International certification process of the ABACC-Cristallini method for UF_6 sampling – current status

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Abstract:

Based on the conceptual development and empirical validation of the Argentine chemist Dr. Osvaldo Cristallini, Brazilian and Argentinean researches developed, with the support of ABACC, a new UF6 sampling method suitable for uranium isotopic determination. This new method, known as the ABACC-Cristallini method, has been successfully tested by ABACC in Argentine and Brazilian laboratories and in pilot plants. The method was renamed as "Standard Practice for Sampling Gaseous Uranium Hexafluoride using Alumina Pellets" and has been submitted to the ASTM International. It is now in its final process of approval.

This paper describes the steps of this process and presents preliminary results associated with the application of the method. This sampling practice offers significant advantages over the conventional sampling practice because it allows handling non-reactive, non-volatile, solid UO_2F_2 sample instead of highly reactive and volatile UF_6. The sample amount is minimum and can be transported with lower radioactivity level and reduced radiological risks. Additionally, there is no risk of airborne uranium particle and HF release.

Uranium isotopic ratios measured with mass spectrometry techniques in UF_6, sampled by both the conventional and the ABACC-Cristallini methods provided results which are in good agreement within the stated uncertainties.

The acceptance of the ABACC-Cristallini method by facility operators is key to the success of this project. Therefore, it is relevant to confirm, by field testing, the practicalities and advantages of the method, which includes the conformance with facility safety procedures, work instructions and training programs.

Keywords: nuclear material safeguards, uranium hexafluoride sampling, uranium isotope composition.

1. Introduction

The ABACC-Cristallini Method for sampling UF6 by adsorption and hydrolysis in alumina pellets inside a Fluorothene P-10 tube has been developed by the Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials (ABACC) [1] [2]. This method has advantages compared to the currently used sampling method, for which UF6 is cryogenically transferred into a stainless-steel vessel for transportation, with hydrolysis and isotopic analysis being performed after shipping to the analytical laboratory.

Facility operators and safeguards inspectors routinely take UF_6 samples from processing lines or storage cylinders to determine the uranium isotopic composition, most important its major ratio ($^{235}U/^{238}U$). The conventional sampling method collects gaseous samples containing 5-10g of UF_6 and requires the use of liquid nitrogen.

UF_6 samples must be safely transported to external laboratories for analysis. Transport includes, among others, public roads and international air shipment. Due to the hazards of UF_6, air transport has become difficult with many transport operators and regulators refusing to carry the material.

The proposed method results in sample vessels suitable for transport, because contain no UF_6, but just a significantly smaller amount of uranium, in the form of UO_2F_2, sufficient to prepare the solution for the determination of the isotope composition. Once the sampling process is complete, the vessel can be transported and handled in a less restrictive manner due to the lessened hazard of handling non-volatile, non-acid UO_2F_2 versus UF_6.

Another advantage of the method using P-10 made of PCTFE, a change in colour of the alumina pellets, from white to yellowish, will be visible as UO_2F_2 is formed. The degree of colour change is a rough indicator of the sufficient amount of uranium adsorbed as presented in Figure 1.

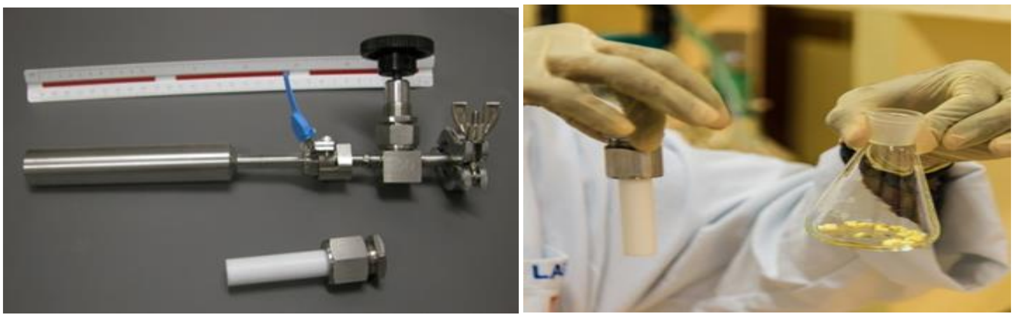

Figure 1: Sample vessels and alumina pellets

2. Qualification for safeguards application

ABACC proposed a rigorous validation program to establish the reliability of the method for nuclear safeguards applications and ^{235}U enrichment determination. The primary evaluation objective of the validation exercise was to determine if the ABACC-Cristallini and direct hydrolysis sampling methods give uranium isotopic measurements in agreement with each other. This program has been successfully carried out under a framework of international collaboration.

This included using four UF_6 Certified Reference Materials (CRM) showed at the table 1, as a source of uranium hexafluoride, and sampling each of the four CRMs by using two different sampling methods: adsorption on alumina (ABACC-Cristallini method) and the standard direct hydrolysis method. Additionally, the two sampling methods measurement results were compared with the certified values for the CRMs to ensure sample integrity.

CRM	$n(^{235}U)/n(^{238}U)$	U	% rel U	ITV-2010
IRMM-020	0.00209570	0.00000060	0.029	0.70%
IRMM-022	0.0072562	0.0000012	0.017	0.28%
IRMM-023	0.0338810	0.0000060	0.018	0.14%
IRMM-029	0.044052	0.000014	0.032	0.14%

Table 1: IRMM UF_6 n(235U)/n(238U) certified values with their expanded uncertainties

The worldwide joint validation program was started in 2016. The samples were distributed to following participating laboratories:

- CNEA (Laboratorios de Control Químico y Físico y de Espectrometría de Masas, Argentina)
- IAEA (Safeguards Analytical Services, Nuclear Material Laboratory, Austria)
- JRC-Geel (Directorate G - Nuclear Safeguards and Forensics, European Commission, Belgium)
- CTMSP (Laboratório de Caracterização de Urânio, Brazil)
- LANIE-CEA/Saclay (Laboratoire de Development Analytique Nucleaire, Isotopique et Elementaire, France)
- JRC- Karlsruhe (Directorate G - Nuclear Safeguards and Forensics, Analytical Service, European Commission, Germany)
- ORNL (Nuclear Analytical Chemistry and Isotopics Laboratory, USA) and NBL (New Brunswick Laboratory, USA)

These samples were measured by these laboratories using their mass spectrometric methods for uranium isotopic composition, particularly $^{235}U/^{238}U$. The conclusion of the validation program for the purpose of nuclear material accountancy (e.g. safeguards), the ABACC-Cristallini UF_6 sampling method provides comparable results to a direct hydrolysis method for uranium isotopic determinations [3].

The Cristallini method was proposed to ASTM International in 2017 with the collaboration of NBL under the framework of the technical cooperation between ABACC and DoE and with the support of specialists of Brazil and Argentina.

3. The process at ASTM International

ABACC is proposing a new procedure to be verified independently by ASTM experts and to be approved by consensus as an official ASTM standard.

The related procedure “Standard Practice for Sampling Gaseous Uranium Hexafluoride using Alumina Pellets”, commonly referred as “ABACC-Cristallini Method”, describes a technique for sampling gaseous uranium hexafluoride (UF_6) with subsequent recovery of the uranium in the sample for use in the determination of its isotopic composition, in particular, its major amount ratio ($^{235}U/^{238}U$).

The practice involves the use of a small sample vessel filled with aluminum oxide (Al_2O_3) pellets which serve as a substrate upon which UF_6 gas hydrolyzes predominantly to uranyl fluoride (UO_2F_2). After pumping the remaining volatile compounds, the vessel contains no UF_6 and may be handled and shipped under appropriate conditions just for UO_2F_2.

Uranium is then leached from the alumina pellets to yield an aqueous solution suitable for the determination of uranium isotopic composition, which can be performed by several mass spectrometric techniques.

Figure 2 illustrates a set-up for sampling gas from a process line or a UF_6 cylinder using a typical manifold system and a P-10 tube containing alumina pellets.

The “Standard Practice for Sampling Gaseous Uranium Hexafluoride using Alumina Pellets” is under analysis by the Committee on Standards Review and if approved the procedure may be published by ASTM International by July 2019.

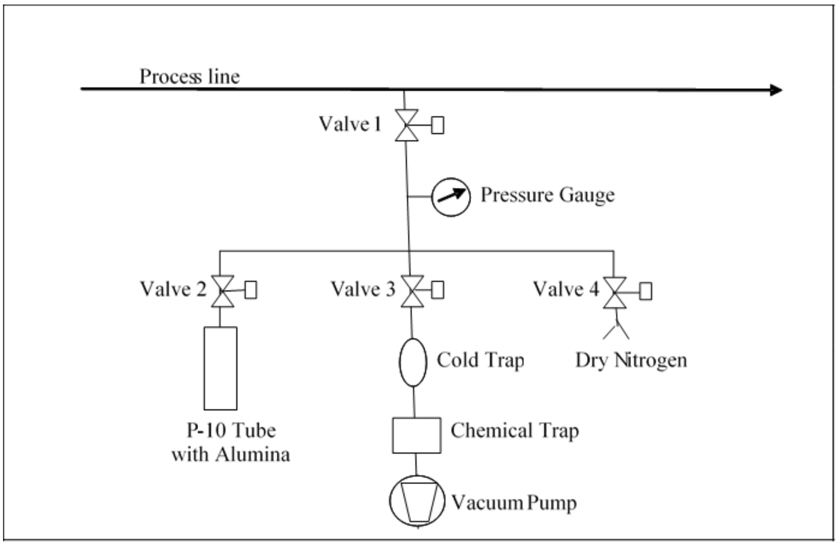

Figure 2: Scheme of equipment setup for UF_6 sampling using alumina pellets

4. UF_6 Sampling Procedure

The principle of the method was first demonstrated at the "Comisión Nacional de Energía Atómica (CNEA)" laboratories in Buenos Aires, Argentina. UF_6 sample bottles with isotope composition in the range of 0.31 and 4.05 ^{235}U % in mass were used to evaluate the influence of UF_6 pressure and sampling time on the amount of uranium absorbed by alumina pellets loaded in P-10 fluorothene tubes. An amount of 1 g of alumina and a sampling time between 10-30 minutes were considered sufficient to collect the amount of U needed for isotope ratio measurements by thermal ionization mass spectrometry (TIMS) [1] [2]. A procedure to recover the U adsorbed was also developed.

Although the first results obtained at the bench were encouraging, concerns were raised whether the method could effectively work in an isotope enrichment facility, mainly due to different gas flowrate and pressures ranges verified in a typical facility.

The proposed standard practice is applicable to sampling gaseous uranium hexafluoride (UF_6) from processing facilities, isotope enrichment cascades or storage cylinders, using the sorbent properties of aluminum oxide (Al_2O_3).

The sampling procedure consider that a tared sample vessel is filled with a weighed quantity of alumina pellets, attached to a sampling manifold, and exposed to gaseous UF_6 for a timed period, typically 10-30 minutes depending on the gas pressure in the installation and the desired uranium amount in the sample. UF_6 readily hydrolyzes in contact with alumina pellets generating predominantly uranyl fluoride (UO_2F_2).

After the required amount of UF_6 has been hydrolyzed by the alumina pellets, the vessel and the manifold are evacuated to remove remaining volatile gas. The valve that connects the installation to the manifold is closed and the vessel and the manifold are pressurized to atmospheric pressure with dry nitrogen (N_2). The vessel can now be safely removed from the manifold and sealed. The amount of uranium contained in the vessel can be determined by reweighting the vessel.

Using a P-10 vessel loaded with 1 g of alumina pellets, and sampling from a UF_6 cylinder or processing lines under typical conditions will easily allow the adsorption of 100-300 mg of uranium, depending on the gas pressure, temperature and time of exposure. The maximum adsorption capacity for uranium is approximately 600 mg.

The alumina pellets are then removed from the vessel and leached firstly with distilled water and secondly with nitric acid. The alumina fines produced must be carefully removed from the uranium solution. Finally, the solution can be prepared for the determination of uranium isotopic composition.

5. Analytical measurements

The P-10 tubes containing alumina and uranium fluoride (UO_2F_2) were submitted to alpha and beta particles counting. The average activity obtained in this sampling exercise was 313 cpm, a value 10-100 smaller than the values usually obtained for UF_6 samples collected using the conventional method.

First P-10 tubes were reweighted; then safely disassembled under a fume hood. Alumina pellets were transferred to an Erlenmeyer flask and leached initially with distilled water and finally with nitric acid. The alumina fines were carefully removed from the solution so that it could be prepared for the further measurements. The U contained in the solution was separated by the use of an ion exchange resin. The U recovery was in the range of 80-85%.

The amount of U collected in the UF_6 sampling exercise for the three streams (F, P and T) was in average equal to 187 mg. It is important to say there were differences in flowrate and pressure between these three streams. Despite, this value is much higher than the 200 ng needed to perform the U isotope ratio measurements by total evaporation method (TE) applied to TIMS.

This method samples a much smaller amount of UF_6 than the traditional method, in the order of a few milligrams instead of grams. This small amount of UF_6 combined with the procedure of pumping and flushing the P-10 bottles with dry nitrogen to the atmospheric pressure, that assures that no volatile gas or UF_6 are present in the P-10 tube, will facilitate the characterization of the sample to be transported under the IATA regulations [4].

The number of pellets in each P-10 tube was also counted, resulting in 32 pellets in approximately 1 g of Al_2O_3. This means each pellet absorbed about 6 mg U. This is an important value because the objective is to recover U from just few pellets, or at least the most yellowish ones, instead of the whole set of pellets within the tube. The goal of this initiative is to reduce the sample waste.

The isotope measurements were easily carried out using the total evaporation method with a thermal ionization mass spectrometer. CRM materials from NBL-DOE-USA were used to correct mass discrimination. $(n^{235}U)/(n^{238}U)$ isotope ratio typical expanded uncertainties were in the range of 0.02 - 0.05%.

6. Conclusions

The procedure “Standard Practice for Sampling Gaseous Uranium Hexafluoride using Alumina Pellets” is under analysis by the Committee on Standards Review. It is expected that the procedure may be published by ASTM by July 2019.

The procedure for sampling gaseous UF_6 in P10- tubes using alumina pellets was easily executed. The procedure is safe, simple and straightforward, with no impact on the safety and in the process operation of the facility. It was repeated in slightly different gas flowrate and pressure conditions, proving to be also flexible and robust, requirements to be successfully implemented worldwide in facilities operating at unpredictable process conditions.

The ABACC-Cristallini sampling practice offers significant advantages over the conventional sampling practice because it allows handling non-reactive, non-volatile, solid UO_2F_2 sample instead of highly reactive and volatile UF_6. The sample amount is minimum and can be transported with lower radioactivity level and reduced radiological risks. Additionally, there is no risk of airborne uranium particle and HF release.

U adsorbed in alumina pellets could be readily recovered by repeated washings with good yields. The suggested sampling time provided U amounts much higher than the amount needed for isotope ratio measurements by thermal ionization mass spectrometry.

The U amount recovered was enough even if repetitions of isotope ratio measurement were needed. There was no need to know details the process parameters of the isotope enrichment facility, which preserved its data confidentiality.

7. Recommendations

Extensive testing and validation exercises of the ABACC-Cristallini UF_6 sampling method have been carried out since Dr. Osvaldo Cristallini envisaged the absorption of UF_6 gas in alumina pellets to analyze UF_6 uranium isotopic determination in nuclear material samples for safeguards purposes more a decade ago.

ABACC in cooperation with prestigious high-level recognized organizations and laboratories demonstrated that ABACC-Cristallini UF_6 sampling method is equally effective and safe for the operation of the nuclear installations as the traditional UF_6 gaseous method and has significant advantages than the traditional method. Therefore, ABACC has a great expectation that stakeholders could use this method in lieu of the traditional one.

ABACC encourages the use of ABACC-Cristallini UF_6 sampling method to relevant stakeholders, like the enrichment facilities operators and safeguards organizations since this new method for sampling gaseous UF_6 using alumina pellets is much more efficient in reducing the quantity of sampled nuclear material, minimizes waste production at the facility and laboratories, it has advantages from the radiation protection viewpoint and solves the issue of the transport of UF_6 samples.

The advantages of this method are such that we encourage relevant parties to consider facing safety authorities´ and operators’ requirements to obtain pertinent authorizations to try and use the ABACC-Cristallini method.

ABACC with the cooperation of NBL has been proposing this method to be considered by ASTM as a standard practice. The ASTM procedure “Standard Practice for Sampling Gaseous Uranium Hexafluoride using Alumina Pellets” is under ASTM´s review and the approval process and it should be finalized with the ASTM publication of this standard by July 2019.

8. References

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