# Analysis of Fission Gas Release Kinetics by On-Line Mass Spectrometry

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*Abstract*—The release of fission gases (Xe and Kr) and helium out of nuclear fuel materials in normal operation of a nuclear power reactor can constitute a serious limitation of the fuel lifetime. Moreover, radioactive isotopes of Xe and Kr contribute significantly to the global radiological source term released in the primary coolant circuit in case of accidental situations accompanied by loss of fuel rod integrity. As a consequence, fission gas release investigation is of prime importance for the nuclear fuel cycle economy, and is the driving force for numerous R&D programs. In this domain, for understanding current fuel behavior issues, preparing the development of new fuels (e.g., for Gen IV power systems) and for improving modeling prediction capability, there is a marked need for innovations in the instrumentation field, mainly for:

- Quantification of very low fission gas concentrations, released from fuel sample and routed in sweeping lines,
- Monitoring of quick gas release variations by quantification of elementary release during a short period of time,
- Detection of a large range of atomic masses (e.g., $H_2$, HT, He, CO, $CO_2$, Ne, Ar, Kr, Xe), together with separation of isotopes for Xe and Kr elements,
- Coupled measurement of stable and radioactive gas isotopes, by using mass spectrometry and gamma spectrometry techniques in parallel.

To fulfill these challenging needs, a common strategy for analysis equipment implementation has been set up thanks to a recently launched collaboration between the CEA and the University of Provence, with the support of the Liverpool University. It aims at developing a chronological series of mass spectrometer devices based upon quadrupole mass filters and 2D/3D ion traps with Fourier transform operating mode. These devices have superior performance to match the previous challenges for out-of-pile and in-pile experiments. The final objective is to install a high performance on-line mass spectrometer coupled to a gamma spectrometer in the fission product laboratory of the future Jules Horowitz Material Test Reactor. An intermediate step will consist of testing prototype equipment on an existing experimental facility in the LECA-STAR Hot Cell Laboratory of the CEA Cadarache.

This paper presents the scientific and operational risks linked to fission gas issues and summarizes the current state of art for analyzing them in nuclear facilities. It details the skills gathered through this collaboration and the development approach of the mass spectrometer set-up to overcome technological problems. Finally the paper describes a proposed implementation strategy for the nuclear research facilities of CEA Cadarache.

*Index Terms*—2D/3D ion trap mass spectrometry, in-pile and out-of-pile fission gas release kinetics measurement, material testing reactor, multiphoton ionization, on-line mass filter.

## I. INTRODUCTION

IN the nuclear fuel cycle, major scientific, technological and economic challenges are associated with the fuel behavior under irradiation in nuclear power plant. A severe technological obstacle, having a major impact on the cost of the fuel cycle and hence the production cost of the energy generated, comes from the fission products (FP) and the alpha decay (helium nuclei) generated in the fissile material and partly released in the inner free volumes of the fuel element.

Among the very large number of chemical elements constituting the fission products, a privileged family consists of the Xe and Kr gases, with which gases from ternary fission (mainly tritium and helium) are associated. This so-called family of "fission gases" (FG) is considered as the most reliable indicator of the behavior of the fissile matrix because of:

- Their behavior (distribution, release) closely linked to the local heat transfer and the microstructure (microcracking, grain boundaries, etc.) of the fissile material,
- Their insensitivity to physicochemical reactions with other chemical elements (fission products, oxygen, etc.),
- The absence of trapping or adsorption on the surfaces which may be encountered after they leave the fissile matrix (first barrier, sweeping lines, volumes, filters, etc.), even during sharp drops in their initial temperature,
- The many radioactive or stable isotopes making up this family, making them useful as genuine "radioactive clocks" to trace the processes governing their generation, migration and release over various timescales (from a few minutes to a few years).

A recent and important R&D area has been opened up by the study of the creation and release of He produced by the alpha decay of certain transuranic isotopes. This can lead to large quantities of He nuclei in the case of specific fuels, such as mixed oxide (U, Pu) materials called "MOX fuel", or in that

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of fuel targets mainly consisting of isotopes of minor actinides, for their irradiation in fast breeder reactors or dedicated to their destruction by "incineration". Moreover, the interest in He and its low temperature behavior has strengthened in recent years due to studies on the disposal and long-term storage of spent fuels. These various topics consequently encouraged the launch of basic research on the behavior of He, a field in which many issues are still outstanding.

Even at a level of a few percent, the release of fission gases (Xe and Kr) and helium out of nuclear fuel materials in normal operation can constitute a serious limitation of their lifetime in nuclear power reactors. On one hand, the internal pressure increase in the fuel element caused by the FG release could reach high values in operation, values not compatible with safety criteria, expressed as maximum internal pressure threshold at the fuel end of life, limiting internal mechanical stresses and ensuring the fuel element tightness. Moreover, radioactive isotopes of Xe and Kr contribute significantly to the global radiological source term released in the primary coolant circuit in case of accidental situations accompanied by fuel rod loss of integrity.

As a consequence, it is crucial to identify the mechanisms and laws governing the behavior of fission gases generated in the fuel matrix in order to trace the reaction mechanisms of atom coalescence and migration under the form of atoms or bubbles. These mechanisms depend on a large number of parameters (fuel material type, microstructure type, irradiation conditions including power transients, etc.) and govern the use conditions of the irradiated fuel.

Today, these studies are carried out mainly through two types of experiments:

1. Separate effect irradiation experiments in material test reactors on monitored gas tight fuel samples [1].
   These programs deal mainly with the nominal conditions (base irradiation and power variations) and some incidental situations (e.g., power ramps). For measuring fission gas release, they use mainly integrative measurements (e.g., total or differential pressure sensors connected to the internal free volume of the sample). In some cases, it is possible to sweep the released fission gases thanks to a specific gas line and to route them in a dedicated facility (fission product laboratory, analysis unit etc.) where on-line and delayed measurements on samples can be made, either by gamma spectrometry or by gas chromatography.

2. Experiments on small fuel samples in hot cells, designated to simulate accidental conditions.
   The objective is to gain data on gas release values and kinetics in various temperature time histories and atmospheres. For this aim, the gas release kinetics are mainly monitored by on-line gamma spectrometers and gas chromatographs by a sweeping gas previously in contact with the sample, and off-line mass spectrometers sampling gases accumulated in pre-voided capacities [2]. Implementation of on-line mass spectrometers is not yet widespread.

Off-line analyses suffer loss of data concerning the parameters and dynamic processes of formation and release, due to the integrative nature of the analysis. They are in particular not well

adapted to monitor fission gas release kinetics and threshold identification, resulting from a power or a temperature transient applied to the sample. Moreover the delayed measurement of short half-life radionucleides causes practical constraints (handling, radioprotection …) in order to avoid a total radioactive decay of the atoms before the start of measurement.

On-line measurements can be applied only with a sufficient detection level; this means either when the gas release rate is significant, or when the required time resolution is not too great and allows accumulating sufficient information during a given period. In this case the release phenomenon is supposed to be constant during accumulation. This measurement method is relevant for base irradiations or when the experimental protocol provides steady-state periods.

## II. CURRENT STATE OF ART FOR FISSION GAS RECOVERING AND ON-LINE MEASUREMENT IN NUCLEAR R&D FACILITIES

Recovering of fission gases released from the sample is certainly the most relevant method for gaining valuable scientific results, because the measurement can be done quantitatively on isotopes in order to be able to calculate continuously the isotope release rate (atoms/s). At present, in order to measure the widest possible range of fission gas isotopes, often combined with the gases of alpha decay and ternary fission (mainly tritium and helium [3]), various methods are employed in a nuclear R&D facility. They can be divided into two classes according to the target isotopes: (1) methods for counting radioactive gas isotopes, such as gamma spectrometry [4] or beta spectrometry (for tritium) for example; (2) methods for counting stable or long-lived gas atoms, mainly by gas chromatography and mass spectrometry, with several means for concentration of atoms before injection into the measurement chamber. Moreover, the application/installation (on-line and/or off-line) of these two classes and their coupling are different according to the type of nuclear facility, out-of-core: hot cell laboratory, or in-core: MTR (experimental Material Test Reactor), TRIGA-type reactor (Training, Research, Isotopes, General Atomics), safety dedicated reactor for example, etc.

### A. Out-of-Pile Facilities

Today, the analytical systems associated with experiments conducted out-of-pile in post-irradiation examination in hot cell laboratories are the most complete. They often serve to analyze the release of fission products of different types of fuels in incidental conditions (power or thermal transients), accidental conditions (loss of primary coolant or local injection of reactivity) or severe accidental situations causing fuel relocation. The platforms associated with these experiments are accordingly made up of a fluid loop which, in addition to the measurement devices, comprises a set of processing elements (condenser, filter, cold trap, carrier gas feed, etc.), a set of conventional sensors (flow rate, pressure, temperature) and a annealing test furnace (induction furnace or heating element according to the target temperature range) in which a sample of fuel to be analyzed is inserted.

The main experimental platforms in the world are: Horizontal Induction (HI)/Vertical Induction (VI) [5] (1981–1993)
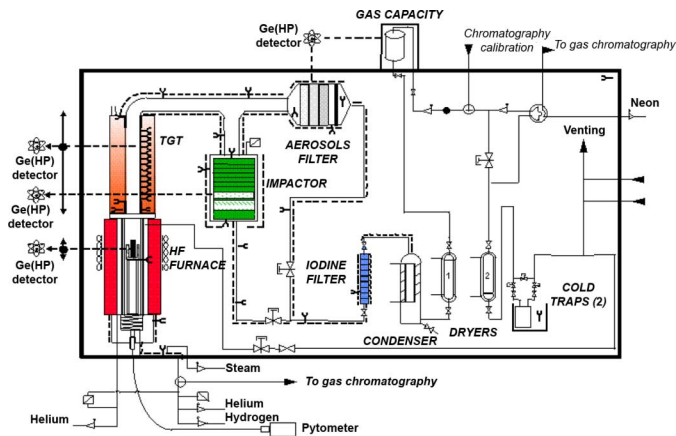
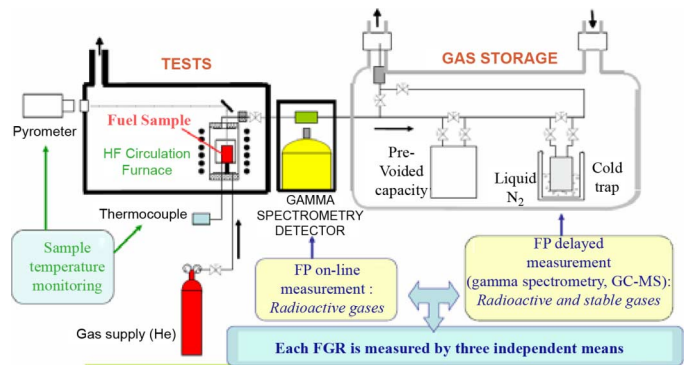Fig. 1. Schematic of the VERCORS HT facility at the CEA Grenoble.



Fig. 2. Fluid schematic of the MERARG facility at the CEA Cadarache.
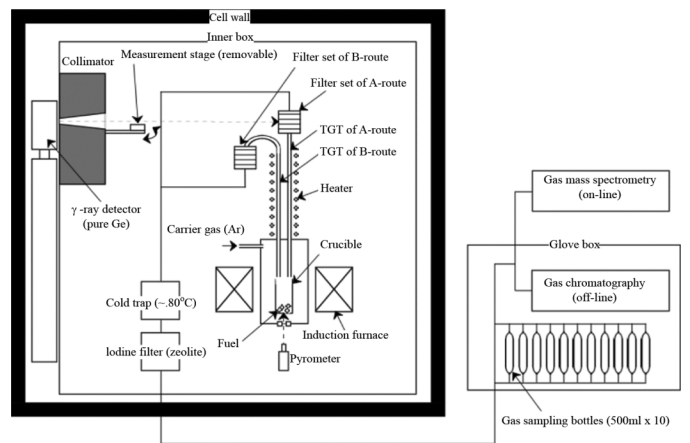


Fig. 3. Experimental circuit of the FP measurement platform in Japan (Reprinted from J. Nucl. Sci. Technol. [11] with permission from The Atomic Energy Society of Japan).

of the Oak Ridge National Laboratory (ORNL) in the United States; chronologically HEVA [6], then VERCORS [7]–[9] then VERDON and MERARG (Moyen d'Etude par Recuit et Analyse des Relâchements Gazeux) of the CEA in France; VEGA of JAERI (1999) in Japan, and the Chalk River Laboratories (CRL) facility of Atomic Energy of Canada Limited (AECL). We shall provide details of some of these platforms by focusing on the associated measurement methods.

The (HI)/(VI) platform of ORNL has a system for collecting fission products [5] adapted to the Zircaloy clad $UO_2$ fuel highly irradiated in light water reactors (LWR) for which on-line and off-line analyses are conducted. This is because this line has a cold trap to collect the fission gases, which are then measured by a radiation detector. The target species are radioactive isotopes of caesium and $^{85}Kr$. Moreover, all the long-lived compounds for each test are sampled and analyzed off-line by various techniques: gamma spectrometry, neutron activation analysis of iodine and bromine, spark-source mass spectrometry (SSMS) to analyze heavier elements (e.g., heavier than neon) and emission spectrometry for Mo, Te, Ba and Sn.

The CEA VERCORS (1983–2002, CEA Grenoble) (Fig. 1) experimental platform [7]–[9], developed for better quantification of volatile fission product release in accidental conditions on PWR type fuel, also comprises on-line and off-line instrumentation.

A gas chromatograph (for measurement of the hydrogen emission kinetics and CO quantification) and three additional gamma spectrometers are installed to measure on-line the release kinetics of the fission products. The first spectrometer measures the FP leaving the fuel. It provides access to differential data on the release rate of each FP, but with a low sensitivity of about 10% of the initial inventory for each FP. Although the method displays drift during degradation of the fuel at high temperature, it is very useful for measuring the release of each FP. The second one, located above an aerosol trap, is used to measure deposited fission products, usually the most volatile and in small amounts (often less than 1% of the initial quantity released). The third detector is used to measure fission gases such as isotopes of Xe ($^{133}Xe$, $^{133m}Xe$, $^{135}Xe$, generated during a short re-irradiation run in the SILOE experimental reactor)

and krypton ($^{85}Kr$ created in a nuclear power plant) with very high sensitivity and an excellent measurement dynamic range (from $10^{-9}$ to $10^{-1}$ of the initial inventory per minute).

The MERARG platform [10] (Fig. 2), currently being operated in the hot laboratory at the CEA Cadarache, is used to qualify fuels in simulated incidental conditions (i.e., thermal transients), also has the feature of comprising on-line measurements, in addition to a gamma spectrometry detector, and a micro-gas chromatograph ($\mu$-GC). The only radioactive isotope analyzed by gamma spectrometry in this facility is $^{85}Kr$. In the same way as for gamma spectrometry, the $\mu$-GC allows measurement of the gas kinetics and release rate. However, it provides additional elementary data on the fission gases (Kr and Xe) and He. Besides, the fission gases are collected in vessels for off-line analysis by GC-MS (using a linear quadrupole type analyzer). This analysis helps determine the stable and active gases by their atomic weight.

The Japanese platform (Fig. 3) dedicated to the measurement of FG (Kr, Xe) release, also in incidental thermal conditions, for MOX fuels previously irradiated in the JOYO fast research reactor in Japan [11], has the original feature of the installation of an on-line mass spectrometer coupled with a gamma spectrometer focusing on the radioactive products. The mass spectrometer (ULVAC, MASSMAT-200) measures the concentrations of the various FP in argon (carrier gas). At the same time, part of

the gas is stored in sampling cylinders, and then analyzed by an off-line chromatograph (G2800T YANAGIMOTO). The results presented concern the detection of $^{84}$Kr and $^{132}$Xe only. The quantities detected are $\sim 100$ ppm for Kr and $\sim 250$ ppm for Xe.

### B. In-Pile Facilities

At present, the loops associated with the experiments carried out in pile, namely, directly in the research reactor, are as varied as those out-of-pile, despite specific constraints related to work in an operating nuclear reactor.

Firstly, in MTR reactors such as Osiris (France), HFR (Holland), ATR (United States), the only measurement method routinely used in-pile is on-line gamma spectrometry. This is used for example for continuous monitoring of the isotopes released in automatic mode. Moreover, it was recently employed in connection with various international programs for the investigation of new fuels (in the form of compact geometry or pebbles) dedicated to HTR (High Temperature Reactor) power systems. Mass spectrometry is then only employed in the case of off-line analyses of gases previously sampled during irradiation of the fuel to be qualified, and so far with relatively low sensitivity when the measurements are taken on site. This sampling of carrier gas sweeping the fuel takes place on smaller pre-voided capacities, sometimes with a previous "trapping" concentration stage demanding a large scale refrigeration installation (with liquid nitrogen), and only providing integrated data. As examples, recent or on-going experiments on this subject concern the programs EU1 and EU1bis in HFR, the programs AGR1 and AGR2 in ATR (United States). One can also mention the design on an on-line gamma spectrometry bench for the HTR SIROCCO program in Osiris, but the irradiation has not started.

In a similar manner, the measurement of the stable gases during a fuel experiment in MTR has been the subject of the European "MTR $+$ I3" program (Integrated Infrastructure Initiative of the 6th PCRD, 2006–2009) bringing together teams from NRG (the operator of the HFR reactor and the experiments conducted therein, Petten, Holland), ITU (Institut des Transuraniens, Karlsruhe, Germany), PSI (Paul Scherrer Institute, Villigen, Switzerland), IRSN (Institut de Radioprotection et de Sûreté Nucléaire, Cadarache, France) and the CEA. The objective was to use an installation for measuring stable gases directly connected with the circuits of the HTR EU1 experiment in HFR. This led to the design of a sampling and analysis rack based on a concentration on a cold trap owing to the very low concentrations to be measured (about $10^7$ to $10^8$ at/cm$^3$ of carrier gas, leading after trapping to inventories of $10^{12}$ to $10^{14}$ atoms depending on trapping time), and a selected mobile mass spectrometer model. The prolonged shutdown of the HFR for repairs prevented the transition to the construction phase of the system and its use in a schedule compatible with the progress of "MTR+I3". However, a conceptual design report details the results obtained on the preliminary calculations of the experiment, the technological aspects (choice of components, integration in an analysis rack), the experimental protocol, the safety analysis demanded by the reactor operator, the financial assessment of the equipment, the analysis method of the results, the liability,
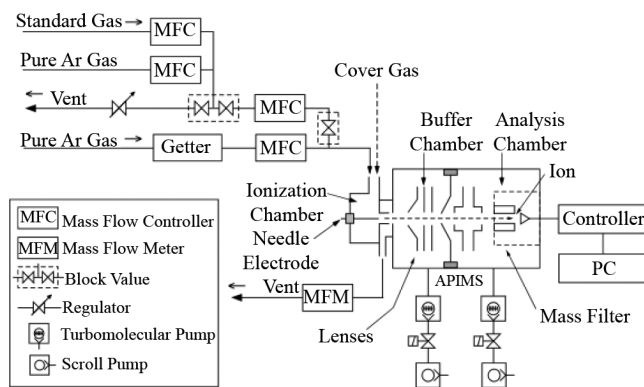


Fig. 4. Principle of the Atmospheric Pressure Ionization Mass Spectrometer (Reprinted from Nucl. Instrum. Methods Phys. Res. Sect. A-Accel. Spectrom. Dect. Assoc. Equip. [16] with permission from Elsevier).

confidentiality, and ownership aspects of the results. This European document can serve as a reference basis for creating new equipment in a MTR and in the future Jules Horowitz Material Test Reactor (JHR) [12], [13].

Second, a TRIGA-SPEC loop which incorporates two types of measurement: one in laser spectroscopy and one in mass spectrometry is being installed on the TRIGA-Mainz reactor [14], [15] in Germany. Mass spectrometry combines a mass spectrometer with a double Penning trap, a magnetic resonance cell (FT-ICR) and a TOF-ICR type analyzer. This loop has been developed so as to start by measuring heavy nuclei ($^{252}$ Cf) off-line and then subsequently, it will be used for the on-line quantification of FP emitted by targets. This loop will be a highly original installation with a mass spectrometer having high sensitivity (ultrasensitive measurement: 1 ion detected), but which is very bulky.

In addition, Hideki Harano and Chikara Ito [16] examined the solution of an atmospheric pressure ionization mass spectrometer (APIMS) (Fig. 4) for application of on-line and real time monitoring of the fission products release in the headspace of fast reactors. This solution was validated at the laboratory scale on a device with dilution and mixing of standard gases. This unit is capable of measuring quantities of Kr and Xe down to 1 ppt.

Its principle is based on the ionization of the gas at atmospheric pressure by a corona (or other) discharge of 1.25 kV. This type of ionization serves to eliminate most of the interfering elements, impurities, and thereby increase the concentration of the fission gases. APIMS uses a linear quadrupole (ULVAC, UG-500) with an operating pressure of $10^{-4}$ Pa. The system has a calibration loop using a 99.9999% pure argon carrier gas and two-step dilution method with four mass flow controllers. The results obtained are 65 ppt for $^{84}$Kr and 7.5 ppt for $^{132}$Xe. The detection limit for quantitative analysis is estimated at 20 ppt for $^{84}$Kr and 2.3 ppt $^{132}$Xe. However, this instrument has a number of drawbacks. On the one hand, during the ionization phase, some isobaric interfering elements are created, obscuring the detection of $^{78}$Kr, $^{80}$Kr, $^{124}$Xe and $^{126}$Xe. In addition, this type of analyzer introduces a background level increase of the spectrum.

Iwata et al. [17] examined another solution for measuring traces of Xe and Kr isotopes at 1 ppt in argon: the "Resonance
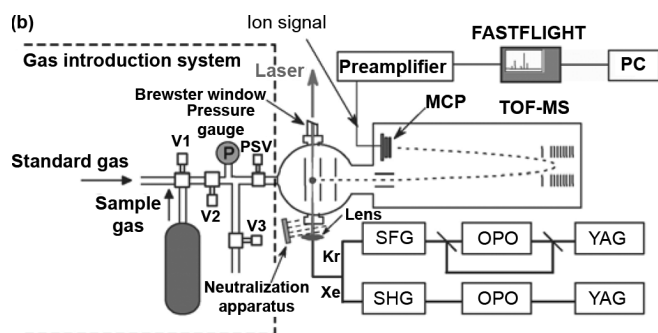
Fig. 5. Loop for measuring the isotopes (Xe, Kr) by Resonance Ionization Mass spectrometry (Reprinted from Int. J. Mass Spectrom. [17] with permission from Elsevier).

Ionization Mass spectrometry" (RIMS), with a time-of-flight analyzer (Fig. 5). This solution is still feasible for the localization and detection of damaged fuels in fast reactors. The device was tested with 100 ppt of Xe and 100 ppt Kr in Ar carrier gas. They observed and avoided the formation of $Ar^+$ and $Ar_2^+$ created by photo electrons due to reflections of the laser beam inside the vacuum chamber. The detection limit for quantitative analysis of Xe and Kr isotopes is 1 ppt.

## III. CURRENT ISSUES AND IMPROVEMENT NEED

For understanding current fuel behavior issues, developing of new fuels (e.g., for Gen IV power systems) and improving the modeling prediction capability and accuracy, there is a marked need for innovations in this instrumentation field, mainly for:

- Quantification of very low fission gas concentrations in fuel sample sweeping lines, with a magnitude order of $10^8 - 10^{10}$ at/cm$^3$,
- Monitoring of quick gas-release variations by quantification of elementary release during short periods (about 1 min),
- Detection of a large range of atomic masses (e.g., $H_2$, HT, He, CO, $CO_2$, Ne, Ar, Kr, Xe), together with isotope separation for Xe and Kr elements,
- Coupling of measurement of stable and radioactive gas isotopes, to obtain the complete status of the released isotopes, by using mass spectrometry and gamma spectrometry techniques in parallel.

The determination of the kinetics of fission gas release requires a sampling system and a mass spectrometry device having on-line and real time functionalities. Particular attention must be paid to the delay and segregation that process sampling and mass spectrometer sampling device can induce.

The detection of Xe and Kr isotope traces, at some tens of ppt for the lowest threshold level, in a carrier inert gas, e.g., He, Ne or Ar depending on the experiment constraints, requires a very high sensitivity mass spectrometer. Also the qualitative and quantitative identification of low mass isotopes in the mass-over-charge ratio range m/z 1–6 requires a high-resolution mass spectrometer. For example, to separate HT and $^4$He, resolution must be greater than 188, and to separate HT and $D_2$, greater than 930.

The trace detection of a targeted isotope among other compounds to be detected, isobaric compounds and the carrier gas leads to gain high-level performances at each stage of the mass spectrometer.

The selectivity criterion can be highlighted when the gaseous compounds are neutral, for instance, by the use of a getter pump to remove spurious compounds from the gas flow to be injected into the mass spectrometer. In the ion source, both the ion creation must be selective and the ionization yield very high. For example, the carrier-gas ion creation must be avoided as far as possible. With an Ar carrier gas, the creation of $Ar_2^+$ ion, an isobaric ion of the $^{80}Kr^+$ ion, can occur [17]. An ion mass-selective stage located before the mass analyzer reduces the number of spurious ions injected into the mass analyzer and consequently reduces possible shifts in mass identification of this latter stage. The mass analyzer must achieve both high-sensitivity and high-resolution performance.

## IV. SKILL IN MASS SPECTROMETRY

Two research groups at the Aix-Marseille Université and at the University of Liverpool are involved in the collaboration with the CEA. They will develop the on-line quadrupole mass spectrometer instrumentation including ion sources, 3D/2D ion traps and mass filter according to their complementary skills.

### A. Aix-Marseille Université

Whereas Fourier Transform (FT) techniques are common in Ion Cyclotron Resonance (ICR) mass spectrometry [18], and more recently in the Orbitrap™ instrument [19], only a few studies refer to non-destructive FT techniques applied to a Radio Frequency (RF) quadrupole 2D linear ion trap [20] or 3D ion trap [21], [22]. The advantage of FT techniques is the high sensitivity of detection. For many years, the research group of the Aix-Marseille Université has developed a mass spectrometer using a 3D quadrupole ion trap running a Fourier Transform operating mode, denoted as FTQIT-MS [23]. A 3D ion trap is chosen, in so far as it is a relatively simple tool requiring only an RF electrodynamics field.

This operating mode employs a destructive measurement technique with a total ejection of the confined ions and the recording of a Time-Of-Flight (TOF) histogram of the ejected ions by means of a fast electron multiplier [23]. Hence, a signal image of the simultaneously confined ions as a function of confinement time is extracted from a set of TOF histograms related to elementary experiments statistically the same and repeated for increasing confinement times. Typically the number of elementary experiments is some thousands. The image signal is a superposition of the axial secular frequencies of the simultaneously confined species. The frequency spectrum is obtained by Fourier transformation of this signal. The mass-over-charge ratio of the confined ionic species is connected to their detected axial secular frequencies.

With FT techniques, as ion motion trajectory depends on initial conditions in position and velocity of the confined ions, either ion motion must be rendered coherent prior analysis [24], [25] or ions must have particular distributions of initial positions and velocities [26] to increase the signal over noise ratio of the detected image signal. With the Steady Ion Flow Injection Mode (SIFIM is an injection mode discovered by the research group)

initial conditions can be chosen such as the detected signal dynamics is optimal [27].

Despite the fact that the mass spectrometer uses an RF quadrupole ion trap, it has been proved in experiment that high resolution can be achieved: e.g., Xe isotopic ions in natural composition have been measured with a resolution of c.a. 4000 [28].

Earlier works of the group concern the development of ion sources using a selective technique to create negative ions by attachment of Rydberg electrons of a noble gas to electrophylic molecules in a crossed beam experiment [29]. The noble gas was excited in Rydberg states by a spectroscopic method using YAG + DYE lasers [30] or by electrons. Later, this creation technique was applied to pollutant molecules, such as dioxins, and a Rydberg electron capture source for a quadrupole mass filter spectrometer has been proposed [31].

### B. University of Liverpool

A high resolution mass spectrometer for low mass analysis poses difficulty for a portable instrument within a process environment. Recent simulation work has demonstrated that a portable quadrupole mass spectrometer (QMS) can be configured for high resolution operation to attain the required performance [32]. To achieve this there are a range of options that may be used: e.g., operation in zone 3 of the Mathieu stability diagram [33] and/or use of hyperbolic electrodes and /or application of a static magnetic field [34]. Operation in zone 3 requires the use of a specialist electronic control unit, since in this case the operational voltages on the quadrupole electrodes are higher than for normal operation (i.e., in zone 1 of the Mathieu stability region). Capture of spectra in the low mass regions requires the use of high dynamic range analogue to digital converters (ADCs). Use of hyperbolic electrodes is advantageous in many respects in that higher sensitivity and instrument resolution may be achieved [35]. Recent work has shown that a magnetic field applied in the axial direction can enhance QMS resolution by 30% for a 200 mm long quadrupole mass filter. This results in a predicted resolution in excess of 3000 for m/z 40 [36]. To achieve the required performance for on-line fission gas monitoring using a portable QMS, a combination of some or all the above techniques will be necessary.

Implementation of portable mass spectrometers for on-line monitoring is mainly driven by the miniaturization of the mass analyzer. This is because smaller analyzers can be operated at higher pressures using miniature and low-weight vacuum systems. Also they require lower drive voltages to achieve the targeted mass range, which allows low-power battery operation. Mass analyzers that have been successfully miniaturized are quadrupole mass filters [37], [38], ion traps [39], [40] and time-of-flight analyzers [41]. Among miniaturized mass analyzers, both quadrupole mass filters (QMF) and linear ion traps (LIT) have already been used for portable environmental applications, such as on-field oil-in-water monitoring [42] and rapid hydrocarbon analysis in air and water [43]. Compared to QMF, the LIT analyzer can operate at higher pressures, providing much faster mass scan rates and significantly higher mass range [40], [44]. LIT implementation results in the smallest footprint portable mass spectrometers allowing an increased number of applications.

## V. DEVELOPMENT APPROACH OF THE MASS SPECTROMETER SET-UP

The mass spectrometer set-up should comprise stages having the following functionalities: gas calibration, gas inlet, ion creation, mass-selective ionic filter or enrichment and mass analysis.

Less than 1 ppm detection threshold for Xe or Kr in Ar gas carrier can be achieved by an on-line mass spectrometer composed of a sampling device at 1–2 bar, an electron impact closed ion source, a triple-quadrupole mass analyzer and a dynode electron multiplier as detector. A mass scan is performed over mass range 2–200 u with mass resolution 1 u for 1 min. The sensitivity is increased by filtering the spurious ions prior mass analysis and using the most sensitive type of ion detector. The isotopes of Xe and Kr can be then detected, as well as $H_2$, and $^4He$ at mass 2 and 4, respectively. This on-line device fulfils the needs of measurement at MERAG facility, where it will be implemented soon.

To respond to the measurement exigencies in the Jules Horowitz Material Testing Reactor (trace detection and high-resolution low-mass analysis of rare gas and some molecules) a high-performances mass spectrometer will be required by combining different specific mass-spectrometry techniques. Here, in the following paragraphs, we detail a development approach that highlights some interesting techniques according to the stages of the device that require specific clarifications.

### A. Multiphoton Ionization Ion Source

Electron impact ion sources are the most commonly used in mass spectrometry. However they have a poor selectivity of ion creation. Multiphoton ionization with photons at a same wavelength seems to be the most effective method to selectively create ions of interest. It has been used for ionization of rare gas [45], [46] and molecules [47] for many years.

Depending on the ionization scheme (according to the laser wavelength) the ionization can occur for more than one targeted compound. For instance, with an ArF excimer laser at 193 nm, Xe and Kr atoms can be ionized according to a two-photon non-resonant and a three-photon $(2 + 1)$ resonant scheme, respectively [48]. Other molecules of interest such as, HCl, $H_2O$ (vapor) and $O_2$ can also be ionized according to a non-resonant two-photon scheme.

A resonantly $(2 + 1)$-photon scheme can be used to exclusively ionize Xe or Kr atoms. For instance, a laser wavelength of 256.02 nm was chosen to resonantly adsorb two photons from ground state to $6p[5/2]_2$ excited state of Xe and one at 216.67 nm to $5p[5/2]_2$ state of Kr, for failed fuel detection and location technique in fast experimental reactor JOYO [17], [49], [50]. A laser wavelength at 249.6 nm has been used to resonantly adsorb two photons from ground state to $6p[1/2]_0$ excited state of Xe, for measuring isotope ratio in terrestrial and extraterrestrial materials [51], [52]. Another excited state $(6p[3/2]_2)$ of Xe and a laser wavelength at 252.5 nm have been proposed to detect trace amounts of transuranics by Xe measurement [53].

Despite the fact that resonant excitation and ionization has been first developed for isotope separation [54], the radiation full-width-at-half-maximum of the common lasers is too large

to gain an isotopic selectivity: generally all the isotopes of one element can be ionized simultaneously.

Ionization yields are estimated from the rate equations describing the population evolutions of the ground, excited and ionized levels of the element submitted to laser irradiation [45], [55].

For a two-photon non-resonant ionization, the population evolution can be modeled by a two level system. The ionization yield $R$, deduced from the rate equations, is given by:

$$R = \frac{n_I(\tau_L)}{n_0} = 1 - e^{-W_I\tau_L} \approx W_I\tau_L \tag{1}$$

where $\tau_L(\mathrm{s})$ is the duration of the laser pulse, $n_I(\tau_L)$ the number of ions created by the laser pulse, $n_0$ the initial number of atoms or molecules on ground state and $W_I(\mathrm{s}^{-1})$ the ionization rate.

For a non-resonant multiphoton excitation or ionization, the expression of the rate for N-photon absorption can be approximately calculated by the expression [56], [57]:

$$W_N = \sigma_N \phi^N \tag{2}$$

where $\sigma_N$ $(\mathrm{cm^{2N}.s^{N-1}})$ is the N-photon absorption or ionization cross-section and $\phi$ $(\mathrm{photons.cm^{-2}.s^{-1}})$ the photon flux. Consequently, in the case of a two-photon non-resonant ionization, the ionization yield can be expressed by [56]:

$$R \approx \sigma_{I,2}\phi^2\tau_L \tag{3}$$

where $\sigma_{I,2}$ $(\mathrm{cm^4.s})$ is the two-photon ionization cross-section.

With $\tau_L = 10$ ns, $\phi = 10^{+26}$ photons.cm$^{-2}$.s$^{-1}$ and $\sigma_{I,2} = 10^{-49}$ cm$^4$.s at 193 nm [58], [59], the ionization yield of Xe gas have a low value of c.a. $10^{-5}$. Franks *et al.* reported a probability of ionization of about $10^{-6}$ at same flux and duration of the laser pulse and for a wavelength at 250 nm [53].

Generally, rate equations of a three level system are [45], [55]:

$$\frac{dn_1(t)}{dt} = -W_a n_1(t) + (W_S + \Gamma_{21} + \beta)n_2(t)$$
$$\frac{dn_2(t)}{dt} = +W_a n_1(t)$$
$$\quad - (W_S + \Gamma_{21} + \beta + W_I)n_2(t)$$
$$\frac{dn_I(t)}{dt} = +W_I n_2(t), \tag{4}$$

where: $n_1(t)$ and $n_2(t)$ are the number of atoms in the ground state and excited level, respectively; $n_I(t)$ is the number of ions; $W_a = \sigma_a\phi$, $W_S = \sigma_S\phi$, $W_I = \sigma_I\phi$ and $\Gamma_{21}$ are the absorption, stimulated emission, ionization and spontaneous rates $(\mathrm{s^{-1}})$, respectively, and $\beta$ $(\mathrm{s^{-1}})$ a spontaneous decay constant. $\sigma_a$, $\sigma_S$, and $\sigma_I$ $(\mathrm{cm^2})$ are the absorption, stimulated-emission and ionization cross-sections, respectively.

For a three-photon resonant ionization scheme (two photons for excitation plus one for ionization), the absorption rate is replaced by $W_a = \sigma_{a,2}\phi^2$, with $\sigma_{a,2}$ $(\mathrm{cm^4.s})$ the two-photon absorption cross-section from ground state to excited state. With $\beta \approx 0$, and if the solution of the 3rd rate equation of (4) is limited to the 2nd order development of exponential expressions, ionization yield can be expressed by [55]:

$$R \approx \frac{1}{2}\sigma_{a,2}\sigma_I\phi^3\tau_L^2 \tag{5}$$

where $\sigma_I$ $(\mathrm{cm^2})$ is the one-photon ionization cross-section from the excited state.

For Xe and a $(2+1)$-photon scheme with photons at a same wavelength of about 250 nm, it has been found that: $\sigma_{a,2}$ is about $4.0 \times 10^{-45}$ cm$^4$.s for the excited states 6p[1/2]$_0$, 6p[3/2]$_2$ and 6p[5/2]$_2$ [60], [61] and $\sigma_I = 4.3 \times 10^{-18}$ cm$^2$ [62]. Consequently, with $\tau_L = 10$ ns and $\phi = 10^{+26}$ photons.cm$^{-2}$.s$^{-1}$, the ionization rate of Xe atoms is then about 10%. Generally, data available at different articles give values between 1 and 10% for the ionization rate [60], [63]. Payne *et al.* reported values up to 55% for on-line analysis of rare short-lived isotopes [64]. Saturation of the resonance transition is the condition for the highest ionization efficiency (100%). In $(2+1)$-photon scheme saturation occurs when: $W_a\tau_L \gg 1$ [45].

For the Xe, another resonantly enhanced three-photon ionization scheme has been proposed by using XeF and ArF excimer lasers at wavelength 351 and 193 nm, respectively [65]. One photon at 351 nm and one at 193 nm excite the atom on state 6p[1/2]$_0$ and then a third one (either at 193 or 351 nm) ionizes the excited atom. In the same experimental set-up, the detected peak electron density is more than an order-of-magnitude larger than that obtained with non-resonant two-photon ionization with solely an ArF excimer laser [59].

For Kr and with an ArF excimer laser at 193 nm, $\sigma_{a,2}$ is about some $10^{-49}$ cm$^4$.s and $\sigma_I = 4.3 \times 10^{-18}$ cm$^2$ [66], [67] leading to an ionization yield for the resonantly three-photon ionization of about $10^{-5}$.

Relative multiphoton ionization rates for Xe, NO, NO$_2$, N$_2$O, O$_2$, N$_2$, CO, CO$_2$, H$_2$O, ... have been measured as a function of laser power at 193 and 248 nm. Relative ionization rates varied among these molecules by more than six orders of magnitude [68].

Resonantly $(2+1)$-photon schemes are the best way to achieve both ionization selectivity and high ionization yields of rare gas atoms and other molecules of interest. However these kinds of scheme require complex laser apparatus. Generally, they consist of a Nd:YAG, an optical parametric oscillator (OPO), and a sum frequency generation (SFG) or a second harmonic generation (SHG) system according to the wavelength generated. The most suitable and commonly used lasers are Excimer lasers: they have a fixed wavelength depending on the used dimmer gas, here, for instance, XeF and ArF. They are robust as they are commercialized in industrial and medical fields. Moreover they have the highest repetition rates (greater than 100 Hz instead of 10 Hz for YAG laser) allowing a greater number of mass measurements per minute.

### B. Gas Inlet

With a multiphoton ionization source, the gas sample at atmospheric pressure is generally introduced directly in the mass spectrometer using a fast pulsed supersonic valve [69]. This results in a collimated high-density jet of neutrals in the interaction zone with the laser beam due to the supersonic nozzle (with a single channel or multi channels). The fast pulsed valve reduces the global amounts of injected gas and then avoids the use of high-speed and large pump group.

With 1–2 bar and $3 \times 10^8$ atoms.cm$^{-3}$ to be detected in the sweeping lines and $10^{-1}$ torr estimated value for the pressure

in the neutral beam, the density of atoms to be detected in the neutral beam is $\rho_0 = 3 \times 10^4$ atomes.cm$^{-3}$. The number of ions created per laser pulse is then expressed by: $n_I = RV\rho_0$. With an ionization yield $R = 10\%$ and an interaction volume between the laser and neutral beams $V = 0.07 \, \text{cm}^3$, the number of ions created per laser pulse is c.a. 200.

### C. Mass-Selective Filter and Enrichment Stage

A quadrupole mass filter with hyperbolic-shaped electrodes can be added prior mass analysis stage to serve as a mass-selective ion guide.

Without mechanical modifications, the mass filter function can be switched to a 2D linear ion trap (LIT) function according the potentials applied to the entrance and exit lenses of the quadrupole [70]. An LIT has the advantage of confining ions that move along the transfer (axial) direction. Furthermore an LIT can generally accumulate larger amounts of mass-selected ions than competing trap technologies [71].

Another possibility is to directly create the ions inside the mass filter [72] or linear trap by either electron gun [73] or laser pulse [74], [75]. The overlap between laser and atomic beams can be increased with a frontal beam experiment along the axial direction of the trap: hence creation occurs in the whole volume of the trap. By this method the interaction volume can be increased by more than one decade. With a 2D trap, in addition to mass-selective accumulation, preparation of the ions (according to their energy of translation) can be performed to increase injection yield in the mass analyzer [76]–[78]. However the trap requires additional He buffer gas in order to move the ions toward the centre of the trap during confinement by collisional cooling. With segmentation of the electrodes and by using different switched potentials applied to the electrodes ions can be located in the last segment close to the exit of the trap [79].

### D. Mass Analyzer

The new techniques proposed of operating a quadrupole mass filter and 3D ion trap for mass analysis developed by the two partners and described in the above paragraph "Skill in mass spectrometry" will be improved to gain both higher resolution and sensitivity. The success of these studies depends mainly on the design and the implementation of specific electronic control units with high performance to supply the respective electrodes of the filter and trap.

The FTQIT mass analyzer exhibits an inherently high sensitivity of detection [26] due to the Fourier transformation principle. Moreover, a better resolution at low masses is expected as the axial secular frequency difference between two species separated by 1 u increases with the decrease of the mass. The challenge is to inject, then to confine low-mass ions in the 3D trap.

For instance, the confinement of low masses in the FTQIT mass spectrometer will require power supplies delivering waveforms of AC (at 1 MHz) and DC voltages of amplitude varying from 0 to $\pm 90$ V with amplitude stability less than 0.1% and slew rates greater than $3000 \, \text{V}.\mu\text{s}^{-1}$. A resolution greater than 1000 can be then achieve at mass 4.

In the case of QMFs and LITs used in portable mass spectrometers, there is generally a trade-off in design to achieve de-

sired sensitivity, resolution, mass range and scan speed, which will depend on application. It was found that electrode fabrication errors can significantly reduce sensitivity and resolution in QMFs [80]. This can be compensated by using higher drive frequency, hyperbolic electrodes, operation in zone 3 and/or application of axial magnetic field. Compared to QMFs, LITs can operate at lower drive frequencies and still achieve identical mass resolution or better. This reduces voltage demand for mass scanning and enables low power operation. For example, an LIT with $r_0 = 2 \, \text{mm}$ driven up to 1500 $V_{\text{p-p}}$ at 1 MHz can provide up to m/z 2000 mass range if needed.

### E. Mass Spectrometer Set-Up

The mass spectrometer set-up will integrate some of the previously described techniques. High-level performance needs to have multi on-line analyzers in parallel, each of them for either the detection of a specific component or a set of components.

The use of multiphoton ionization techniques allowing selective ion creation requires a specific laser set-up for each trace level compound to be detected.

The part of the device comprising mass-selective filter or enrichment stage and mass analyzer can have a same structure for the detection of all the compounds. However, each device must run (1) at different operating points depending on the targeted mass-range and (2) over the smallest mass-range for the fastest mass-scan for real time analysis with high resolution. Consequently, each device will require different electronic control units according to the compounds to be detected.

Moreover, size reduction in quadrupole mass spectrometers is an on-going requirement driven by the reduction of both process flow and fluid consumption, and complementary measurement devices located in a limited place.

## VI. NUCLEAR RESEARCH FACILITIES BENEFITING FROM THE COLLABORATION

### A. Technical Breakthroughs and Innovations

Such new equipment in nuclear research facilities has to solve the present difficulties of implementation of continuous or off-line measurement methods of stable gaseous isotopes.

One of the major difficulties is the frequent need for isotope concentration and detection by trapping at the temperature of liquid nitrogen, in order to obtain concentrations measurable by mobile or fixed mass spectrometry. This implies:

- A cold trap installation, source of a specific safety analysis: management of additional circuits coupled with the experiment, use of nitrogen, risk of ice clogging due to residual humidity, concentration associated with radioactive isotopes, etc.
- A result producing a mean value of the isotope concentration during the concentration period. This measurement strategy can only be used for "base" irradiations not exhibiting variable or "threshold" release mechanisms. Experiments on operation in transients or safety can be feasibly monitored with this method.

Another major difficulty is the need to transport the sample to the "delocalized" analytical measurement instrument inducing cost, deadline, radiation protection, effluent management, etc.

In terms of innovation, the development of small-sized, high-sensitivity on-line mass spectrometers is a major breakthrough for measurements in nuclear environments. It helps open up a greater field of use by circumventing the standard restrictions for use in a controlled zone, such as:

- Equipment in close proximity to experimental gas lines,
- Easier radiation protection (instrument and carrier gas),
- Real time monitoring of the mechanisms, even during transients (which is a great advantage for modeling e.g., in nuclear safety),
- Tests or surveillance of objects after long decay times or after low irradiation runs, for which activity measurements are no longer relevant.

Now, the $^{85}$Kr isotope is commonly measurable quantitatively with off-line mass spectrometry and gamma spectrometry. The development of on-line mass spectrometry technique will provide additional information regarding the existing measurement by gamma spectrometry of certain radioactive fission gases, allowing a direct comparison of the two methods and their respective improvements. It will be possible for the first time to gain a complete understanding of the behavior of the fuel sample throughout the experiment: emission zones, type of fissioned heavy nuclei, realistic fission product source terms or envelope, etc.

### B. Partnership Development Opportunity

Linked with R&D facilities in which the devices will be implemented, this development program will be carried out together with the following partners:

*1) The JHR Operation and Service Unit of the CEA Cadarache (SERJH) and the Reactor Design Department (DER, Département D'Etudes des Réacteurs) for Measurements in the JHR Facility:* The main result of this program will indeed correspond to the increase of the offer of experimental services associated with the Jules Horowitz Reactor. The scientific results will be exploited directly by the scientific community, by industrial customers (fuel designers, power plant operators) or by the national safety authorities or international organizations (through joint international programs) because the completeness and scientific quality of the results of an experiment are often decisive selection criteria for clients of this type of service. The final objective is to install a nuclearized mass spectrometer and a gamma spectrometer in a unique experimental platform located in the ELF Fission Products Laboratory of the JHR [81]. The technical environment for the installation and use of this measurement platform is one of the most favorable, because the interfaces with the JHR facility are managed by it: connection to experiments with "fluid" safety elements and associated nuclear safety, supply of fluids required by the platform (various grades of water, clean gases, electricity, liquid nitrogen, etc.), circuits leading to the effluents (liquid and gas), ventilation on shielded containments, local management of radiation protection, data transmission and archival network, handling and maintenance facilities, etc. The scientific equipment is dedicated to the measurement of active and stable gases passing through a flushing circuit of the sample (generally an experimental fuel rod equipped with flushing minitubes) with an inert gas. This is the "medium level gas" circuit of the ELF laboratory.

The fission products laboratory itself is a monitored room in the JHR controlled area and is completely dedicated to on-line and off-line measurement, and to the storage of fission products. However, in normal periods, it allows access for employees assigned to the experiments or to maintenance. Eventually it will have a set of hot cells each dedicated to the measurement of a specific carrier fluid: coolant of the irradiation loop, or carrier gas flushing either the sample or a headspace. The connecting circuits between the experiment and the future hot cells (fluid intakes to be measured) and those leaving to the experiment or to the wastes, are provided in the laboratory equipment, in the same way as the associated safety elements (radiological monitoring, ventilation, leak collection, etc.) and the radiation protection required around the circuits and the equipment.

*2) The Laboratory for the Analysis of the Migration of Radioelements (LAMIR), Belonging to the Fuel Research Department of the CEA Cadarache for Post-Irradiation Measurements in a hot Cell Laboratory:* The LAMIR is the scientific manager for investigations of the release and transport of the fission products contained in nuclear fuel elements in accident situations involving the nuclear reactor cores, and also during the storage or transportation of nuclear fuels. From the experimental standpoint, the laboratory has separate effects annealing test (TTA-Traitements Thermiques Analytiques) facilities, in hot cells, used to measure the release kinetics and rates of the fission products from nuclear ceramics irradiated in controlled historical conditions of temperature, pressure and atmosphere. Thus several experimental platforms have been designed, developed and operated in the laboratory: MERARG for Analytical annealing test, VERDON for experiments simulating a severe reactor core accident (fuel meltdown) and DURANCE for fuel/clad thermo mechanical coupling, etc.

More specifically, and given the particularly innovative nature of continuous measurement by mass spectrometry, a portable on-line prototype will be installed and qualified in the CEA high level laboratory "LECA-STAR" (INB No 55), in an existing annealing test facility: the MERARG II equipment. It will be installed in the gas recovery glove box located in the rear area of cell No C7, where the experiments are carried out and where an on-line and off-line gamma spectrometry station is already operational. The MERARG II facility is currently deployed in a concrete cell of the LECA-STAR facility. It is used to characterize irradiated nuclear fuels for the behavior of the fission gases during thermal transients. The temperature levels reached allow the extraction of part or the entire gas inventory contained in the analyzed sample. The experimental assembly consists of three main parts: the actual heat treatment furnace located in the high level cell, the gamma spectrometry detector, the glove box including the micro-gas chromatograph and finally the active gas recovery devices, all located in the rear area.

*3) Other Opportunities:* Moreover, this program will be included in the common wall-less laboratory LIMMEX, set up between the CEA and the Université de Provence, which will help consolidate the collaboration between the two partners in the nuclear instrumentation field, a promising topic in the French PACA region, where many large research infrastructures or cutting-edge instruments with high added technological and scientific value are installed or under construction (e.g., in the fission

domain: CABRI, EOLE, MINERVE, JHR, RES, ASTRID, and the ITER facility in the fusion domain).

Finally, the prototypes developed in this program will be able to be deployed in other research reactors. In France, for example, on the future Gen IV ASTRID prototype with the problem of measurements in the presence of sodium (which will enhance the analyses of the reactor vessel upper gaseous blanket) and in Europe at least on two MTR type reactors that will still be operating in parallel with the JHR: BR2 in Belgium and HFR in Netherlands. Outside of Europe, other facilities could take profit from these developments, such as the TRIGA-type reactors and/or in a country where nuclear power is emerging, such as Morocco, with associated technological and training requirements.

## VII. Conclusion

The chosen implementation strategy favors an approach that progressively will open up the technological bottlenecks to obtain eventually an on-line mass spectrometer suitable for a high level on-line and real time gas analysis on irradiation experiments in the future Jules Horowitz Reactor.

Prior to nuclearization purposes, the research studies will be conducted on various investigations of devices in an unirradiated environment, not restricted by safety purposes, handling or integration constraints linked to operation in Nuclear Controlled Area.

The strategy thus relies first on the less-ambitious and closer-deadline step associated with the issue of on-line measurement by mass spectrometry in post-irradiation out-of-pile, on the MERARG facility at the CEA-Cadarache hot cell laboratory. The structure of the mass spectrometer set-up is defined. Further studies will be conducted to adapt the mass spectrometer and define operating protocols and conditions to gain an optimal sensitivity of detection of noble gas in an on-line sampling condition, before nuclearization and implementation.

For an implementation in the Jules Horowitz Reactor, the first scientific approach of the development has given possible techniques to be employed at different stages of the mass spectrometer set-up which will present a realistic chance to target the challenging needs requested by the experimenters. The next steps of the program will concern the definition of (1) its structure, (2) on-going research studies and (3) necessary material support of these studies. This will be possible thanks to the available scientific skill of the partners (the coordinating partner at Aix-Marseille Université and the group at University of Liverpool) and by applying for research support grants.

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