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Qualification for Safeguards of the Sampling of UF₆ using Alumina – “ABACC-Cristallini Method” – Progress Achieved

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Summary

During the procedure currently used to sample material from process lines in uranium enrichment plants, the uranium hexafluoride (UF₆) in gaseous phase is collected by desublimation inside a metal sampling cylinder cooled with liquid nitrogen or in a fluorothene P-10 tube type in certain facilities. A new method has been proposed [1], [2], [3] to collect the UF₆ (gas) by adsorption in alumina (Al₂O₃) in the form of uranyl fluoride (UO₂F₂) (solid). This procedure receives the name “ABACC-Cristallini method” (A-C method).

This paper describes the progress achieved in the technical certification process that ABACC is pursuing for qualification of the UF₆ sampling A–C method for uranium isotopic determination. This method uses a fluorothene P-10 tube type containing alumina pellets that absorb and hydrolyze UF₆ directly during the sampling.

This method has been proven effective for ABACC safeguards purposes and potentially for IAEA safeguards as well. The activities being undertaken with the IAEA in the framework of the Brazilian and Argentinean Safeguards Support Programs with the coordination of ABACC represents a significant step towards the ultimate goal of using ABACC-Cristallini UF₆ method in place of some or most of the traditional UF₆ sampling for safeguards.

The intercomparison results obtained from different laboratories will be the basis of the validation process to confirm that the new method can be used for routine safeguards application at the enrichment plants. It was previously verified that there is not a loss of

¹ Dr. Osvaldo Cristallini (In Memoriam), widely renowned Argentine radio-chemist, has developed the “ABACC-Cristallini” method for UF₆ sampling.

accuracy for the uranium isotopic determination with real UF₆ samples taken from enrichment plants. This new method has advantages compared to the usual method with less residual material left at the facility and also less constraint related to nuclear material transport regulation.

The UF₆ sampling for safeguards comprises the taking of the samples from the enrichment plants processes to their analysis for total U concentration and isotopes. It is worthy to note that the focus of this intercomparison is the validation of the sampling technique. The next step will be to carry out another intercomparison exercise by taking UF₆ samples with the ABACC-Cristallini method at enrichment plants from Argentina, Brazil and any other facilities and related laboratories from elsewhere that could be interested in participating.

1. ABACC-Cristallini Method Description

The method uses a fluorothene P-10 tube type containing alumina pellets that absorb and hydrolyze UF₆ directly during the sampling. The alumina pellets retain up to few hundred milligrams of U (in a solid compound UO₂F₂) without the need of using liquid nitrogen during sampling. With this new method the UF₆ sample content left at the installation (archive sample) will be lower and less reactive as the actual, the laboratory procedures for manipulating the sample will be much easier (no need for hood, gas sampling, vacuum system, nitrogen cleaning, etc), the residual uranium retained at the laboratory will be much lower, the sampling device is less expensive compared to the sampling metallic bottle type, there will be savings in transport cost as well, and it is relatively safer concerning radiological protection aspects during transportation. Potential changes in IATA transport regulations for UF₆ may eliminate the possibility of air transport of traditional UF₆ samples. Therefore the A-C method may become the only alternative for air transport UF₆ for safeguards. The Figure 1 shows the two types of UF₆ sampling device and the alumina pellets.

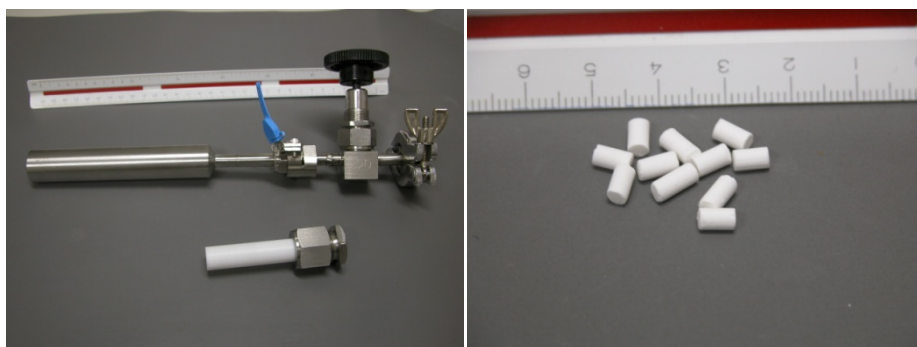
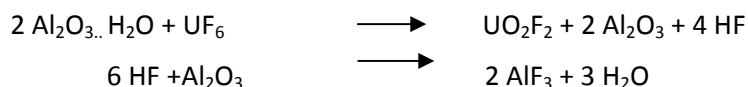


Figure 1: UF₆ sampling devices – Hoke tube / fluorothene P-10 tube and alumina pellets

1.1. Reaction Mechanism

The chemical traps are commonly employed in enrichment plants to remove UF₆ from various gas streams of the process. The effectiveness of the chemical trap largely depends on the particular absorbing material that is used to fill the trap. As these traps are the final barriers

between the process and the environment, they should assure the total elimination of UF₆. The materials normally used in these traps are alumina (Al₂O₃) and sodium fluoride (NaF). The election of the appropriate absorber is made comparing different performance factors as: reaction kinetics, absorber regeneration / uranium recovery requirements, absorbing capacity, pressure losses, and effects of other system components such as HF and F₂. These factors do not have the same importance in every application. For the UF₆ sampling method proposed the predominant factors are reaction kinetics and uranium recovery. The effectiveness of the alumina relies on the hydrolysis of the UF₆ with the available lattice water. The reaction is the following:



The UF₆ alumina trapping mechanism depends on the hydrolysis reaction with subsequent retention of the uranyl fluoride (UO₂F₂) in the porous structure. The UO₂F₂ is a non-volatile solid and soluble in water if uranium concentration is low. This facilitates the preparation of an adequate solution to carry out the isotopic analysis.

Due to the characteristics described above, alumina pellet was chosen as the material to be used for UF₆ sampling.

2 Advantages – Beneficial Aspects of the ABACC-Cristallini Method

ABACC and the IAEA are always looking for more effective and efficient methods to perform safeguards inspections at nuclear facilities. The current safeguards approaches for enrichment facilities are based on a combination of routine announced and unannounced inspections, in which several verification activities take place, including environmental sampling (ES) and destructive assay (DA) sample collection from UF₆ in-process material and selected cylinders. Samples are then shipped offsite for subsequent destructive analysis at specified laboratories. The main objective of the UF₆ analysis is the determination of isotopic enrichment. As previously said, the ABACC-Cristallini method reduces the challenges and increasing complications that the UF₆ traditional samples pose in transportation, it is also simpler and safer in terms of the storage of UF₆ DA samples and also optimizes the time for the sample taking process.

Among the benefits, the amount of UF₆ taken during the sampling is much less than in the method currently in use. The laboratory procedures for manipulating the sample will be much easier (no need of hood, gas sampling, vacuum system, nitrogen cleaning, etc), the residual uranium retained at the laboratory will be much lower, the sampling device is less expensive, and not less important, there will be savings in transport costs as well, and the A-C samples will be much easier to ship from the view point of transport regulations.

2.1 UF₆ Samples Transport and Storage

The UF₆ sampling technique using A-C method in enrichment plants has been demonstrated and the quantities in mass involved in this new process have been reduced by a factor 10 to the current process, so this reduction of nuclear material in samples allow the flight transport of the UF₆ samples without restrictions imposed by the safety transport regulation. During experiments carried out at constant and decreasing pressure using experimental setup

presented in Figure 2 [2] the retained UF₆ mass (mg) by the alumina pellets range from 110 to 947. The quantity of nuclear material was enough to carry out an isotopic analysis.

Regarding this transport issue, the transfer of bottles with less than 0.1 kg of UF₆ are considered exempted material, considering the “Regulations for the Safe Transport of Radioactive Material” from IAEA. This consideration is a general framework for all radioactive material transport and the IATA (International Air Transport Association) include that limit in its own regulations, but each flight company can reduce the exemption limit. Taking into account the above information, if the amount of nuclear material to be transported is small and the chemical compound is less reactive than UF₆, the transport regulations are easier to fulfill.

The remaining UF₆ samples, in the form of UO₂F₂, retained in the alumina pellets kept at the facility can be discharged after a certain time, so consequently the reduction of waste realized by this new method is more cost-effective in safeguards, safety and operational perspectives.

2.2 UF₆ Sample Taking Process Control

Regarding to the UF₆ sample taking from enrichment installations, the A-C method is much simpler than the current method. A P-10 tube containing at about 1.0 g of alumina pellets was weighed and installed at the conventional sampling position. It was pumped for approximately 30 minutes using the installation’s vacuum system until a pressure of at least 1.0×10^{-3} mbar was reached.

Sampling started when the UF₆ stream was directed to the P-10 tube. It is important to stress that no liquid nitrogen was employed in this operation. After a sampling period of 30 minutes the normal UF₆ stream was reestablished in the installation. The tube was then evacuated for 10 minutes to remove volatile compounds formed. After that it was pressurized with dry nitrogen and the tube was removed from the installation and closed with a Teflon blind gasket and a monel nut. Finally it was weighed to determine the mass of UF₆ effectively collected.

The sampling experiment described above was realized at a Brazilian ultracentrifugation enrichment facility. Samples were collected in triplicate at the enriched and depleted sampling positions. The whole procedure required at about 4 hours and was repeated three times along the same week. It is clear the length of time spent in this procedure can be greatly reduced with some optimization studies.

Another study conducted at the same facility addressed the concern of possible process line contamination. First, it was proved that under high vacuum, even before the contact with UF₆, no measurable gas has evolved from alumina pellets. Second, despite of the pumping operation realized before sampling, alumina pellets remained very well kept within the P-10 tube. Third, after the contact with UF₆, no gas impurity has been detected in the region near to the sampling positions.

The new process establishes a more rigid time control for the sample taking for different extraction lines (feed, product and tails) and cylinders, while in the current UF₆ sampling method the time and quantities taking during process are not well established, so the mass will be measured after the sample process is finished, that it is also inconvenient for operator if the minimum sampling mass is not reached.

It is known, that the UF₆ sampling kinetics strongly depends on the system pressure. In the A-C method it is also a relevant parameter, but at the same time, this information may be considered commercial sensitive information, thus, it will be not available when the lines

process piping are sampled. This constraint is not an issue in the A-C method since the saturation of the alumina pellets is reached relatively fast, mainly due to the small amount of nuclear material to be collected over a wide range of line pressure.

3. Tests and Results of the ABACC-Cristallini Method.

The analytic results gathered from the comparison between UF₆ hydrolysis process in conventional and A-C methods were presented in 13th Workshop on Separation Phenomena in Liquids and Gases (SPLG)[4]. The results show that no significant differences in the isotopic analysis by mass spectrometer were found between the direct hydrolysis method and the alumina pellet method.

4. Qualification Program of UF₆ Samples Collected on Alumina – A-C Method

ABACC has established a program to validate the A-C method for safeguards routine use. The main objective of the program is to ensure the new sampling procedure using alumina is suitable for use in taking samples for isotopic analysis.

An intercomparison exercise coordinated by ABACC to validate the A-C method has been underway for sometime. This exercise has been performed in cooperation with NBL and Argentinean and Brazilian laboratories and experts. In addition, efforts have been made within the ABACC-IAEA cooperative framework as well as by Argentina and Brazil in the IAEA's Safeguards Support Programme to advance in the validation of the A-C method for IAEA safeguards use.

Between 2013 and 2014, ABACC gave new impetus to the validation of the A-C method. A meeting between ABACC, NBL, Argentina and Brazil experts engaged in the program to certify the A-C method with ASTM to update the plan and actions were performed. A fruitful exchange of views between ABACC and the IAEA in the way forward took place. The updated version of the intercomparison exercise was produced, including the participation of the IAEA Laboratory, as well as others. The working plan proposal is still being assessed by the participating laboratories.

The plan includes taking of samples of the UF₆ reference materials by the current procedure and by the A-C method. They will be sent to internationally recognized laboratories for isotopic analysis by high accuracy mass spectrometric methods. A statistical evaluation and comparison of the results of these U isotopic abundance determinations will be performed to ensure there is no detectable difference in the isotopic between identical samples obtained by the two methods.

The sample materials will be IRMM UF₆ certified reference materials. The goal of the study is to demonstrate that the A-C sampling technique has no detectable effect on the isotopic composition of UF₆ material.

One laboratory will perform the sampling and four laboratories will utilize the same procedures, as detailed below, for retrieving the uranium from the sample containers and performing isotopic measurements. All laboratories will agree on sample processing and analysis methodologies before the intercomparison begins.

4.1 Sampling of UF₆ Certified Reference Material

Four ampoules, each containing approximately 20 grams of certified reference materials in the form of UF₆ are available at the Laboratorio de Control Físico y Químico, CAC, CNEA (Argentina). They were prepared and supplied by the IRMM. The materials and their certified n(235U)/n(238U) isotopic ratios are the following: IRMM 020 (0.0020930), IRMM 022 (0.0072535), IRMM 023 (0.033863) and IRMM 029 (0.044039). These CRM ampoules will be used for the qualification program.

These available UF₆ CRM ampoules will be sampled to produce 9 subsamples by the direct hydrolysis sampling method and 9 subsamples by the A-C method. The sub-sampling procedure will be performed in the “Laboratorio de Control Físico y Químico (CAC, CNEA, Argentina). ABACC, in coordination with ARN and CNEN will be responsible for shipping the samples to the participating laboratories.

The participating laboratories will be invited to witness the sub-sampling operation with schematic representation of equipment setup for UF₆ sampling with alumina pellets in Figure 2.

The sub samples will be shipped to the participating laboratories including ORNL, IAEA, CTMSP (Brazil), and CNEA (Argentina). Each laboratory will receive 2 subsamples by direct hydrolysis and 2 subsamples by the A-C method obtained from each CRM. The ninth sub-sample of each CRM and sub-sampling method will be kept as an archive sample.

In order to eliminate the risk of isotope cross contamination coming from different CRM materials flowing in the same sampling system, a different manifold set-up will be used for each reference material.

4.2 Direct Hydrolysis and Hydrolysis over Alumina

The standard procedures to obtain a sample from a metal reference cylinder, which utilizes direct hydrolysis of the sample in a P-10 tube loaded with distilled water and the procedure, as proposed in the A-C method, to obtain a sample by hydrolysis over Al₂O₃, are described in the working plan for qualifying A-C method. [5]

4.3 Recovery of Uranium Retained in the Alumina

As the uranyl fluoride (UO₂F₂) is a very soluble salt, much of the U retained in the alumina pellets can be effectively removed with distilled water. However, due to the high material porosity, several washes with small water volumes and some washes with 0.3M nitric acid are necessary for complete dissolution of the uranium.

A high solution acidity, intense heating or prolonged contact times are not recommended, because the alumina can be partially dissolved and the final solution will have a high aluminum content that may affect the isotopic analysis procedure.

The recommended procedure for U recovery from the alumina pellets will be send to the participating laboratories. With this procedure, it is possible to recover around 85 % of the original U, without dissolving a significant quantity of alumina. Each laboratory should inform and explain any change or extra step in the procedure followed to prepare the samples. Each laboratory will agree on sample handling, processing, filament loading and isotopic analysis methodology prior to the start of the intercomparison.

4.4 Statistical Evaluation and Report of Results

A plan for statistical evaluation has been prepared in advance by NBL, in order to establish the quantity of measurements to be performed for each sample, what reference materials will be used for calibration and quality control, and how the data will be evaluated. Each laboratory will perform the required quantity of measurements (as derived from the plan for statistical evaluation) for each sample received. The results and uncertainties for each measurement will be reported independently.

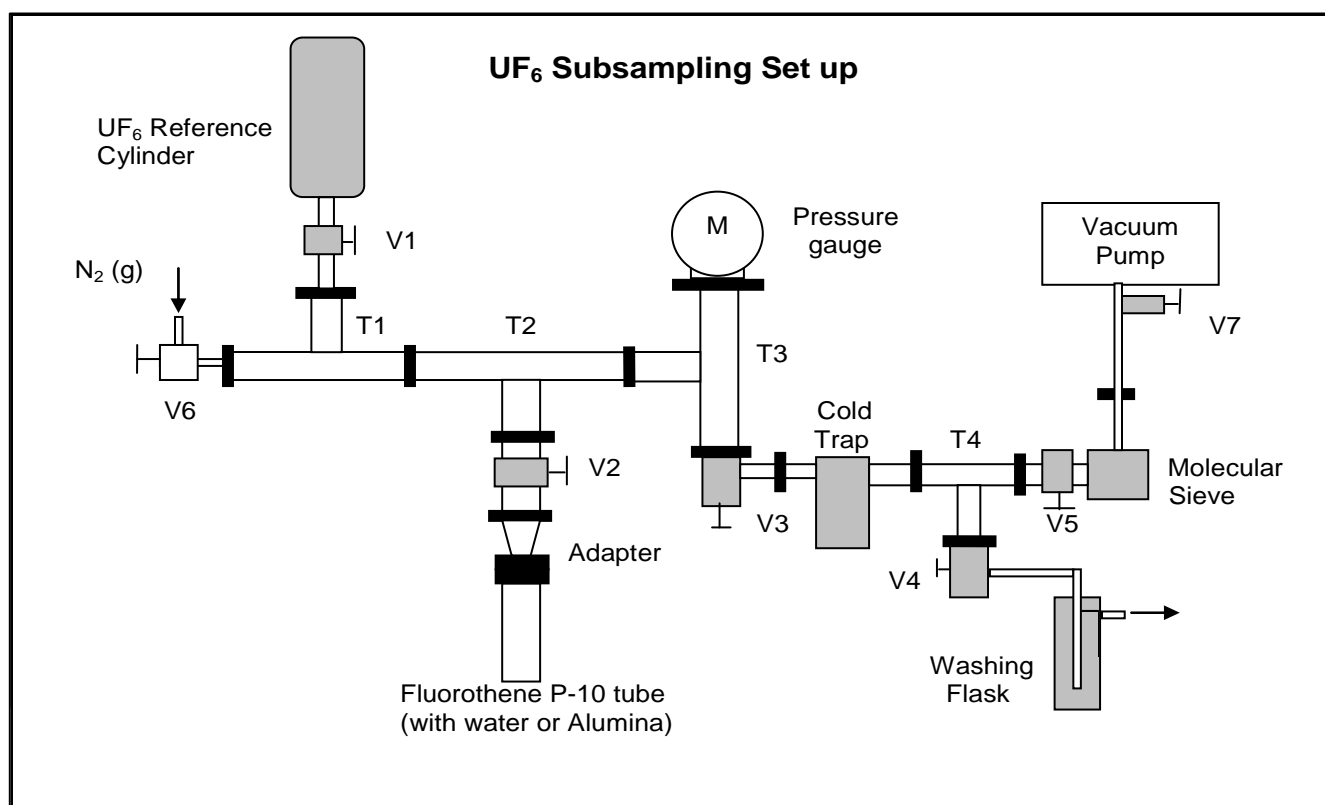


Figure 2: Scheme of equipment setup for UF₆ sampling with alumina pellets

Each laboratory will produce a report of results to be submitted to ABACC. The report will indicate:

- Analytical technique (e.g. TIMS or MC-ICP-MS) and method (e.g. conventional, total evaporation, modified total evaporation) for isotopic determination;
- CRM used for correction;
- CRM used for Quality Assurance;
- Measurement date and analyst name;
- Measured sample identification;
- Isotopic ratios, including at a minimum ²³⁴U, ²³⁵U, and ²³⁶U data, for each sample analyzed including calibration and quality control samples;
- Overall value and GUM-compliant measurement uncertainties for each of the sample types. An uncertainty budget will be supplied including an explanation of how the value and uncertainties are determined.

The reported results will be organized by ABACC and submitted to NBL for statistical analysis. The evaluated results will be submitted to the participant laboratories for comments. The final report and support documentation containing the method description and the inter-comparison data will be submitted to ASTM to start the qualification process.

5. Future: A Field Trial involving the use of the ABACC- Cristallini method at laboratories and Enrichment Facilities.

The other goal of the project is to demonstrate and document further that the Cristallini sampling technique does not disturb the U isotopic composition of depleted, natural and low enriched uranium hexafluoride, thus showing that this sampling method can be safely use in any commercial uranium enrichment facilities for the determination of the isotopic composition. The tasks to develop this phase of the project are still ongoing.

To this end, a second step after the validation by ASTM of the A-C methodology is achieved is to organize another intercomparison exercise involving more sampling at the enrichment facilities and laboratories in Brazil, Argentina and other interested operators from other countries to further demonstrate the technique in the real operational environment.

Conclusions

The implementation of safeguards at enrichment facilities requires the taking of UF₆ samples during interim and PIV inspections for isotopic determination. On a case-by-case basis, and depending on the safeguards approach for each individual facility, the use of the A-C method would be appropriate to meet safeguards objectives. In other instances, a combined scheme of UF₆ A-C and current methods sampling and analysis would not be excluded a priori, for instance in the case the IAEA requires taking higher UF₆ mass for other analytical determinations, such as Uranium concentration measurement.

At this stage it is not adventurous to say that the A-C method is a very positive development for safeguards implementation at enrichment facilities worldwide. For all the advantages that the A-C method has shown and the results already obtained, ABACC has proven that this method serves the purpose and it represents a tangible contribution to more efficient safeguards and thus, it is determined to start using the A-C method in the near future.

In the framework of the Quadripartite Safeguards Agreement, under the IAEA Safeguards Support Programms and the cooperation between ABACC and NBL together with the participating laboratories of Argentina, Brazil and IAEA, the intercomparison exercise is of utmost importance to progress towards the approval of the A-C method for safeguards.

In order to verify that the method is suitable for sampling for isotopic determinations, identical samples of several standard UF₆ materials will be sampled by both A-C technique and by conventional UF₆ sampling technique. These ‘paired’ samples will be analyzed by high accuracy TIMS or MC-ICP-MS analyses and a statistical evaluation of the results for the Cristallini samples and the standard samples will be performed. This evaluation will include independent analysis of each laboratories result and a combined evaluation of all laboratories results. Each laboratory will use the same reference material (IRMM uranium isotopic standard) to serve as calibration and Quality Assurance (QA) samples.

Moreover, the tasks foreseen in the validation program would also demonstrate that the A-C method could be use a safeguards technique in any nuclear facility where UF₆ samples for DA analysis for isotopic determination is appropriate.

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