

Development of a Gas Trapping System for Xenon and Krypton Fission Products throughout Dissolution of Irradiated Targets and Fuels in hot cells

Pierrick Menegon^{1*}, Nathalie Herlet¹, Yves Pontillon², Gilles Ferlay¹, Jean-Philippe Dancausse¹

1: DEN/VRH/DRCP/SE2A/LEHA
CEA Valrho – Site de Marcoule
BP 17171 30207 Bagnols sur Cèze CEDEX
France

2: DEN/CAD/DEC/SA3C/LAMIR
CEA Cadarache
13108 St Paul lez Durance Cedex
France

Abstract

In the frame of full characterisation of irradiated targets and/or nuclear fuels, the analysis of the fission products including gases is required. Nowadays at Atalante laboratory thanks to the specific dissolution process of irradiated targets and fuels used, gaseous forms of iodine or carbon can be quantitatively desorbed from dissolution solution and trapped for isotopic analyses. This was until now not achievable for krypton and xenon linked to dissolution step. As future studies will need such data, a gas trapping system for these rare gases is under development.

Up to now, two trapping ways were retained and evaluated: one where gases are physically trapped inside a storage capacity and the other one where xenon and krypton are chemically absorbed into organic oils or n-heptane.

These systems have to take into account the requirement of previous gas traps (iodine and carbon dioxide). Moreover the Kr and Xe quantities are usually quite small and isotopic proportion data have a great interest. Thus this trapping system must avoid interferences with Xe et Kr air components (airtightness) and loss (adsorption, iodine traps). These constraints are defining the materials and the design that will be used.

In the present paper, the developed experimental loops are presented together with the methodology and the first results obtained during the “cold” (i.e. not in hot cells) qualification and calibration phases.

KEYWORDS

Gas trapping system, krypton, xenon, dissolution, irradiated fuel, irradiated target, oil, heptane, organic, Atalante

1 Introduction

Nuclear energy industry is nowadays working on new kinds of reactors in the scope of Gen. IV systems. In order to define such reactors, better knowledge of particular physical constants (such as efficient cross sections of many elements inside the fuel) is required. As a consequence, dedicated programs have been launched where exhaustive characterisation of some irradiated nuclear fuels and/or targets is needed. That is including the analysis of gaseous fission products. Currently some of these gases are trapped and analysed, such as iodine and carbon isotopes, but it is not the case of krypton and xenon. The difficulty of trapping these noble gases

* Tel.: +33 4 66 79 77 57 fax: +33 4 66 79 16 48 mobile: +33 6 25 68 06 91 e-mail: pierrick.menegon@cea.fr

comes from the fact they have a very low chemical reactivity and consequently are participating only in few chemical reactions. Therefore a specific gas trapping system has to be defined and developed in order to specifically capture these rare gases. It will be implemented at the Atalante facility, where dissolution of irradiated fuels and targets are regularly carried out.

2 Design of the gas trapping system

The design of the gas trapping system has to take into account several restrictions. Some of them are related to the work in hot cell facility where the system will be finally implemented, the others are linked with the further analyses that will be realised.

Various methods are described in literature in order to trap and to recover krypton and xenon. The main are cryogenic distillation playing with ebullition temperature of krypton and xenon gases [1], absorption in organic solvent [1, 2], adsorption on active char or on zeolith [3, 4], permselective membranes [5] that are more permeable to krypton and xenon than to other common air components and physical trapping[6].

Atalante shielded cells are not equipped and designed with cooling fluids leading to obtain temperatures lower than 0°C. In the same way, due to safety reasons, the use of high pressured devices is not allowed without a specific risk study. As authorisation and modification delay are therefore not suitable with the need of the noble gas trapping system use, only two of the literature's methods seem to afford the hot cell restrictions.

The first method is a physical trapping concept [6] that is to fill a capacity regularly in order to capture the remaining dissolution gases outgoing from soda traps, which are pushed in direction of the capacity by a sweeping gas. The main difficulty is to fill as slowly as possible the capacity without losing gases, in order to avoid a too high dilution of the fission gases in the sweeping gas.

The second way is a chemical trapping method [2, 7]. The concept is the use the oils and n-heptane selective absorption properties for heavy noble gases, within ambient temperatures. The fission gases are again pushed through an absorption column by a sweeping gas. The phenomenon responsible of krypton and xenon absorption in oil is not yet fully understood [8]. Thus it remains unknown, it has to be checked if desorption of noble gases could occur when pure sweeping gas will pass through the krypton and xenon filled organic solvent.

3 Apparatus set-up description

Rare gas trapping system should be complementary with actual required iodine and carbon gas analyses [9], which also will be performed. Thus the experimental setup is divided into two modules. The main module is the common part of the two trapping methods. The two remaining modules are each specially designed for the trapping method used: the physical or the chemical one. Here after a description of each module is given.

3.1 Main module

The main module is composed with the dissolution process, the iodine/carbon isotope traps and nitrogen oxides traps. Iodine analysis prevents the use of neither grease substances nor plastics in the gas trapping device.

The characterisation of some targets includes the dissolution of the stainless steel cladding, banishing its use as material for dissolution vessel. A glass apparatus design with connections that can support the adjunction of metal devices (pressure transducer, etc.) has thus been chosen.

The air contains some krypton (1.14 ppm) and xenon (0.089

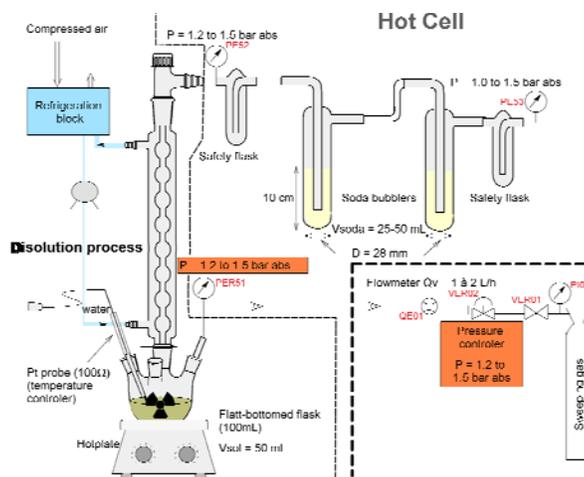


Figure 1: main component scheme

ppm). The concentration and isotopic distribution of both gases in the air are high enough to interfere with the predicted isotopic composition of fission gases, depending of initial chemical and isotopic composition of targets and of their mass. Thereby the trapping system has to be airtight.

Since the apparatus works under a pressure slightly higher than atmospheric one and because of the need to be airtight, the different parts of the apparatus should be tightly bound. In order to decrease the risk of leakages and gases loss by adsorption on joints, the number of parts composing the apparatus has been optimized and lowered, taking into accounts hot cells specificities (dimensions of material gateway, risk of breakage during manipulations, ...).

According to these considerations, the device schematically illustrated in Figure 1 has been built up together with the two trapping systems shown in Figure 2 **Error! Reference source not found.** and Figure 3 and described in the sections 3.2 and 3.3 respectively.

For a more detailed description, the main module is made of a pressure-equalizing dropping funnel which drops the nitric acid solution into a flat-bottomed flask. The top of the dropping funnel is the inlet of the sweeping gas. The flat-bottomed flask is welded to a reflux condenser for nitric acid vapour. The condenser is then bound to two bubblers with their safety flask. These bubblers are filled with a soda solution which is acting as an iodine and carbon dioxide trap as well as NOx trap.

In order to bind the different parts together, a special system with modified ball and socket joints has been designed: on the standard ball joint, a groove has been made in order to add an O-ring joint, to respect greaseless. The modified ball and socket joints provide airtightness at least for 4 bar rel. and allow some flexibility for the alignment.

3.2 Capacitive trap module

Following the main module, a 3 liters stainless steel cylinder capacitive trap is added (**Error! Reference source not found.**). This cylinder possesses a way to obtain vacuum inside, an analytic outlet, one pressure transducer, a pressure security device and a gas inlet. A three-ways valve, linked at the inlet, controls if the gas flow is stocked in the gas cylinder or sent towards gas outlet. Before this valve, a mass flow controller insures a pressure break between the main module and the cylinder. Therefore the mass flow controller allows filling up regularly the gas cylinder until there is no more sufficient pressure gradient (*ie.* a nearly equal pressure in all modules of the apparatus).

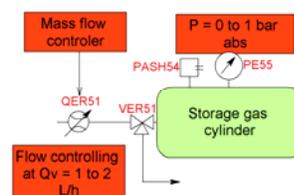


Figure 2: capacitive trap scheme

3.3 Oil trap module

The alternatively trap module is the oil/n-heptane trap, composed of an absorption column equipped with a multi-knit filling. It has been chosen because of the very low gas and oil flow that will be used. A pump will make a recirculation of the organic solvent from the bottom of the column towards its top if needed. The absorption column will be tested with and without recirculation in order to evaluate its impact. The literature provides some data on the absorption capacity of different oils and hydrocarbon [7]. The n-heptane and corn oil have been chosen in correlation with their good absorption capacity for Kr and Xe [10]. Specific tests on this module have to be done in order to see if there will be a desorption effect when pure sweeping gas will pass through the krypton and xenon filled organic solvent, since there will be no way to know exactly when dissolution of target is completed.

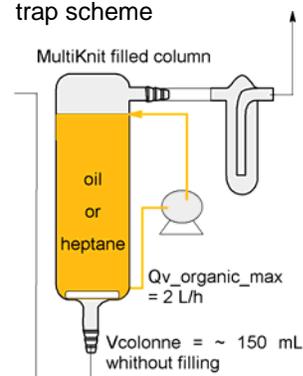


Figure 3: oil trap scheme

4 Experimental procedures and validation

Once the apparatus has been designed and a prototype made for each trapping method, the validation of the system performances is needed. The different modules are then tested in a “cold” calibration and qualification step actually in progress. Oil trap module needs to demonstrate its performance and needs to be optimized

(recirculation, height of filling, etc.). Capacitive trap module should be easier to test and qualify. Anyway, for both methods, the main module will have to be really airtight on one hand; and on other hand to avoid the noble gas losses especially on the joint surface, and in soda solution (iodine and NOx traps).

Before to describe the so-called “validation step on non-irradiated samples” procedure for the two trapping devices, the first point of the qualification (i.e. Kr and Xe adsorption on joints) is presented.

4.1 Kr/Xe adsorption on joints

Since krypton and xenon would be present in few quantities in most of the targets to be studied, and since elementary quantities and isotopic composition must be determined, every gas loss possibility must be eliminated. In that purpose, the number of joints has been minimized, as well as their visible surface for the gas since the literature shows that krypton and xenon may adsorb in plastics [7, 11].

The joint material choice has been made taking into account operating conditions (oxidizing fumes (NOx), known adsorption of krypton into plastics). Kalrez® material has finally been selected after an adsorption test conducted with a sheet of Kalrez® whose surface has been measured.

This experience has consisted in a metallic airtight gas cylinder filled at 2 bar rel. with a 1000 ppm krypton-xenon gas in a helium matrix. Analyses of the evolution of the gas composition inside the cylinder (without Kalrez® sample and with Kalrez® sample) have been made. Measurement points have been regularly sampled with a micro gas chromatography. Results comparing the blank and sample analyses show, regarding the measurement incertitude, a comparable evolution, that is, the experience does not show a significant krypton and xenon adsorption effect on Kalrez®.

With a conservative approach of these results, we can determine a maximum adsorption kinetic for both gases: 5.10^{-4} ppm_v.h⁻¹.mm⁻² for Kr and 10^{-3} ppm_v.h⁻¹.mm⁻² for Xe, that is, for a 2 hour dissolution in the apparatus, a loss of approximately $3.1 \cdot 10^{-3}$ ppm_v of Kr and $6.5 \cdot 10^{-3}$ ppm_v of Xe, what is low enough compared to Xe and Kr amount to be analyzed.

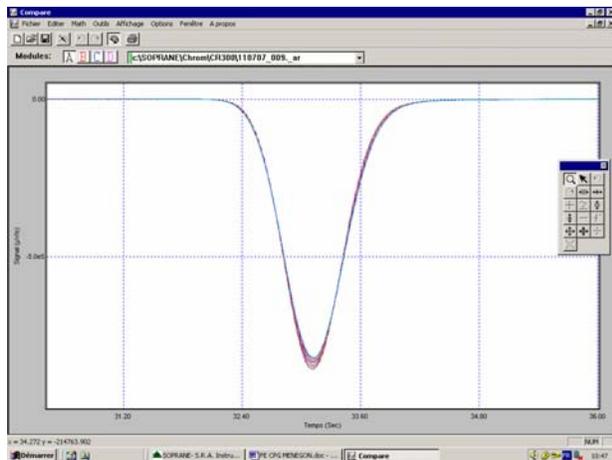


Figure 4: krypton pic; credits SECM/LMPA

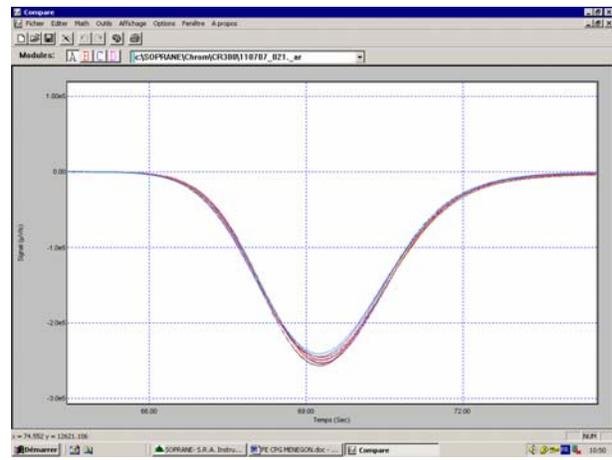


Figure 5: xenon pic; credits SECM/LMPA

4.2 Validation step on non-irradiated samples using µGC

The validation step will use a micro gas chromatography (Agilent 3000 Micro GC) in order to validate the whole setup using reference gases containing various relative concentrations of rare gases. More precisely the µGC is able to realise measurement on two different lines. One will be placed before and the other after the tested module.

Main trap module will be either tested in order to make sure the airtightness is obtained, in both ways (inside to outside and vice-versa), and if needed to locate more accurately gas loss location (in bubblers, at joints ...).

Oil trap module will be tested under this configuration for the following reasons:

- to know if the absorption column efficiency is as expected (absorption of krypton and xenon);
- to check if a krypton and xenon free sweeping gas will lead to desorption of the krypton and xenon trapped in organic solvent;
- to determine the impact of different parameters of the absorption column: recirculation flux, nature of organic solvent, height of the filling and determine the contact time needed to obtain a saturation of the organic solvent.

Capacitive trap module will also be tested using μ GC through mass balance between what is going out from the main module and what is found trapped inside the gas cylinder.

Other analytical tools may be used in order to confirm or explain the μ CPG results such as ICP AES and mass spectrometry.

5 Conclusion

The capture efficiency using both methods is currently under way:

- the glass material has been designed and received;
- the whole device has been realized;
- remote controlling and monitoring system of the pressure transducers, flow meter and pressure and flow controllers has been designed.

[1] Pence (D. T.), "Technology assessment and cost estimates for applying removal techniques for tritium, carbon-14, krypton-85, and iodine-129 from the nuclear cycle". Final Report, Science applications, inc., October 1978

[2] Russ (W. R.), Valentine (J. D.), Rooney (B. D.) and Gross (K. C.), "Fluid transfer concentration of airborne radionuclides to enhance monitoring capabilities", *Nuclear Instruments and Methods in Physics Research A*, vol. 422, 1999, p. 820–825.

[3] Wilhelmová (L.), Tomášek (M.) and Dvůrák (Z.), "The modified cryogenic adsorption method for the laboratory separation of ^{85}Kr from the atmosphere", *Journal of Radioanalytical and Nuclear Chemistry, letters*, vol. 95, n^o 1, 1985, p. 45–54.

[4] Munakata (K.), Kanjo (S.), Yamatsuki (S.) *et al.*, "Adsorption of noble gases on silver-mordenite", *Journal of Nuclear Science and Technology*, vol. 40, n^o 9, September 2003, p. 695–697.

[5] Rainey (R. H.), Carter (W. L.) and Blumkin (S.), "Evaluation of the use of permselective membranes in the nuclear industry for removing radioactive xenon and krypton from various off-gas streams". Completion Report, Oak Ridge National Laboratory, April 1971.

[6] Pontillon (Y.), Bonnin (J.), Adde (E.) *et al.*, "Fission gas release under normal and off-normal conditions: New analytical device implemented at the CEA-Cadarache", in *43rd Plenary Meeting of the European Working Group "Hot Laboratories and Remote Handling"*, Petten, May 2005

[7] Liu (K. V.), Gabor (J. D.), Holtz (R. E.) and Gross (K. C.), "Fluid-based radon mitigation technology development for decontamination and decommissioning", *International Conference on Nuclear Engineering*, vol. 5, 1996, p. 111–117.

[8] Rooney (B.), Gross (K. C.) and Nietert (R.), "A fluid-based measurement system for airborne radionuclides surveillance", in *19th Seismic Research Symposium on Monitoring a Comprehensive Nuclear Test Ban Treaty*, September 1997

[9] Esbelin (E.), Vaudano (A.), Dancausse (J-Ph.), "C-14, I-129 and Cl-36 Gaseous LLRN Analysis in Spent Nuclear Fuel: Results and Perspectives", *Global 2005, Tsukuba (Japan)*, 2005.

[10] Steinberg (M.) and Manowitz (B.), "Recovery of fission product noble gases", *Industrial and Engineering Chemistry*, vol. 51, n^o 1, January 1959, p. 47–50.

[11] Masson (M. B. R.) and Taylor (K.), "Solubility of krypton-85 in olive oil and human fat", *Physics in Medicine and Biology*, vol. 12, n^o 1, 1967, p. 93–98.

Acknowledgment: special thanks to SECM/LMPA for conducting tests on Xe-Kr adsorption on Kalrez®.