He and Fission Product Release from Irradiated Nuclear Fuels: MERARG 2 capabilities

Boris MEUNIER[*], Yves PONTILLON[**], Sidonie CLEMENT, Jacqueline DEBARGE, Julien PIQUEMAL, Marina PONTILLON, Guillaume VOLLE, Sebastien BERNARD

Commissariat à l'Energie Atomique, Centre d'Etudes de Cadarache, DEN/DEC/SA3C, BP1,
13108 Saint Paul les Durance, France

Abstract: In order to increase fuel rod performance, the basic mechanisms that promote gas (i.e. He, H_2, N_2, Kr and Xe) release from irradiated nuclear fuel must be studied. The CEA fuel study department at Cadarache decided to improve its experimental facility devoted to fuel behaviour under thermal transient by modifying the existing annealing device, called MERARG, to extend the studies of fission gases to He. As a result, a micro-gas chromatograph (µ-GC) has been integrated into the MERARG 2 facility. The device can analyse gas concentrations from a few ppm (1.5, 0.9, 3, 2.6 and 5.3 ppm respectively for He, H_2, N_2, Kr and Xe) up to several thousands of ppm in under two minutes. Regarding the quality of the measurements (limits of detection, fidelity and linearity), the µ-GC is very well adapted to measure the absolute level and the time dependence of all gases released from the fuel during a representative thermal transient.

Keywords: He Release, Fission Gas Release, Gamma Spectrometry, Chromatography

1. INTRODUCTION

Under both normal and off-normal conditions, fission gas release (FGR) is known to have repercussions on fuel performance. Up to now, the correct evaluation of FGR from high-burn-up fuel in these conditions remains an important challenge [REF 1]. More recently, He release has also been identified as an additional factor [REF 2]. For instance, in some conditions it may contribute, in the form of fission gases, to pressurization inside fuel rods. These phenomena may impact directly on the average life of nuclear fuel, because the internal rod pressure must be kept lower than the design criterion.

However, in order to allow a better understanding of the basic mechanisms that promote gas release from irradiated nuclear fuel, the studies previously performed on fission gases need to be extended to include He. In this context, the CEA fuel study department at Cadarache decided to improve its experimental facility devoted to fuel behaviour under thermal transient, and ended up developing new equipment around the MERARG[1] annealing device.

Basically, MERARG operates on irradiated fuel (typically one pellet) at temperatures that range from room temperature up to 2800°C, with temperature ramps between 0.1 and 200°C/s [REF 3]. The released gases are swept by a regular "carrier" gas (Ar, He or air according to the experiment), which is then analysed by on-line gamma spectrometry. A micro gas chromatography (µ-GC) device has now been added to this equipment in order to extend analysis to the stable gases (for instance He, H_2, N_2, Kr and Xe). Like the gamma spectrometry station, the micro gas chromatograph makes it possible to study both the kinetics and total release of the measured gases. To gain a better understanding of the fuel, a gamma spectrometry device with a direct sighting on the fuel specimen was also added to MERARG facility for the purpose of studying the behaviour of volatile fission products (Cs, I, etc.).

The main goal of this paper is to give a concise review of the main aspects of the MERARG 2 facility as implemented at the Cadarache CEA Centre's LECA-STAR Laboratory, and then to focus on MERARG 2's new capabilities provided by the µ-GC. After a general description of the facility, the global qualification and calibration phases of the µ-GC are presented.

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[*] Tel: 0033 4 42 25 25 67, Fax: 0033 4 42 25 44 79, e-mail: boris.meunier@cea.fr
[**] Corresponding author: Tel: 0033 4 42 25 72 26, Fax: 0033 4 42 25 44 79, e-mail: yves.pontillon@cea.fr
[1] A French acronym for "Means of Study by Annealing and Analysis of Gaseous Releases"

2. MERARG 2: GENERAL DESCRIPTION

   This type of experiment is designed for the study of gas releases through the annealing of an irradiated fuel sample (typically one pellet) up to temperature levels allowing the extraction of all or part of the gaseous inventory it contains. More precisely, the MERARG 2 ("2" for the second version) facility uses a high-frequency (HF) furnace to heat a sample at temperatures ranging from room temperature up to 2800°C, with temperature ramps between 0.1 and 200°C/s. Measuring equipment associated with this induction furnace allows the specific analysis of FGR and He releases (Figure 1).
   During the experiment, the released gases are retrieved in a tight circuit swept by a circulation gas called "carrier gas". This can be neutral (helium or argon) or oxidizing (dry air), and its flow rate is low at roughly 60 cm^3/min. The carrier gas transports the released gases to the back zone, where the "Fission Product circuit measurement" is located with a gamma spectrometry station (online analysis of gamma emitter gases) and a μ-GC (online analysis of stable gases). Finally, all these gases are accumulated in capacities (6, 15 or 20 litres according the type of experiment), located in the glove box along with the μ-GC. In addition, a gamma spectrometry device with a direct sighting on the fuel specimen is integrated into the facility in order to study the behaviour of volatile fission products (Cs, I, etc.).

   In the following section, the main components of MERARG are described in more detail.
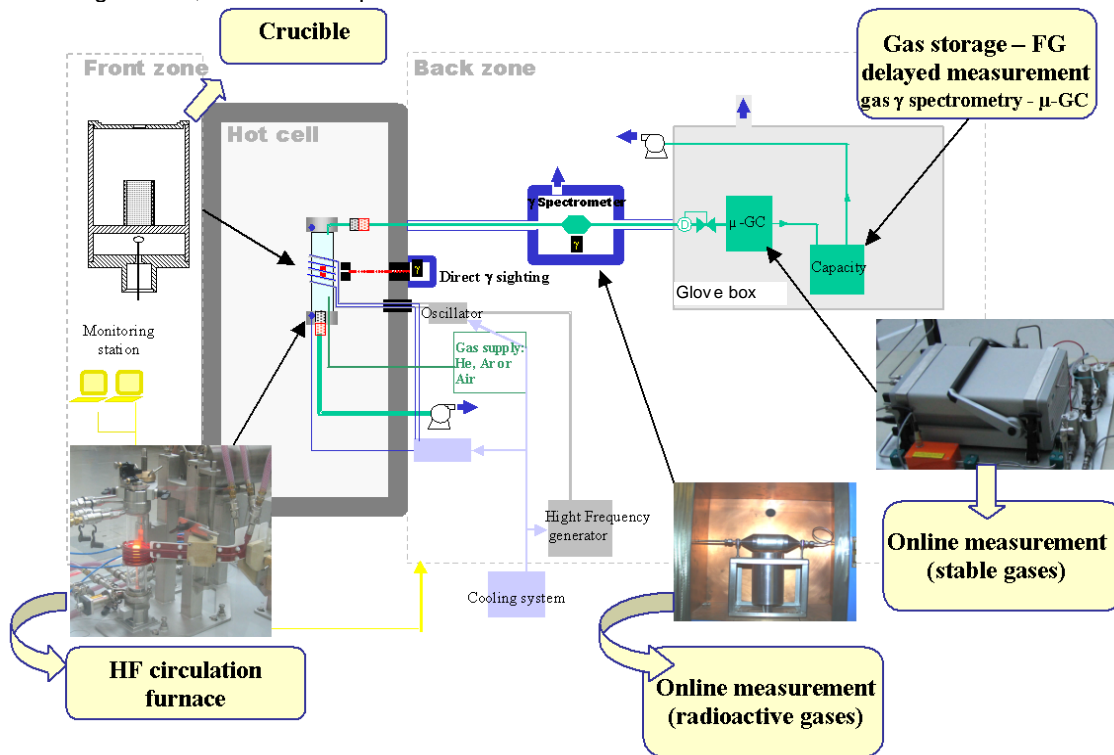

Figure 1: Simplified diagram of MERARG 2 facility

   The induction furnace, located within a shielded hot cell shown in Figure 1, uses six coils to heat a suceptor by induction. This suceptor is a metallic crucible with a fuel pellet located inside. The crucible heat is transferred to the fuel pellet by conduction, convection and radiation (indirect annealing).
   Tungsten, molybdenum or platinum crucibles are available according to the type of experiment. The choice depends on the specific experiment requirements in terms of the level of temperature reached and the atmosphere of the test. The crucible, located in the centre of the induction coil, is composed of two dissociated chambers (Figure 1): (i) an upper one, which contains the fuel pellet and is covered by a removable lid with a

central hole. The pellet temperature is monitored by a pyrometer, which sights the top of the pellet through the lid hole. (ii) a lower one containing the instrumentation, i.e. a thermocouple. The thermocouple allows the inductance furnace piloting. A correlation law links the temperature of the lower chamber to the upper one [REF 3].

The furnace enclosure in which the crucible is placed is kept airtight by a quartz tube. This one is squeezed between the lower and the upper bases of the furnace. The induction coils, the bases of the furnace are cooled by water. The entry of the "carrier gas" (He, Ar, or dry air) is on the lower base of the furnace, while the gas outlet (the "carrier gas" charged with the released gases from the pellet) is on the upper one.

The gamma spectrometry device with a direct sighting on the fuel specimen is integrated to the hot cell. This detector is aimed at the top of the fuel and records the departure of all the fission products from the fuel. Since that is a differential measurement, the station has the drawback of low accuracy in the release measurement. The FPs releases lower than 10% are of low significance on this measurement station [REF 5]. However, it has the advantage of quantifying the kinetics of all the FPs, including those which do not reach the "gas gamma spectrometry station". Besides, it allows one to **follow fuel degradation**, since it "records" the loss of signal, corresponding to no or low volatile FPs, due to the collapse of the fuel and its bulk relocation at the bottom of the crucible.

The gas gamma spectrometry station, located in the back zone, monitors the kinetics of the fission gases released during the experimental sequence. The measurement devices (capacity and detector) are designed to be able to quantify very low release of the ^{85}Kr contained in a pellet of UO_2 fuel [REF 4].

The glove box includes: (i) a flow-rate regulator at the glove-box inlet to ensure the required gas circulation (60 cm^3/min); (ii) the μ-GC for analysing stable gases; (iii) the storage capacities (25, 12 and 6 litres as a function of the test requirements), in which the gases are accumulated during the experiment. At the end of the experiment, gases stored in the capacity can also be analysed by gamma spectrometry and gas chromatography to study the total release (i.e. delayed measurement).

The μ-GC extends the analysis of active gases to all the stable gases. Within the context of MERARG 2 programs, the μ-GC can analyse He, H_2, N_2, Kr and Xe. Like gas gamma spectrometry, this device allows the kinetic studies of all these gases (online measurement). More items about its functioning are given in the following section.

3. μ-GC IMPLANTED IN MERARG 2 FACILITY

3.1. GENERALITIES

The purpose of a μ-GC is to separate the different gas components contained in a sample [REF 5] and to measure each of them. This device is composed of an injection system, a column and a detector as shown in Figure 2 [REF 6].

The injection system injects a gas sample passing inside the injection loop into the column.

The column, a capillary one for the μGC of MERARG 2, separates the different components of the sample. The capillary column, developed by Golay [REF 7], is destined for the application of gas chromatography by interaction between two phases. The "mobile phase", consisting of the gas sample and the μ-GC carrier gas (Ar in the case of MERARG 2), goes through the column. The "stationary phase", typically the column, delays the different components more or less according to their various chemical and physical properties.

The detector, a katharometer (i.e. thermal conductivity detector [REF 8]) for the μ-GC of MERARG 2, detects and measures all components that come out of the column. It measures the difference between the thermal conductivity of the μ-GC carrier gas alone and the one charged with the sample (Wheatstone bridge). The response of the detector is proportional to the concentration of the component going through the detector, allowing quantitative measurements after calibration.

Finally, data are presented in the shape of a chromatogram. This gives the detector response (y-axis) as a function of the retention time (x-axis). The retention time is the time taken after the injection of the sample to reach the peak maximum. Each peak is characteristic of one component of the sample and the area under this peak is proportional to its concentration.
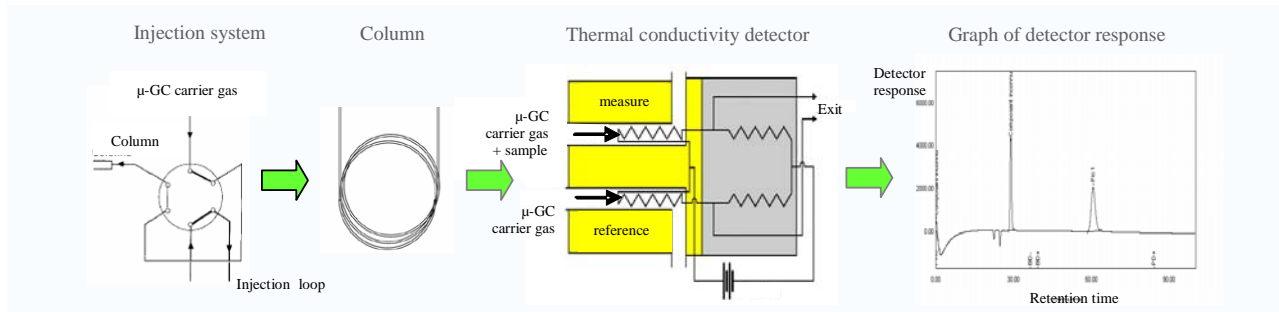
Figure 2: The different elements of a µ-GC

An experimental approach has to be followed before processing analyses with the µ-GC. It aims at defining:
- **an analysis method**. This method specifies the operating conditions of the µ-GC in order to separate the different components of a sample: column temperature (in °C) and column pressure (in psi[2]). According to these conditions, the retention time will be more or less fast;
- **an integration method**. This makes it possible to calculate the area under a peak, by using the mathematical function of integration, for a scale of concentration;
- **the calibration of the µ-GC**. The calibration makes it possible to perform quantitative analysis by linking the area of a peak to the associated concentration. Calibration bottles are used for this phase;
- **the limits of detection**. The goal is to specify the low scales of concentration that can be analyzed using the µ-GC.

3.2. µ-GC PERFORMANCES TO BE ACHIEVED

A preliminary study was carried out to verify that the gas chromatograph was adapted for analysing the gas releases that occur during a typical "MERARG" experiment [REF 9]. Figure 3 illustrates the corresponding estimation of the Kr and Xe instantaneous releases for UO_2 irradiated at 50 GWd/t. This study concluded on low rates of release: 2 ppm of Kr, 2 ppm of He and 15 ppm of Xe have to be online-detected inside the "carrier" gas. Note that only a few points are concerned by the low rates of release (in range of 2 ppm), typically at the very beginning and at the end of the experiment.
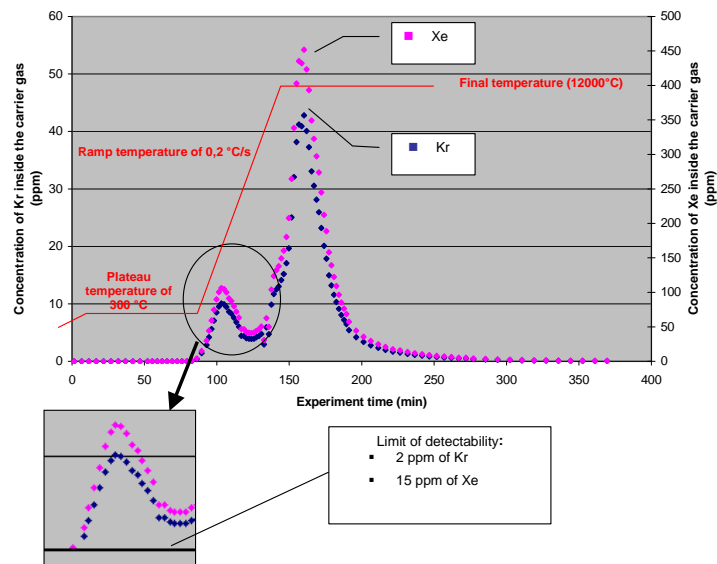

Figure 3: Estimation of the Kr and Xe instantaneous releases for UO_2 irradiated at 50 GWd/t

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[2] pressure unity : 1 psi = 0.69×10^5 Pa

Thus, the μ-GC has to be able not only to measure these rates of release, but also to follow their kinetics. Therefore, similarly to gamma spectrometry, the μ-GC has to be able to analyse a sample every one or two minutes (for online measurement).

4. μ-GC QUALIFICATION

The qualification of the μ-GC device was performed in three main phases:
- "the cold qualification phase" (i.e. not in hot cell), which consists principally in identifying the performance of the μ-GC in both configurations (online analysis and delayed analysis). Its purpose is to verify that the μ-GC meets the requirements. In order to facilitate this phase, the μ-GC is separated from the rest of the MERARG 2 facility;
- "the modification phase", which consists in making modifications to the device in order to allow its use within the LECA-STAR constraints. After that, the μ-GC performance is checked again to be sure that the modifications do not have any repercussions on the analysis quality;
- "the hot qualification phase" (i.e. inside the LECA-STAR Laboratory), during which all the equipment from MERARG 2 facility is fully operational and assembled to form the final facility, as illustrated in Figure 1. This phase is devoted principally to checking the complete facility, and is still in process at the present time.

The "cold qualification" phase concluded on the good performance of the μ-GC regarding the gas-release rates during an experiment (cf. **3.2**), but showed some inconsistencies with glove-box use. As a consequence, the μ-GC has been modified.

The next section will focus on the qualification and calibration phases of the modified μ-GC. The cold qualification will not be described in this paper.

4.1. PERFORMANCE OF THE MODIFIED μ-GC

A specific installation was developed to check the performance of the modified μ-GC, as illustrated in Figure 4 and Figure 5. This specific installation allows both analysis configurations: (i) online measurement and (ii) delayed measurement. The first one simulates the configuration where the μ-GC is coupled to the outlet of the induction furnace: a calibration bottle and a first flow regulator reproduce the gas flow circulating in the furnace enclosure (Line 1). A second flow regulator allows the gas flow in the μ-GC injection loop (Line 2), necessary for the injection phase before analysis. In the second case, the gas stored in the capacity re-circulates into the circuit, thanks to a dedicated pump, through lines 3 and 1.

According to these configurations, the μ-GC analyses are performed in two different ways. Concerning the online measurements, the gas flow of Line 2 assures the continuous circulation of the sample into the μ-GC injection loop. For the delayed measurements, the circulation of the sample into the μ-GC injection loop is assured before each analysis by a pump system that is intrinsic to the μ-GC.
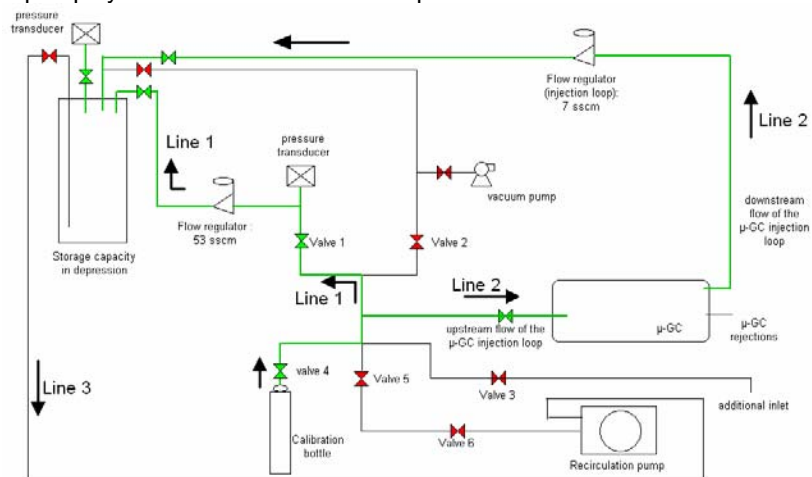

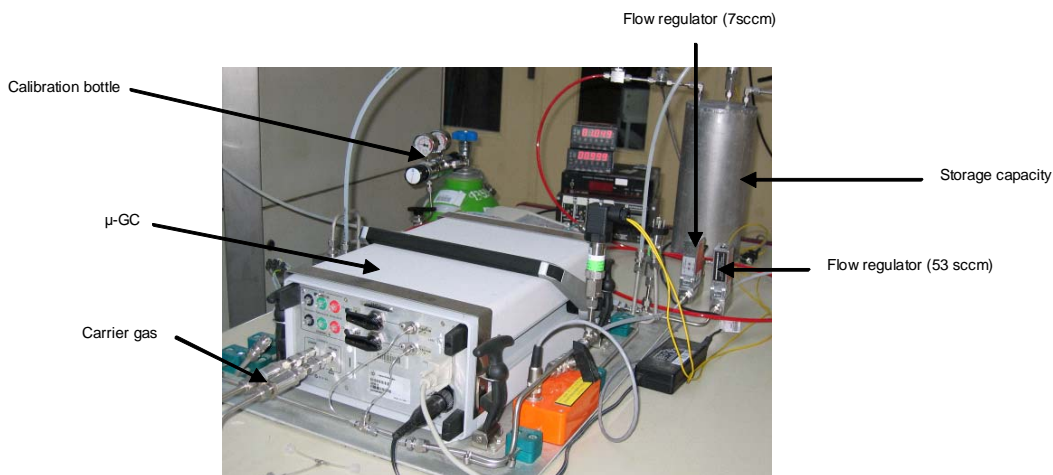Figure 4: Scheme of the installation used for the qualification (online measurement configuration)

Figure 5: Photograph of the installation used for the qualification

In accordance with the experimental approach (cf. **3.1**), an <u>analysis method</u> is determined in order to separate each component in under two minutes. A column temperature of 100°C and a column pressure of 35 psi allow a good separation of the He/H_2/N_2/Kr/Xe, as illustrated in Figure 6. The corresponding retention times are 18.6, 20, 29.3, 34.6, and 90.6 seconds, respectively, for He, H_2, N_2, Kr and Xe. This method is called P35T100.
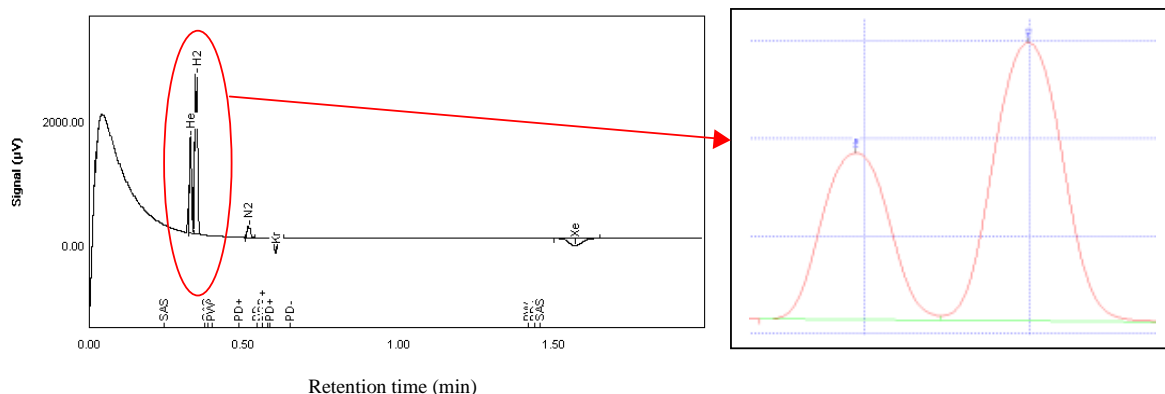

Figure 6: Graphs obtained with the P35T100 analysis method

An appropriate <u>integration method</u> is then determined to ensure that the integration is reproducible for all chromatograms of the concentration scale (typically 1 to 300 ppm for MERARG 2 experiments).

The next step, <u>calibration processing</u>, is completed on four points using calibration bottles: 0, 10, 50 and 300 ppm. For each of these points, fifty identical analyses are made in order to decrease the uncertainty of measurement.

The <u>limits of detection</u> are identified by continuously decreasing the component concentrations until the µ-GC is no longer able to integrate the corresponding peaks.

Following these steps, the µ-GC is ready to make measurements.

Table 1 and Table 2 sum up the performance results of the µ-GC for online and delayed measurements. They give notably:

- the limits of detection, which correspond to the lowest concentration that the µ-GC can analyse (Table 1);
- the repeatability standard deviation, which qualifies the reproducibility of measurements (Table 2);

- the R^2 coefficient, which evaluates the linearity of measurements: the closer R^2 is to 1, the better the calibration is. For example, Figure 7 shows the calibration curve for He.

	He gas	H$_2$ gas	N$_2$ gas	Kr gas	Xe gas
Low limits of detection (ppm) -delayed measurements-	0.45	0.48	-	2.95	7.60
Low limits of detection (ppm) -online measurement-	1.50	0.87	3.00	2.62	5.25

Table 1: Low limits of detection with the P35T100 analysis method

Component	Concentration of analysed gas (ppm)	Delayed measurement		Online measurement	
		R² Coefficient	Repeatability standard deviation (%)	R² Coefficient	Repeatability standard deviation (%)
He	299,80	0.999993	1.6	0.999984	0.3
	49.90		2.3		0.9
	10.01		2.9		3.3
H$_2$	300.02	0.999990	1.6	0.999992	0.3
	49.96		2.2		0.8
	10.02		2.9		3.3
N$_2$	300.00	0.992716	2.8	0.996813	1.4
	49.95		9.3		5.9
	10.02		21.5		19.4
Kr	300.20	0.999959	2.7	0.999907	1.3
	50.00		5.8		5.1
	10.03		49.6		16.9
Xe*	300.40	0.999723	2.7	0.999668	2.1
	50.00		10.4		8.8
	10.04		68.2		47.2

* *For Xe, another calibration point was completed at 1000 ppm.*

Table 2: Repeatability standard deviation with the P35T100 analysis method
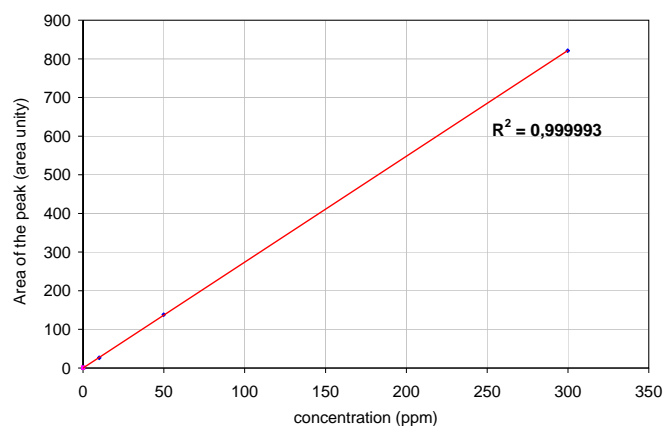

$R^2 = 0,999993$

Figure 7: Calibration curve for He

The results from Table 2 show that the repeatability standard deviation coefficients of online measurements are better than those for delayed measurements. This phenomenon is a consequence of the analysis configuration. As explained previously, the analyses (performed in two different ways, as described in section 4.1) correspond to a much higher injected quantity of sample for the online measurement.

We also note that the repeatability standard deviation coefficients are high for the low concentrations of N_2, Kr and Xe (around 10 ppm). The responses of the detector are in fact low for these few levels of concentration, with repercussions on the accuracy of integration. However, with respect to Figure 3, only a few points from an experiment are concerned by such a level of release. Therefore, these phenomena have a negligible impact on the total release measurements.

Taking into account these results, the µ-GC meets the requirements of MERARG 2 programs completely:
- the time of analysis is less than two minutes, making it possible to follow the release kinetics (Figure 6);
- the limits of detection are low in accordance with the rates of release: 1.5, 2.62, 5.25 ppm, respectively, for He, Kr and Xe. The detection limits for Xe are not as good as those for the other gases, because the thermal coefficient of this gas is lower than the others. However, the detection limits for Xe are good enough in comparison with the requirements (15 ppm);
- the fidelity and linearity, as illustrated in Table 2 by the repeatability standard deviation coefficient and R^2 coefficients, are globally good.

4.2. HOT QUALIFICATION PHASE

The next and last step of the qualification program is devoted to "the hot qualification phase" where the MERARG 2 facility is fully operational. During this phase, the global performances of the facility are checked: gamma spectrometry, annealing test (level of temperature and ramp temperature) and µ-GC, but also all the sensors and regulators. At this step, the µ-GC and all the equipments (gamma spectrometry, measurement instruments, etc.) are coupled to the furnace. The last step of this phase is to operate on irradiated fuel and to check the measurements of MERARG 2. This hot qualification phase is scheduled to start before the end of 2007.

5. CONCLUSION

The MERARG 2 facility offers accurate results for fission-gas and He measurements, notably thanks to online gamma spectrometry and µ-GC. Both of these devices allow studying the kinetics of He and fission-gas releases accurately: online measurements can be made every two minutes using the µ-GC, and typically every minute using gamma spectrometry.

Moreover, the total gas released during an annealing test can also be analysed by means of delayed measurements: the spectrometry gamma and the µ-GC have a wide scale of functioning (from the ppm to several thousand of ppm).

To conclude, the µ-GC is not only a perfect device for analysing all the stable gases, but also totally adapted to the rest of the MERARG 2 facility.

REF 1: A.E. VOLKOV, A.I. RYAZANOV, "Theory of gas bubble nucleation in supersaturate solution of vacancies, interstitials and gas atoms", Journal of Nuclear Materials, Vol. 273, Pages 155-163 (1999) ; P. VAN UFFELEN, "Modelling the influence of the athermal open porosity on fission gas release in LWR fuel", *Proc. of the Fission Gas Behaviour in Water Reactor Fuels*, *Nuclear science OECD NEA* , p. 151 , OECD, Cadarache, France (2000) ; B. V. DOBROV, O.V. KHORUZHII, Z. Yu. KOURTCHATOV, V. V. LIKHANSKII, "The development of a mechanistic code fission product behaviour in the polycrystalline UO2 fuel" Nuclear Engineering and Design, Vol. 195, Pages 361-371 (2000) ; R. E. VOSKOBOINIKOV, A. E. VOLKOV, "Effect of point defect interaction with bubble surface on the nucleation and growth of gas bubbles", Journal of Nuclear Materials, Vol. 297, Pages 262-270 (2001) ; P. LÖSÖNEN, "Modelling intragranular fission gas release in irradiation of sintered LWR UO2 fuel", Journal of Nuclear Materials, Vol. 304, Pages 29-49 (2002) ; J. REST "The effect of irradiation-induced gas-atom re-solution on grain-boundary bubble growth", Journal of Nuclear Materials, Vol. 321, Pages 305-312 (2003) ; L. NOIROT, Ph. GARCIA and C. STRUZIK, "A mechanistic fission gas behaviour model for UO_2 and MOX fuel," *Proc. of the Fission Gas Behaviour in Water Reactor Fuels*, *Nuclear science OECD NEA* , p. 131 , OECD, Cadarache, France (2000).

REF 2: E. FEDERICI, A. COURCELLE, P.BLANPAIN, H. COGNON, "Helium production and behaviour in nuclear oxide fuels during irradiation in LWR", Proceedings of the 2007 International LWR Fuel Performance Meeting, San Francisco, California, September 30th – October 3rd, 2007, Paper 1057

REF 3: Y. PONTILLON, J. BONNIN, E. ADDES, J-J. COCHAUD, J. PIQUEMAL, M. PONTILLON, C. ROURE, G. VOLLE, "Fission Gas Release Under Normal and off-Normal Conditions: New Analytical Device Implemented at CEA-Cadarache", European Working Group, "Hot Laboratories and Remote Handling", Plenary Meeting, Petten, the Netherlands, May 23rd – 25th, 2005

REF 4: Y. PONTILLON, P. P. MALGOUYRES, G. DUCROS, , G. NICAISE, R. DUBOURG, M. KISSANE, M. BAICHI, "Study of the Active Role Played by UO_2-ZrO_2-PF Interactions on Irradiated Fuel Collapse Temperature from VERCORS Tests", J. Nucl. Mat., 344, (2005), 265

REF 5: P.G. JEFFERY, P.J. KIPPING, "Gas Analysis by Gas Chromatography", PERGAMON PRESS, 1964

REF 6: SRA Instruments, instruments supplier, www.sra-instruments.com

REF 7: M. J. E. GOLAY, "Gas Chromatography", ACADEMIC PRESS, 1958

REF 8: P. H. RAY, J. Appl. Chem. 4, 1954

REF 9: F. ASPE, "Mise en place d'une méthode chromatographique de caractérisation en ligne des gaz occlus dans une céramique nucléaire", mémoire de DRT, CEA, 2004