DEC 2017 CONTAMINATION INCIDENT AT THE IAEA SAFEGUARDS ANALYTICAL LABORATORY INVOLVING A SMALL QUANTITY OF NP-237

David Amaraggi, Markus Kohl, Mika Sumi, Steven Balsley, David Tissington, Diego Ortiz-Trujillo

International Atomic Energy Agency Laboratories, Friedensstrasse 1, A-2444 Seibersdorf, Austria

ABSTRACT

Since December 2015, the International Atomic Energy Agency (IAEA) completed the modernization and replacement of its vintage Safeguards Analytical Laboratory (SAL) by commissioning the new Nuclear Material Laboratory (NML) to maintain and enhance verification activities of the Office of Safeguards Analytical Services (SGAS). The commissioning of the new NML involved the transfer of thousands of nuclear material items including a broad range of Certified Reference Materials routinely used to ensure the quality of analyses performed. Some of these reference materials were already stored for more than 20 years as being extremely rare, seldom produced and therefore extremely valuable for the laboratory operation. On December 11th, 2017, an incident later described as INES below scale/level 0 occurred in the Pu storage area of the NML during physical status checking of a set of glass ampules containing standards solutions of neptunium-237. At 14:48, one of the ampules spontaneously burst whilst in the hands of a staff member. This resulted in the spread of Np-237 and broken glass in the room. The most likely cause of the burst ampule was an overpressure induced by alpha radiolysis inside the ampule, which caused disassociation of water and hydrogen/oxygen build up in the headspace of the ampule. This paper describes the root cause leading to the incident as well as its consequences and the actions to prevent other similar incidents to occur.

INTRODUCTION

The NML performs destructive chemical analysis of nuclear material samples taken by inspectors in nuclear facilities as part of the IAEA Safeguards mission. Nuclear material analysis is governed by the precision goals established by the International Target Values (ITV-2010) [1]. These constitute quite ambitious objectives and necessitate elaborate quality assurance and quality control measures. The Verification of appropriate compliance with ITV values is done by analysing well-characterised specimen so called Certified Reference Materials (CRMs) for which actual results can be compared with certified values. NML has a large inventory of such nuclear CRMs of various compositions and concentrations to allow these control measurements on a routine basis. Typically, CRMs in liquid solutions are conditioned in flame-sealed ampules to ensure integrity of the material. Since the radioactive substance causes radiolytic decay of the aqueous solution resulting in build-up of gases, pressure in the sealed vial gradually increases. The NML incident involved Np-237 in nitric acid solution, where pressure build up ultimately caused bursting of the vial and subsequent wide spread contamination of the storage room area with low level contamination of 2 staff members (intakes less than 0.25 mSv). Laboratory ventilation safety controls worked according to design and safety procedures were accurately followed by the staff members which resulted in the containment of the contamination preventing nuclear material release outside the room or outside the building (no contamination release to the environment). Identification, safe interim storage and final destruction of all other high-pressure ampules became a major effort, which was successfully completed as a priority task within 7 months after the incident. In parallel, further investigations were conducted to improve the algorithm used to estimate the pressure build-up due to radiolysis inside the glass-sealed ampules.

1 ROOT CAUSE AND FIRST IMPROVEMENT ACTIONS

1.1 INCIDENT

At approximately 14:40 on December 11th, 2017, staff members entered the Pu storage room in the NML and opened a nuclear material safe to check the empty space in thirteen sealed glass-sealed ampules of 6mL volume containing each 5mL of Np-237 dissolved in 1M nitric acid. Each ampule contained approximately 690 mg ($1.8x10^7$ Bq) of Np-237 enclosed in heavy double-plastic bags welded shut and contained in an aluminium can with a screw top lid. One of the thirteen ampules was removed from the safe and the aluminium can for inspection. Although no incident occurred during the inspection, at 14:48, a loud snap was heard and the ampule burst energetically in the hand of one of the staff members when the ampule was placed back in the aluminium can. The room was immediately evacuated to an adjoining room for immediate hand decontamination with water and contamination monitoring (approximately 0.5 Bq/cm^2 alpha measured by a contamination monitor device after removal of gloves and first wash, approximately 0.1 Bq/cm^2 measured on feet). At 15:00, both member staff went to the NML first aid room for further assistance by the First-Aid Warden, the Radiation Protection Officer (RPO) and the local medical service. The NML logistics areas affected by the incident were electronically locked down by the NML Security Officer as a preventive measure (area potentially contaminated, Continuous Air Monitor showing 14 Bq/m^3 contamination). At 15:49, when sufficient facts were available to confirm the nature and extent of the incident, a summary report was sent to the IAEA Incident Emergency Centre (IEC) as required by internal IAEA regulations. At 16:05, although there was no evidence of a wound and/or internal contamination due to the incident, both staff members were transferred by Red Cross ambulance to Donauspital in Vienna for further investigations. At 18:30 both staff members were discharged from the hospital as the dose assessment based on blood tests and whole body counting confirmed that no further medical treatment was required. Because of the low activity/doses involved (maximum committed effective dose of 0.25 mSv), the event was considered below scale/level 0 in terms of INES rating. To highlight the seriousness of this incident, if a worker had sustained a contaminated wound during this incident, it is likely that the committed effective dose would have been significantly higher than the actual dose received, potentially exceeding a statutory dose limit.

1.2 CLEAN UP ACTIONS

As the contamination was wide spread in the floor area and on table top where Np glass-sealed ampule was inspected (see figure 1), access to the Pu storage room was restricted to prevent any further risk of contamination of staff members until necessary remediation actions would be completed. Floor contamination near the door area was in the range of 0.1 Bq/cm^2 to 1 Bq/cm^2, and contamination levels generally increased closer to the table (spill point) to a maximum of approximately 10 Bq/cm^2. The tabletop was contaminated in its entirety, and had numerous small ‘hot spots’ where solution droplets had spilt of approximately 100 Bq/cm^2.

Figure 1: Glass-sealed ampule after burst (tabletop inside Pu storage room)

As the floor in this room was sealed with an epoxy floor sealant, contamination on the floor could be easily removed using an ‘off the shelf’ bathroom cleaner (Cif). For other areas (mainly the tabletop) Decon Gel was applied, left to dry overnight and then removed the next working day. Cleaning work was done by at least two staff members: one Senior Laboratory Technician and one Radiation Monitoring Technician (RMOT) wearing Personnel Protective Equipment including Tyvek coveralls and full-face respirators. One staff member used hand held alpha detector to monitor decontamination progress while the other staff member was using absorbent wipes (paper towel) and Cif to remove the contamination from the door of the room and working inwards. When the floor monitoring/decontamination was completed, accessible areas of the safes and walls were monitored and decontaminated using the same method as was used for the floor. Once all decontamination was finished, the floor was washed using a dedicated controlled area floor cleaner and wipe test samples were taken of the floor and analysed for non-fixed contamination. Once the above was completed, the room was deemed clean and returned to full operation on 20th December.

1.3 INVESTIGATIONS

During storage of an aqueous solution that contains alpha-emitting nuclides, the energy of alpha particles causes radiolysis of H_2O and the release of H_2 and O_2 in gaseous form. Gaseous hydrogen and oxygen build up depends on both energy deposited in the solution by the emitted alpha particles and on the free volume above the solution (headspace). The energy released in the solution depends on the solution chemical characteristics (isotopic composition, total mass of radioisotope, molarity of nitric acid solution) and on the time elapsed since the production date. When the solution is stored in a gas-tight glass container, pressure build-up occurs. If not released, the container may rupture and result in an exothermic recombination of H_2 and O_2. Energetic release of radioactive liquid mixed with sharp glass fragments may cause serious injury, and result in internal and external contamination. This risk was well known by SGAS since the first incident that occurred in 2008 [2] and was followed up through monitoring of estimated pressure in glass-sealed containers with aqueous solutions containing alpha-emitting nuclides. A calculated pressure of two bar (0.2 MPa) was set as the action limit for the safe removal of an ampule from the inventory and its destruction using a specific device designed in 2008. In November 2015, the list of CRM in stock (about 1040 vials) was reviewed to identify potential safety hazards before physical transfer from the old SAL to the new NML. The pressure inside the ampules was estimated using an algorithm from previous works [3][4] and with available information in the corresponding certificates. Three glass-sealed ampules belonging to three different series were identified with a risk of bursting and were destroyed using the cracking device. Remaining CRM glass-sealed ampules were transferred with no incident to the NML and were stored with careful monitoring of the pressure build up. The inspection done on 11th December 2017 revealed that the headspace of the Np-237 containing vial was 20 time less than listed in the inventory database (1mL instead of 20 mL) leading to a significant under-estimation of the calculated pressure (7.8 bar instead of 1.3 bar). As the vial was being placed back into the aluminium can, the external force exerted on the vial by the staff member, together with the internal 7.8 bar pressure, probably caused the glass to crack. The movement of glass shards across micro fractures during the crack probably caused an electrical discharge that resulted in the energetic recombination of hydrogen and oxygen in the vial, and hence the flash that was reported.

1.4 IMPROVEMENT ACTIONS

In order to prevent other incidents, investigations were made by the RPO and the NML SAS Office in charge of nuclear material booking to identify other potential hazardous (high pressure) CRM stored at NML. After the incident in 2017, a new application was added to the Laboratory Information Management System (LIMS) of NML to follow up the estimated pressure inside all CRMs stored in glass-sealed ampules (corresponding to 1040 items belonging to 64 different series). Using feedback from the incident, the hydrogen pressure was recalculated for all items assuming a conservative headspace volume. Using a conservative headspace of 1 mL in the algorithm revealed that approximately 100 ampules had an estimated pressure over the limit of two bars. As only 12 ampules could be cleared out using headspace information from the certificates, a physical inspection was prepared to confirm the headspace in the remaining other ampules. A specific procedure was issued by the RPO on 29th January 2018 and the physical inspection took place on 7th March involving four staff members (one Senior Laboratory Technician, two RPOs and one RMOT). About half of the items could be cleared out as having enough free volume over the solution to keep the pressure inside the ampule less than 2 bar for more than one year. These items were returned to their original safe for storage (see table 1).

Table 1: Characteristic of series identified with high pressure inside glass-sealed ampoules – P1: estimated pressure using conservative headspace of 1 mL; P2: estimated pressure using measured headspace; V1: minimum headspace for pressure less than 2 bar; V2: measured headspace

Number of ampules	P1 (bar)	V1 (cm3)	V2 (cm3)	P2 (bar)	Action
2	4.5	4	12	1.3	Return to safe for storage
6	2.1	2	21	1.1	Return to safe for storage
24	8.3	7	63	1.1	Return to safe for storage
10	4.0	4	12	1.3	Return to safe for storage
3	3.3	4	21	1.2	Return to safe for storage
6	2.5	2	42	1.0	Return to safe for storage
3	2.4	2	9	1.2	Return to safe for storage

The other half of items (total 44 ampules including the remaining Np-237 bearing ampules) were confirmed to have a potential internal pressure over two bars (see table 2).

Table 2: Characteristic of series identified with high pressure inside glass-sealed ampoules

CRM Source	**Radionuclide mass per ampule**	**Isotopic Composition**	**Production year**	**Estimated Pressure (bar)**
AEA-1	0.7g Np	100% Np-237	1996	7.8
AEA-2	1mg Pu	97% Pu-239 (2% Pu-238, 1% Pu-240)	1992	2.2
AEA-3	1mg Pu	95% Pu-239 (4% Pu-238, 1% Pu-240)	1992	2.9
IRMM	22mg Pu	2% Pu-238, 56% Pu-239, 27% Pu-240, 7% Pu-241, 8% Pu-242	2013	4.8
NPL	1mg	99.6% Pu-240 (0.4% Pu-238)	2010	3.1

All these ampules were carefully transferred one by one into gas tight storage containers capable to withstand overpressure from a bursting ampule (steel container with a capacity 9.5 litres, maximum pressure 5.5 bar, P3 particulate filter attached to pressure release valve). In addition to the usual PPE to address contamination risks (Tyvek coverall, full-face negative pressure respirator with P3 filter), helmet with protective face visor attached, cut resistant gloves and fire brigade tunic was worn by the staff member who physically handled the high-pressure ampules. In the meantime, the algorithm used to estimate the pressure build-up due to radiolysis was modified to increase the accuracy of hydrogen yield calculation. Firstly, corrections were made in the laboratory database to include contribution of first daughters to energy production by alpha particles (see figure 2). Secondly, linear regression model for logarithm of hydrogen generation yield was replaced by linear interpolation model to better-fit experimental results for the yield, in particular at 1 M nitric acid concentration (see graphic1). The estimated pressure for the five series was recalculated showing significantly higher value with the new algorithm for the Np-237 CRM series mainly due to modification of the hydrogen yield calculation at 1 M (see table 3). Slight increase of estimated pressure could also be observed for the IRMM series because of its initial isotopic composition (7% Pu-241) when including contribution of first daughter (Am-241). As a result, the new algorithm, considering daughter’s contribution used in the inventory database should be an additional countermeasure for the NML to reduce the risk of under-estimating the pressure built up inside stored glass-sealed ampules.

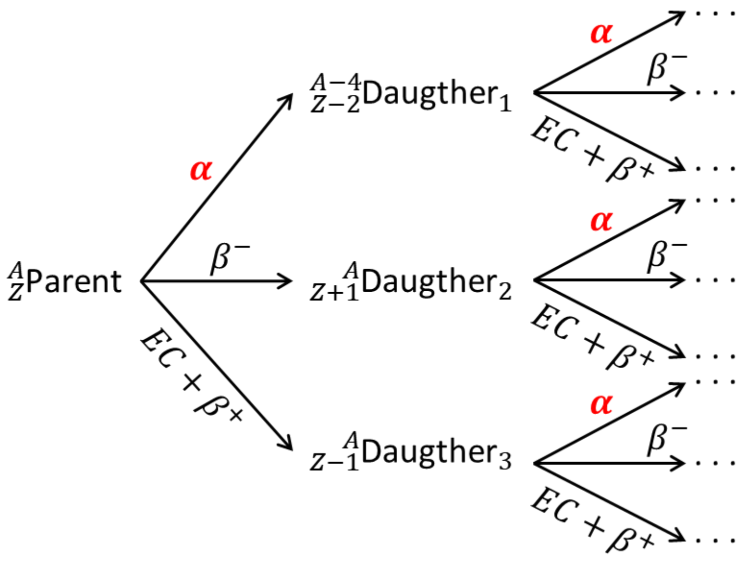
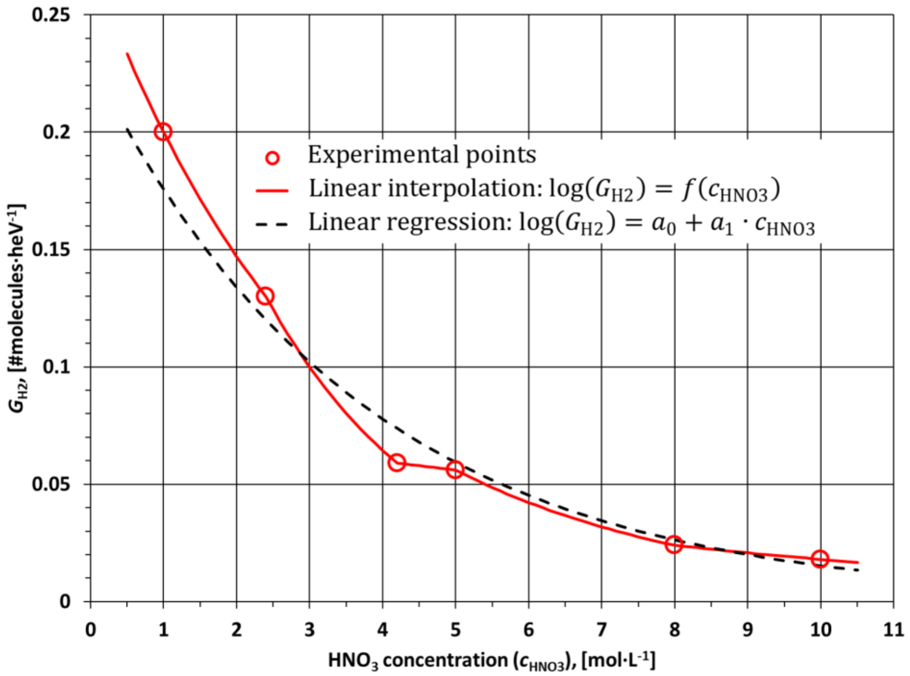


Figure 2: Energy deposited by alpha particles emitted by parents and the daughter nuclei taken into account in the estimation of the pressure build-up due to radiolysis



Graphic 1: Hydrogen yield as a function of molarity of nitric acid concentration\

Table 3: estimation of pressure inside ampules – comparison between different algorithms; (1) linear regression ($\log(G_{H2})$ versus c_{HNO3}) without daughters contribution; (2) linear interpolation ($\log(G_{H2}) = f(c_{HNO3})$) without daughters contribution; (3) linear interpolation ($\log(G_{H2}) = f(c_{HNO3})$) with daughters contribution (selected algorithm in the NML inventory database)

CRM Source	Previous algorithm (1)	New algorithm (2)	New algorithm (3)
AEA-1	7.8	8.7	8.7
AEA-2	2.2	2.3	2.3
AEA-3	2.9	3.1	3.1
IRMM	4.8	4.8	4.9
NPL	3.1	3.3	3.3

2 AMPULES DESTRUCTION PROJECT

2.1 DESIGN FOR A NEW CRUSHING DEVICE

At the end of 2015, a cracking device set up in a glove box was used in SAL to destroy all high pressure CRMs before the move to the NML. At the end of the destruction campaign, it was discarded; at that time there was no foreseeable future use for the cracking device as all known high-pressure vials had been crushed and procedures were in place to open sealed vials before they reached overpressure. At the beginning of 2018, a new cracking device was therefore needed to crush the ampules identified with new algorithm. The design of the new cracking device was studied by SGAS with the aim to optimise some features of the old device, minimizing the need for glove box modification and ensuring the same level of safety protection. Although the old device gave full satisfaction during previous cracking campaigns in 2008 and 2015, its operation was complex (motorization of a piston with movable block inside the glove box) and the equipment was bulky. Smaller motors were available on the market but as none of them provided sufficient torque, the design was completely changed for a simpler system using assembled commercial components and internal workshop capabilities. After several design review meetings, a hydraulic Jack system (commonly used for car repair) was finally selected in March 2018, which had capacity to crush safely any type of ampule (stated force of 4 tons). The hydraulic Jack was mounted on a metal stand dimensions adjusted to the size of an explosive suppressant bag (designed to contain blast and heat from LiPo batteries) with the largest possible ampule from the CRM stock (7.3cm length) put inside (see figure 5). The electrical remote control for pushing was replaced by manual actuation of a hydraulic pump from outside of the glove box. A La Calhene port (type of tight connection for glove-box with 105 mm diameter) was modified so that oil pressure could be transmitted through a hydraulic line passing through an adapted La Calhene cover connecting the pump to crushing jaws (see figure 6). This design offered the safety advantages of remote operation (hands of member staff out of glove box during cracking), tightness of glove box at all times and mitigation of risks associated with ampule blasting (spread of glass fragments and contamination in the glove box contained by LiPo bags). The new design also brought operational benefits from being more compact inside the glove box, using low cost commercial components and required limited modifications of the glove box. The original cracking procedure was reviewed by the RPO with some updates compared to the previous campaigns. The main steps remained the same but temporary storage time in dry ice was extended to 2 days so that cooling efficiency of ampules would be kept even with large size gas-tight containers. The cracking device design was successfully validated in April during inactive tests done with surrogates (empty penicillin glass vials, 60mL) including cooling of ampule in liquid nitrogen and transfer to LiPo bag prior to crushing step (see figure 7).

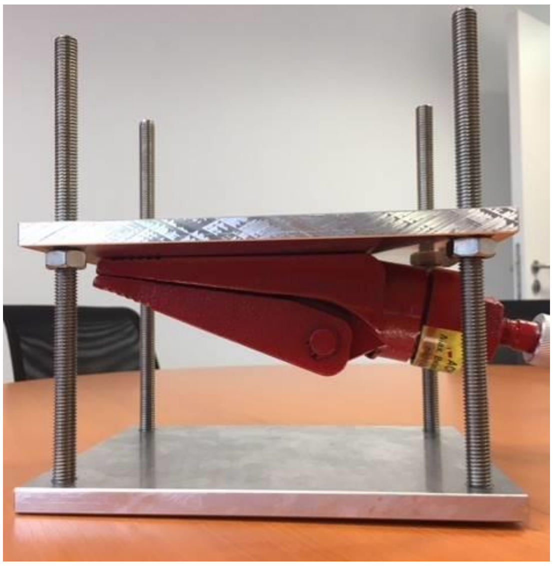


Figure 5: Cracking device (new design)

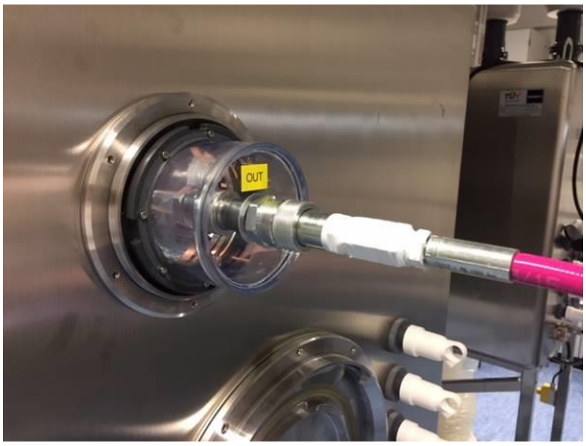


Figure 6: Feedthrough cover for hydraulic cable

Figure 7: Frozen ampule

2.2 AMPULES DESTRUCTION CAMPAIGN

At the end of May 2018, safety authorisation issued by the IAEA Regulator was received by SGAS to proceed with the destruction of the selected 44 ampules using the new design cracking device. The campaign was held in two batches. On 28th June the 13 remaining Np ampules were processed first as considered a priority given the incident and the estimated internal overpressure. Once having enough evidence that the procedure was safe and efficient, the remaining ampules containing Pu CRM solutions were processed on 11th July. Although time was needed to prepare the campaign, the real time needed for cracking was quick and completed with no issues following each step of the procedure: only 1 hour was needed to crack ampules for the first batch, and about 4 hours for the second batch.

3 CONCLUSIONS

Since 2016, algorithms were applied on a routine basis by SGAS to existing CRMs radionuclide solutions inventories at the NML to follow up the risk associated with long time storage of 1040 glass-sealed ampules. Despite of this safety precaution, pressure was significantly under-estimated in 14 Np ampules due to inaccurate information of the free volume space, resulting in the burst of one ampule during a physical safety inspection. The incident at the NML has demonstrated the importance of having good laboratory design and staff members well trained for emergency procedures to prevent contamination release to the environment and limit dose rate intake of personnel attributable to the incident. Clean-up work was completed within a week and preventive actions to reduce risks in the long term were executed within several months after the incident. Potential additional hazardous ampules were identified among the remaining CRM solutions stock and were temporarily safely stored before being finally destroyed 7 months after the incident thanks to a new cracking device internally designed, fabricated and tested at the NML. Since the incident, a new algorithm using linear interpolation and including daughter's contribution has been used at NML and integrated to the laboratory management system; internal pressure inside remaining stored glass-sealed ampules with CRM presenting similar safety risks is recalculated every month including a projection up to one year ahead to anticipate opening of ampules before reaching action limit of 2 bars absolute.

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REFERENCES

[1] "International Target Values 2010 for Measurement Uncertainties in Safeguarding Nuclear Materials", Safeguards Technical Report STR-368, IAEA, Vienna, (November 2010)

[2] "The Aug 2008 incident at the IAEA Safeguards analytical laboratory involving a small quantity of Pu-240", C. Schmitzer, INMM proceedings, (January 2009)

[3] J. R. WEISS, C. E. PIETRI, Radiat. Effects, 19 (1973) 191

[4] Y. KUNO, T. HINA, J. MASUI, J. Nucl. Sci. Technol., 30 (1993) 919