**Fission Gas Release (FGR) from nuclear fuel:**
**Xe-Kr isotope monitoring at 1 ppm by on-line mass spectrometry**

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1. Context and Objectives
During irradiation in Nuclear Power Plant (N.P.P), fission gases are produced in the fuel matrix. It is important both, to investigate the effect of incorporating fission products in the fuel matrix and to understand the corresponding release of these fission gas, mainly composed of Xe and Kr, in order to best characterize the nuclear fuel.

MERARG II device (based at the CEA Cadarache centre) allows to characterizing the nuclear fuel with respect to the behaviour of fission gases during thermal transients [1]. In this device, the fuel is heated in order to extract a part of the gas inventory. FGR is actually monitored by on-line gamma spectrometry and by micro gas chromatography. These two devices record the quantity and kinetics of gas release rate. However they only address \(^{85}\)Kr radioactive isotope and the elemental quantification of Kr and Xe. In addition, fission gases are collected in capacities for off-line analysis by GC-MS, which allows dosing stable and active gases.

The aim of this work is highlight how the measurement of the release kinetics of Kr and Xe isotopes and \(\text{H}_2\) and \(\text{He}\), at masses 2 and 4 u, with a lower threshold of \(\text{ca}\) 1 ppm can be performed by means of an on-line mass spectrometer.

This paper is divided in three main parts. The first one, the specific analyser use in this study is described. Then the experimental qualification is detailed before conclusions are shown.

2. RGA type analyser
   a. Description of the analyser
To match these specifications, a Residual Gas Analyser (RGA) has been chosen as mass spectrometer. It is conventionally used as a smart gauge in a vacuum chamber, when it operates as an analyser of residual vacuum of this chamber. For our application, it is used as a Process Gas Monitor and requires a small-volume vacuum chamber.

The mass spectrometer consists of an open electron-impact ion source, a triple mass filter and two detectors (a Faraday Cage and Electron Multiplier). The triple filter provides high sensitivity, which is increased by a pre-filter operating in Radio-Frequency (RF) only mode [2] and a post filter to have a better focusing of ions toward detector. This device allows us to obtain a mass separation of 1 u, which is sufficient for the separation of Kr and Xe isotopes with high-speed mass scanning. This device is also very robust and compact: it measures 50 cm long and 30 cm wide.
b. Operating principle

The principle of the quadrupole filter has been described first by Paul and Steinwedel in 1953 [3]. The quadrupole filter comprises four cylindrical rods arranged in parallel. A cylindrical shape is easier to manufacture and to assemble than a hyperbolic shape, the latter providing the purest electric fields and better performances [4], [5]. However, the performances attained with a cylindrical shape are sufficient. A DC and RF voltage is applied to a pair of opposite rods, while an opposite voltage is applied to the other pair of rods.

The ions are slightly accelerated (typically 3 eV) and focused by lenses from the source toward the filter along the axis parallel to the rods. Inside the filter, the ion trajectories in the radial plane (plane perpendicular to the bars) can be stable or unstable according to the amplitudes of DC and RF voltage and the masse-over-charge ratio for a given distance separating the rods from the centre.

There are several operating mode for mass analysis. In a typical procedure, the amplitudes of the DC and RF voltage amplitudes are ramped continuously and simultaneously while maintaining their ratio constant. Hence, the ions of different masses are transmitted one after one with mass increase. A straight line passes by zero and the stability diagram apices of all the masses. In this case, mass separation is infinite however the number of ions tends to zero. By decreasing the value of the ratio the number of ions passing through the filter increases leading to mass analysis at constant resolution, but with an increase of the peak width (curve (a) Figure 2). A constant peak width is achieved with a scan line that is a curve starting at zero and increasing with DC to RF voltage ratio (curve (b) of Figure 2). However it is possible to approximate this curve over a reduced mass range by a straight line with a negative DC offset. The analysable mass-range value depends on the amplitudes and the DC voltage.
c. Adaptation for gas sampling to the line

The performance characterisation is performed with a standard bottle containing H₂, He, N₂, Kr and Xe at 100 ppm in Ar carrier gas. The output pressure is calibrated at 1.2 bars, the same pressure than MERARG sweeping line. Two pressure drop devices are used, a capillary and a molecular leak, to enter the gas in the vacuum chamber at 10⁻⁷ torr, typically. A double flow system, each having a separated pumping device, and the molecular leak located the closest as possible to Q_p flow allow us to ensure a fast response to gas inlet without segregation. The main flow is Q_p while Q_a is 100 times lower (Figure 3).

![Figure 3 Adaptation for gas sampling to the line of mass spectrometer.](image)

3. Experimental qualification

The resolution, sensitivity and isotopic ratio will be presented in this experimental qualification for a static and a dynamic gas inlet which simulate respectively off-line and on-line MERARG II measurements. Only results with Xe gas are presented, but similar results have been found for other gases.

a. Static mode
The valves are opened to reach 5 × 10⁻⁶ torr in the mass spectrometer chamber. Then inlet and bypass valves are closed. Hence the gas volume between valves passes through the molecular leak. This process is slow as it concerns a static volume of gas before the leak. This mode is suitable to analyse the total quantities released during annealing and retained in capacities.

As soon as the inlet and bypass valves are closed, the ion signal of each isotope is recorded every second over a period of few hours. Ion signal diminishes with gas quantity, while the isotopic ratios are quasi-constant (Figure 4). As a consequence, no segregation occurs.
In addition, 10 spectra are recorded with sample valve closed with $10^{-7}$ torr in the vacuum chamber for the Xe mass range. The mean value of these spectra is subtracted to each spectrum recorded at different instants with gas inlet on. For spectra recorded at initial time (Figure 5), the relative error between experimental and theoretical results [6] is less than 1.5 % for major isotopes and less than 10 % for isotope 128, the concentration of which is 2 ppm.

### Figure 4: Xe isotope ion signal versus time.

### Table 1: Comparison of Experimental and Theoretical Values

<table>
<thead>
<tr>
<th>Mass (u)</th>
<th>Experimental</th>
<th>Theoretical</th>
<th>Error between exp and theo</th>
</tr>
</thead>
<tbody>
<tr>
<td>128</td>
<td>2.12</td>
<td>1.91</td>
<td>9.98</td>
</tr>
<tr>
<td>129</td>
<td>26.42</td>
<td>26.40</td>
<td>0.08</td>
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<td>130</td>
<td>3.94</td>
<td>4.10</td>
<td>3.97</td>
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<td>10.40</td>
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</tr>
<tr>
<td>136</td>
<td>8.68</td>
<td>8.90</td>
<td>2.52</td>
</tr>
</tbody>
</table>

### Figure 5: Xe spectrum and isotopic ratio in static mode.

b. Dynamic mode

For the dynamic mode the three valves are opened allowing a steady flow entering the vacuum chamber through the molecular leak. The opening of the bypass valve is adjusted to have $2 \times 10^{-6}$ torr in the vacuum chamber. 10 spectra are recorded and the mean background spectrum is subtracted (as described in static mode).
The relative error between experimental and theoretical results is between 0.6 and 3 % for major isotopes and less than 7 % for isotope 128 (Figure 6).

4. Conclusion

The quadrupole mass filter is certainly the mass spectrometer the most widely used in the world since thirty years in many areas. They are widely for analyzing residual gases and more particularly for the isotopic analysis or elemental analysis. Technological advantages include low construction costs, the simplicity, the very compact size and robustness favourable for online process implantation in Hot Laboratory.

The RGA has been adapted to sample gas at high pressure without mass segregation. The dynamic mode (corresponding to on-line sampling) and the static mode (corresponding to capacity analysis of the released total quantity) have been qualified. The sensitivity threshold is as low as 1 ppm. The error between experimental and theoretical isotopic ratios are lower than few % for the 3 major isotopes and than 10 for isotope 128 at 1.9 ppm.

This mass spectrometer will be implemented on a MERARG II replica.

References


