention appears in plasma-facing surfaces. At present, T retention is estimated from the balance between fuel supply into the reactor vessel and its exhaust from the reactor vessel. However, T retention accuracy is quite poor, and hence, the development of techniques to quantify the T retention in the reactor vessel is urgent.

In a whole chapter [Testsuo Tanabe, 2017] different techniques are described to allow a direct measurement of Tritium in the Plasma. Therefore remote and not destructive techniques are systematically considered for fusion application. In these new developments, the measurement corresponds to quite high activities of tritium.

7 Conclusions

Tritium measurement is very difficult because the radionuclide is generally volatile, and the range of the electron produced in air is very short. This radionuclide must be generally quantified with high accuracy. Lots of regulations already exist and naturally must be followed.

The most well-known technique for tritium measurement is known as Liquid Scintillation Counting (LSC) but this can be done only in liquid matrix. Even if this technique is very sensitive, liquid scintillators remain toxic and moreover the tritium measurement produces nuclear wastes that must be treated after.

Other important techniques have been described in this review that can be used for solid and gas investigations. Main techniques correspond to destructive methods and only few of them are non-destructive. Autoradiography is proposed as an interesting non-destructive technique to measure tritium.

Measurement of tritium contamination in depth of a solid material is still a challenge. Ion beam technology and LIBS can theoretically be used but lots of research must be performed to assess the potentialities of the techniques in terms of tritium evolution during the measurement and tritium contamination.

These three techniques Autoradiography, Ion beam technology and LIBS will be developed during the TRANSAT project.

Detection limits for tritium can be very low. The detection limits of several Bq cm⁻² on solid surfaces and 0.01 Bq cm⁻³ in water are attained.

R&D is still going on for tritium analysis for environmental purposes, and decommissioning purposes particularly with reference to ITER. Measurements of tritium in plasma is very important but remain a challenge. In any Tritium handling systems, H-3 accountancy for radiological safety is an important matter, so that it must be monitored and quantitatively accounted.

Problem of contamination and memory effect can be an actual trouble for different tritium analysis.

8 References

Bachelet, Fabre, Salmon, Brix, « Tritium impurities measurements based on gas chromatography », Tritium 2016 conference, Charleston USA

Baglan, Ansoborlo, Cossonnet, Fouhal, Deniau, Mokili, Henry, Fourné, Olivier: «Tritium metrology within different media: focus on organically bound tritium (OBT) », Radioprotection 2010, Vol. 45, n 3, p 369 -390

Bray, Pailloux, Plumeri, « Tritiated water detection in the 2.17 μm spectral region by cavity ring down spectroscopy », Nuclear Instruments and Methods in Physics Research A (2015), 789, 43-49.

Bükki-Deme, Alecu, Kloppe, «First results with the upgraded TLK tritium calorimeter IGC-V0.5) », Fusion Eng. Des. 2013, 88, 2865–2869

Connan, Hebert, Solier, Maro, Pellerin, Voiseux, Lamotte, Laguionie, « Atmospheric tritium concentrations under influence of AREVA NC La Hague reprocessing plant (France) and background levels » Journal of Environmental Radioactivity 177 (2017) 184-193



- DOE Handbook** (2008), « TRITIUM HANDLING AND SAFE STORAGE »
- Fichet**, Bresson, Leskinen, Goutelard, Ikonen, Siitari-Kauppi « Tritium analysis in building dismantling process using digital autoradiography» J Radioanal Nucl Chem 2012, 291, 869–875
- French Authority ASN** « Livre Blanc », 2010
- Friedrich**, Pilz, Sun, «Tritium depth profiling by AMS in carbon samples from fusion experiments. » Phys. Scr. 2001, 94, 98-101
- Grisolia**, Semerok, Weulersse, Le Guern, Brygo, Thro, Coad, Bekris, Stamp, Rosanvallo, Piazza, «In-situ tokamak laser applications for detritiation and co-deposited layers studies» Journal of Nuclear Materials, (2007) 363, 1138-1147
- Harmon**, Knox, Srinivasan, « Detection and profiling of tritium in solids» Journal of Nuclear Materials, 176-177 (1990), 1018-1021
- Haudebourg**, Fichet «A non-destructive and on-site digital autoradiography-based tool to identify contaminating radionuclide in nuclear wastes and facilities to be dismantled» J Radioanal Nucl Chem, 2016, 309, 551–561
- IAEA**, (1970) Technical reports series N°120, « Monitoring of radioactive contamination on surfaces».
- Ion beam analysis** technique. (2018) Retrieve from <https://sites.google.com/a/lbl.gov/rbs-lab/ion-beam-analysis>.
- Ishibashi** et al., «Lunar and Planetary Science Conference» 2014 Abstract #2080
- ISO 13168** (2015), Water Quality « Simultaneous determination of tritium and carbon 14 activities- Test method using liquid scintillation counting »
- ISO 7503-2** (2017), «Measurement of Radioactivity – Measurement and evaluation of surface contamination – Part 2: Test method using wipe-test samples».
- ISO EN 9698** (2015), «Water quality – Determination of tritium activity concentration – liquid scintillation counting method».
- ITER** fusion reactor. (2017) Retrieve from <https://www.iter.org/fr/mach/tritiumbreeding>
- Kresssig**, Grötzel, Behrisch, «Simultaneous measurement of the hydrogen isotopes H, D, T and ³He with HIERD», (1994) Nuclear Instruments and Methods in Physics Research B, 85, 71-74.
- Leo** «Techniques for Nuclear and Particle Physics Experiments» (1994) Springer Verlag
- Leskinen**, Fichet, Siitari-Kauppi, Goutelard «Digital autoradiography (DA) in quantification of trace level beta emitters on concrete» J Radioanal Nucl Chem 2013, 298, 153–161
- LNHB**, www.lnhb.fr
- JR Johnson** (1991) «Recommended tritium surface contamination release guides», DOE 91 016047
- JP Patent 3041386 A** (1991), «Amount of tritium in the concrete in a nondestructive measurement method and apparatus»
- Malaquias**, Philipps, Huber, Hakola, Likonen, Kolehmainen, Tervakangas, Aints, Paris, Laan, Lissovski, Almaviva, Caneve, Colao, Maddaluno, Kubkowska, Gasior, van der Meiden, Q.Xiao, «Development of ITER relevant laser techniques for deposited layer characterisation and tritium inventory», Journal of nuclear materials 2013, 438, S936-S939
- Matsuyama**, Watanabe, Hasegawa «Tritium assay in materials by the bremsstrahlung counting method. » Fusion engineering and Design (1998) 39- 40, 926-936.
- Matsuyama**, Murai, Watanabe «QUANTITATIVE MEASUREMENT OF SURFACE TRITIUM BY B-RAY INDUCED X-RAY SPECTROMETRY (BIXS)» Fusion Science and Technology (2001), 41, 505-509
- Matsuyama**, Chen, Nisimura, Akamaru, Y.Torikai, Y.Hatano, N.Ashikawa, Y.Oya, K.Okuno, T.Hino Trapping and depth profile of tritium in surface layers of metallic materials. » Journal of Nuclear Materials. (2011) Issue 1-3. 900-903.



Matsuyama, Abe «Advanced β -ray-induced X-ray spectrometry for non-destructive measurement of tritium retained in fusion related materials. » Fusion Engineering and Design (2016), 109-111, 1569-1573

Mercadier, Grisolia, Roche, Semerok, Hermann, Pocheau, Thro, Sirven, Weulersse, Mauchien, Sentis «In Situ Tritium Measurements and Control by Laser Techniques», Fus Sci Technol, 2011, 60 1049-1052

NCRP (1976), National Council on Radiation Protection, “«Tritium Measurements Techniques»

NF M60-321 (2005), «Nuclear energy – Nuclear fuel cycle technology – waste – Non-intrusive, non-destructive determination of the tritium activity of a package containing tritiated waste by measurement of helium-3 leakage from the package»

NF M60-312 (1999), «Nuclear energy – Measurement of environmental radioactivity – Air – Determination by liquid scintillation of the activity concentration of atmospheric tritium sampled by sparging technique (air through water) »

NF M60-309 (2001) «Nuclear Energy-Nuclear fuel technology-waste-tritium releasing assay in tritiated waste packages by ionization chamber»

NF M60-327 (2008), «Nuclear energy – Nuclear fuel technology – waste- determination of released tritium from radioactive waste packages»

NF M60-822-0 (2014) «Radioactivity measurement in gaseous effluents – Determination of tritium and C14 activity in gaseous effluents and gas discharge-Part 0: Calculation of tritium or carbon-14 released activities. »

NF M 60-822-1 (2012) «Nuclear energy- Radioactivity measurement in gaseous effluents- Determination of tritium and C14 activity in gaseous effluents and gas discharge-Part 1: Sampling of tritium and C14 in gaseous effluents. »

NF M60-822-2 (2011) «Nuclear energy-Radioactivity measurement in gaseous effluents- Determination of tritium and C14 activity in gaseous effluents and gas discharge – Part 2: Determination of tritium activity in the trapping solution of gaseous effluents or gas discharge sampled by sparging. »

NF M60-325 (2005) «Nuclear energy-Nuclear fuel cycle technology-waste-determination of tritium activity in waste by liquid scintillation. ».

Ochiai, Hayashi, Kutsukake, «Measurement of Deuterium and Tritium retentions on the surface of JT-60 divertor tiles by means of nuclear reaction analysis. » J. Nucl. Mater. 2004, 329–333, 836–839

Oh, Warwick, Croudace, Lee, « Rapid determination of tritium and carbon-14 in urine samples using a combustion technique» J Radioanal Nucl Chem (2014) 299; 187-191

Paris, Butikova, M Laan, M Aints, A Hakola, K Piip, I Tufail and P Veis «Detection of deuterium retention by LIBS at different background pressures», Phys Scr (2017) T170 – 014003

Piip, van der Meiden, Hämarik, Karhunen, Hakola, Laan, Paris, Aints, Likonen, Bystrov, Kozlova, Založnik, Kelemen, Markelj «LIBS detection of erosion/deposition and deuterium retention resulting from exposure to Pilot-PSI plasmas» J Nucl Mater 2017, 489, 129-136

Piip, van der Meiden, Bystrova, Hämarik, Karhunen, Aints, Laane, Paris, Seemene, Hakolac, Brezinsek «Loading of deuterium and helium by Pilot-PSI plasma and their detection by in-situ LIBS», Nucl Mater Energy 2017 12, 694-698

Priester, Klein, «Tritium Activity Measurements with a Photomultiplier in Liquids-The TRAMPEL experiment», Fusion Engineering and Design 2016, 109-111, 1356-1359

Pujol, Sanchez-Cabeza, «Optimisation of liquid scintillation counting condition for rapid tritium determination in aqueous sample», J Radioanal Nucl Chem 1999, 242(2) 391-398.

Röllig, Priester, Babutzka, Bonn, Bornschein, Drexlin, Ebenhöch, Otten, Steidl, Sturm «Activity monitoring of a gaseous tritium source by beta induced X-ray spectrometry» Fusion Engineering and Design. (2013), 88, 1263-1266.



Rudolph, Bauer, Gippner, Grambole, Heiser, Herrmann, Thomas, «Hydrogen determination by means of the $^1\text{H}(^{19}\text{F}, \alpha\gamma)^{16}\text{O}$ and $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ resonance reactions» 1984, Journal of Radioanalytical and Nuclear Chemistry, 83, 99-105

Semerok, Grisolia «LIBS for tokamak plasma facing components characterization: Perspectives on in situ tritium cartography» Nuclear instruments & methods in physics research section A- Accelerators spectrometers detectors and associated equipment, (2013), 720, 31-35

Suchoňová, Veisa, Karhunen, Paris, Pribulaa, Piip, Laan, Porosnicu, Lungu, Hakola, «Determination of deuterium depth profiles in fusion-relevant wall materials by nanosecond LIBS», Nucl Matter Energy 2017 12, 611-616

Suyanto, Lie, Niki, Kagawa, Fukumoto, Hedwig, Rinda, Abdulmadjid, Marpaung, Pardede, Suliyanti, Hidayah, Jobilong, Lie, Tjia, Kurniawan «Quantitative Analysis of Deuterium in Zircaloy Using Double-Pulse Laser-Induced Breakdown Spectrometry (LIBS) and Helium Gas Plasma without a Sample Chamber» *Anal. Chem.*, 2012, 84 (5), 2224–2231

Tarancon, Bagan, Garcia, «Plastic scintillators and related analytical procedures for radionuclide analysis», J Radioanal Nucl Chem (2017), 314, 555-572

Tetsuo Tanabe Editor «Tritium: Fuel of Fusion Reactors» Springer 2017

XP M60-824 (2016) « Nuclear energy – measurement of radioactivity in the environment – Determination of tritium activity in the environment – Test method for the analysis of tritium in free water and organically bound tritium in environmental matrices.

Varlam, Ionita, Stefanescu, Dumitru «Comparative study between external standard method and internal standard method for low level tritium measurements», International Conference Nuclear Energy in Central Europe 2001

Warwick, Kim, Croudace, Oh, « Effective desorption of tritium from diverse solid matrices and its application to routine analysis of decommissioning materials », *Anal Chim Acta* (2010) 676 (1-2), 93-102

Xia, Ding, Zhang, Long, Luo, Peng, Hutton, Shi,* «Cross-section for proton–tritium scattering from 1.4 to 3.4 MeV at the laboratory angle of 165» Nuclear Instruments and Methods in Physics Research B 266 (2008) 705–708

Založnik, Iztok, Cadez, Markelj, « In situ hydrogen isotope detection by ion beam methods ERDA and NRA», Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 2016, 371, 167-173