

IMPROVEMENT OF FISSION GAS ANALYZER

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ABSTRACT

In order to study the Fission Product gas release behaviour in the high burnup fuel in the case of a Reactivity Initiated Accident, gas analysis have been performed on the fission gas released from the fuel rod. The techniques for the volume measurement of Kr were improved to gain its accuracy higher with the hardware and software approaches. This paper describes this measurement technique.

1. Introduction

For the beneficial utilization of the nuclear fuel in Light Water Reactor (LWR), its burnup has been extended and the behaviour of the high burnup fuel must be evaluated to keep its safety during the reactor operation including the accidental conditions. A Reactivity Initiated Accident (RIA) is one of the severe accidental conditions studied as a part of the safety research also for High burnup fuel. In this safety research regarding RIA, the amount of Fission Product (FP) gas release is one of the important parameters to evaluate the safety margin of the high burnup fuel rod. A part of FP gas accumulated in fuel pellets is released from the pellets to the outside to the fuel rod, and its amount of the released FP gas increased due to the burnup increasing affects the rod integrity. Therefore, it is important to know the behaviour of the released FP gas under the various situations especially high burnup fuel.

To understand the behaviour of the released FP gas from the high burnup fuel under RIA condition, simulated RIA examinations have been carried out with the high burnup fuel irradiated in a commercial reactor. The spent fuels were re-fabricated to the dedicate test rods for the pulse irradiation at the Nuclear Safety Research Reactor(NSRR). After that irradiation, the FP gas analysis was performed for the test rod at the Reactor Fuel Examination Facility (RFEF). To collect the released FP gas, the rod puncture test was applied for the non-failure fuel rods, whereas the remained gas inside the irradiation capsule was collected with the known volume cylinders for the failed rods. The Gas Chromatograph (GC, Shimadzu Co./GC-2014AT) and the Gas Chromatograph-Mass Spectrometer (GC-MS) were used to measure the volume and the isotopic ratio of Kr and Xe in the collected FP gas. Regarding the measurement of failed rod by using the GC, large amounts of N₂ in the collected capsule gas affect the measurement accuracy of Kr. The techniques for the volume measurement of Kr are improved to gain its accuracy higher with the hardware and software approaches. This paper describes this improved measurement technique.

2. Improvement of apparatus (hardware approach)

2.1 Trace gas detector

Regarding the failed rods, the released FP gas is diluted with the air in the irradiation capsule. Previous GC used Thermal Conductivity Detector (TCD) to detect the FP gas and air components. However, since the detection sensitivity of the TCD is not high, it was difficult to measure the diluted trace components such as Kr released from the failed rod. In order to improve the detection of the diluted trace gas, a Pulsed Discharge Detector (PDD, Valco Instruments Co., Inc./D-4-I-SH14-R) was added to the gas detector of GC. Additionally, to introduce the collected FP gas to the GC, the induction device which consists of a vacuum pump, pressure gauges and multiway valves was connected to GC. The schematic diagram of the fission gas measurement system with PDD and the gas induction device is shown in Fig 1.

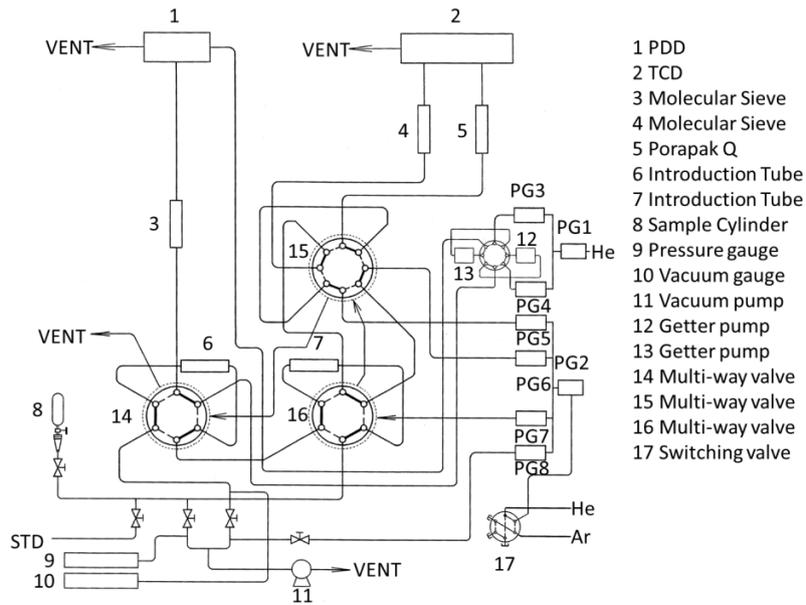


Fig 1. Schematic diagram of the fission gas measurement system

2.2 Measurement results

The volume ratio and the chromatograms of the standard gas with the improved GC are shown in Table 1 and Fig 2. In this figure, vertical axis represents intensity and horizontal axis represents retention time.

Components	ratio(%)
H ₂	0.2873
Ar	0.1014
O ₂	0.1006
N ₂	0.1020
CH ₄	0.1011
CO	0.1004
CO ₂	0.1005
Kr	0.487
Xe	0.493
He	Balance

Table 1: Standard gas ratio

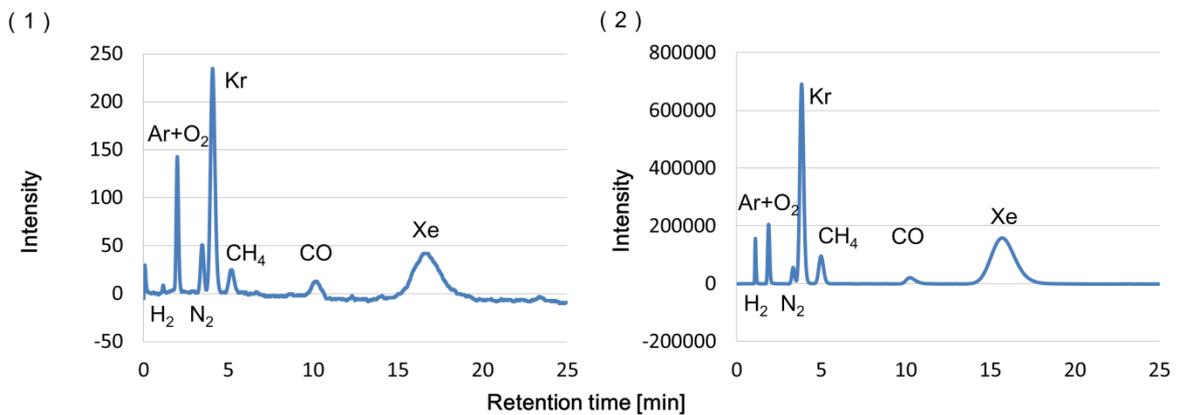


Fig 2. Chromatograms of same gas using (1) TCD,(2) PDD

Table 2 shows the Signal/Noise (S/N) ratio obtained from the standard gas measurement with the TCD and PDD. From these values, it is seen that the improved GC with PDD has higher sensitivity for both of Kr and Xe than GC with the TCD.

Components	Introduction amount (ppm)	S/N(TCD)	S/N(PDD)
Kr	9.95	4.75	2.29×10^3
Xe	9.95	9.17	5.25×10^2

Table 2: Comparison of S/N ratio with TCD and PDD

With the additional measurement of the standard gas, the calibration curve of S/N ratio was obtained by varying the amount of standard gas using the induction device. Table 3. shows the Minimum Detectability of the improved GC estimated from gradient of calibration curves. It is seen that the PDD has 500 times higher sensitivity of Kr compared with TCD.

Component	Detector	Minimum Detectability (ppm)
Kr	TCD	5.27×10^{-1}
	PDD	1.05×10^{-3}
Xe	TCD	2.67
	PDD	4.61×10^{-3}

Table 3: Minimum Detectability of Kr and Xe

3. Peak deconvolution (software approach)

3.1 Peak analysis

Although the detection sensitivity has been improved, the peak overlap of Kr and N₂ still remained. This overlap was caused by the closed retention times of the Kr and N₂. Especially for the failed rods, the released FP gas is diluted with large volume of air from the irradiation capsule, so that N₂ included in air affects the accurate measurement of Kr. Fig 3. shows an example of N₂ affection observed in a previous test. The leading part of Kr peak is hidden by the tailing of N₂ one.

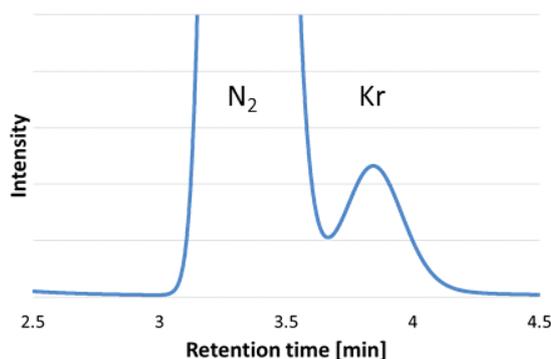


Fig 3. Chromatogram of diluted FP gas with large volume of air from the irradiation capsule.

This overlap significantly affects the quantitative analysis of Kr to determine the volume ratio of Xe / Kr. Therefore, it is necessary to separate the Kr and N₂ peaks. In general, a long column or a decreased column temperature is carried out to increase the clearance between these retention times. However, this method requires the longer measurement time and also the optimization of the measurement condition for each examination. At RFEF, the measurement time is limited by the facility operation and the amount of collected gas is little so that it is not suitable to perform the longer measurement with the optimization for each examination. The software analysis was applied for the measured chromatogram to deconvolute the Kr and N₂ peaks. In the ideal condition, the peak shape of the gas chromatogram has the Gaussian distribution. However, the measured peak shape is deformed from that ideal shape due to the

measurement condition. Therefore four different types of Gaussian functions were compared to adopt as the most appropriate function which can estimate peak shapes to the measured Kr and N₂ peak shapes. For the optimization of the estimated peak, non-linear least-squares method is carried out. [1] Each function is listed below.

(1) Exponentially Modified Gaussian Function (EMG) [2]

EMG Function has been used widely to describe chromatographic peaks.

$$f(t) = A \exp \left[\frac{\sigma^2}{2\tau^2} - \frac{t - t_m}{\tau} \right] \times \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\frac{t-t_m}{\sigma} - \frac{\sigma}{\tau}} \exp \left[-\frac{x^2}{2} \right] dx$$

(2) Empirically Transformed Gaussian Function (ETG) [3, 4]

ETG function is based on the decomposition of Gaussian function into leading and trailing edge functions, and subsequently modified.

$$f(t) = \frac{H''}{\{1 + \lambda_L \exp[K_L(t_L - t)]\}^{(t_L/t)^\alpha} + \{1 + \lambda_T \exp[K_T(t - t_T)]\}^{(t/t_T)^\beta} - 1}$$

(3) Generalized Exponentially Modified Gaussian Function (GEMG) [2, 4]

GEMG function is obtained by convoluting a Gaussian function with the resultant of two exponential functions of different time constants.

$$f(t) = \frac{A}{1+b} \left\{ \sum_{i=1}^2 \left(\exp \left[\frac{\sigma^2}{2\tau_i^2} - \frac{t - t_m}{\tau_i} \right] \times \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{z_i} \exp \left[-\frac{x^2}{2} \right] dx \right) \right\}$$

$$z_i = \frac{t - t_m}{\sigma} - \frac{\sigma}{\tau_i}$$

(4) Polynomial Modified Gaussian Function (PMG2) [2, 4].

PMG2 function is based on a variable standard deviation in Gaussian function.

$$f(t) = \frac{A\sigma_0}{\sigma} \exp \left[-\left(\frac{t - t_m}{\sigma} \right)^2 \right]$$

$$\sigma = \sigma_0 + \sigma_1(t - t_m) + \sigma_2(t - t_m)^2 + \sigma_3(t - t_m)^3 + \sigma_4(t - t_m)^4$$

3.2 Results of peak analysis

The result of peak analysis is shown in Fig 2. The graphs show residuals between the measured peak and the estimated peak. Additionally, these residuals were also evaluated with the minimizing the Sum of Squares of Residuals (SSR) as shown in Table 4.

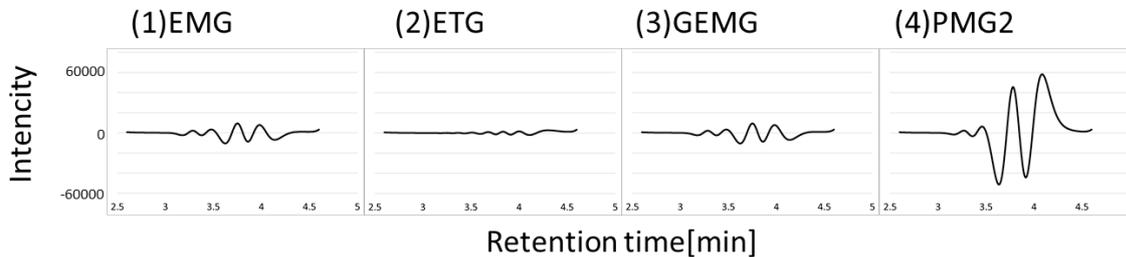


Fig 4. Peak analysis results of four functions. The graphs show residuals between measured peak and estimated peak. (1)EMG, (2)ETG, (3)GEMG, (4)PMG2

Function	EMG	ETG	GEMG	PMG2
SSR	4.37E+10	3.74E+9	4.37E+10	1.46E+12

Table 4: Results of peak analysis using Fig 4. chromatograms.

From Fig 4. and Table 4, it can be said that ETG indicates the best estimation in the four Gaussian functions in order of its smallest residual.

4. Conclusion

For the accurate measurement of the released FP gas during the RIA examination, the Gas Chromatograph was improved with the hardware approach and the software one. As the hardware approach, the PDD was added to the gas detector of GC and it can detect 500 times higher sensitivity of Kr compared with the TCD. As the software approach, ETG function adopted to deconvolute the overlapped two peaks of Kr and N₂. With ETG estimation, Kr volume can be evaluated with the deconvolution from N₂ peak in neither the long measurement time nor the changing measurement condition.

In the next step, the measurement accuracy with the improved GC will be evaluated with the standard gas which simulates the diluted gas component from the spent fuel rods.

References

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