UF_6 SAMPLING METHOD USING ALUMINA

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Abstract

The ABACC-Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials performs safeguard inspections jointly with the IAEA-International Atomic Energy Agency at enrichment plants in Brazil and Argentina. Particularly, at enrichment plants in Brazil that use centrifuge enrichment process, routine and unannounced inspections are performed and UF_6 samples are taken from process lines and cylinders to verify the uranium enrichment conformity with design/operator declarations. ABACC has developed a UF_6 sampling method for enrichment determination (named ABACC-Cristallini Method) which uses a fluorothene P-10 tube type containing alumina pellets that absorb and hydrolyze UF_6 directly during the sampling. The alumina pellets retain up to few hundreds milligrams of U (in a solid compound – UO_2F_2) without the need of using liquid nitrogen during sampling. This new method has advantages compared to the currently used method that uses a Hoke tube as: the UF_6 sample content left at the installation (archive sample) will be lower and less reactive, the laboratory procedures for manipulating the sample will be much easier, the residual uranium retained at the laboratory will be much lower, the sampling device is less expensive, there will be saves in transport cost as well, and it is relatively safer concerning radiological protection aspects during transportation. This paper describes the physical principle of the new method, the experiments carried out at laboratory taking into account different process parameters foreseen in real cases, and the development of a procedure for recovering the uranium retained inside the alumina pellets for the U enrichment measurement. The behavior of the new method is compared to the traditional one, showing no loss of accuracy for the enrichment determination with real UF_6 samples taken from enrichment plants. The qualification strategy applied to the new method for routine safeguard application at the enrichment plants is presented in this paper as well.

Keywords: *UF_6* sampling; enrichment plant safeguard; measurement techniques and standardisation

1. Introduction

A Hoke tube type is normally used for UF_6 sampling. Sampling dwells up to one hour, with the tube immersed in liquid nitrogen, and up to 10 grams of UF_6 are collected. The samples taken in Brazil are sent by ABACC to a Network Laboratory in Argentina for mass spectrometry analysis. The UF_6 sample is hydrolyzed and a very small quantity (some milligrams) is used for the enrichment determination. The residual quantity of UF_6 retained at the laboratory is very large compared to the needs for the enrichment measurement. It is also a costly sampling system, as the Hoke tube type is expensive, it has to be cleaned-up before reutilization, and additional costs are added to the transportation of cleaned tubes from Argentina to Brazil.

Due to the disadvantages of the actual UF_6 sampling method, ABACC has developed a method (named ABACC-Cristallini Method) of sampling UF_6 for enrichment determination. The new method uses a fluorothene P-10 tube type containing alumina pellets that absorb and hydrolyze UF_6 directly during the sampling. The alumina pellets retain up to few hundreds milligrams of U (in a solid compound – UO_2F_2) without the need of using liquid nitrogen during sampling. With this new method the UF_6 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, there will be saves in transport cost as well, and it is relatively safer concerning radiological protection aspects during transportation. Figure 1 shows the two types of UF_6 sampling device and the alumina pellets.

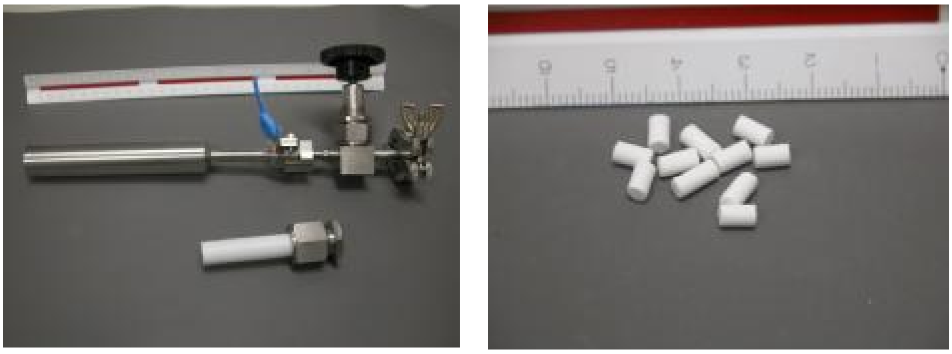

***Figure 1:** UF_6 sampling devices – Hoke tube / fluorothene P-10 tube and alumina pellets*

1.1 Reaction Mechanism

Chemical traps are commonly employed in enrichment plants to remove UF_6 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 UF_6. The materials normally used in these traps are alumina (Al_2O_3) 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 F_2 [1,2]. These factors do not have the same importance in every application. For the UF_6 sampling method proposed in this paper the predominant factors are reaction kinetics and uranium recovery.

The sodium fluoride trapping mechanism involves the reaction of UF_6 to form a solid complex, according to the following reaction:

$$2\ NaF + UF_6 \rightleftarrows UF_6.2NaF$$

The uptake of uranium hexafluoride by sodium fluoride is a chemisorption process forming an $UF_6.2NaF$ complex. This reaction can be readily reversed heating the complex to around 350°C and recovering the uranium as UF_6. Also, it can be dissolved in water, obtaining a solution with the uranium and a high NaF saline content. If the NaF, with the retained complex, is dissolved in water, the high fluoride quantity present in the resulting solution should be eliminated completely by successive evaporations, because its presence affects the isotopic analysis.

On the other hand, the effectiveness of the alumina relies on the hydrolysis of the UF_6 with the available lattice water. The reaction is the following:

$$6\ Al_2O_3.H_2O + 3\ UF_6 \longrightarrow 3\ UO_2F_2 + 6\ Al_2O_3 + 12\ HF$$

$$12\ HF + 2\ Al_2O_3 \longrightarrow 4\ AlF_3 + 6\ H_2O$$

The UF_6 alumina trapping mechanism depends on the hydrolysis reaction with subsequent retention of the uranyl fluoride (UO_2F_2) in the porous structure. The UO_2F_2 is a non-volatile solid and soluble in water. 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 UF_6 sampling.

Some initial quantity of water is essential for the alumina loading mechanism, being a content of 3 to 4% near the optimum [1]. However, if the alumina, in the form of pellet, contains too much water, greater than 7 to 8%, it will be so reactive that the pores leading to the interior of the pellet will become prematurely plugged, and the uranium loading is largely confined to the periphery of the pellet. In this case, the average load can be considerably lower than otherwise expected. These facts shall be taken into account for the material specification and sampling setup.

1.2. Alumina Characteristics

The tested aluminum oxide is type gamma, used as catalyst support, bimodal, with a very high specific surface. The material has form of pellets of 1/8", (cylinders of 3 mm diameter and 5-6 mm high – see Figure 1) with an apparent density of 0.39 g/cm^3 and a total pore volume of 1.14 cm^3/g. The specific area is around 250 m^2/g measured by the BET Method.

The absorbed water was determined as 0.07% by heating at 120°C for 2 hours. The crystallization water was determined as 4.5% by heating at 1200°C for 2 hours. Considering the high specific area of the pellets, the material was not exposed to the atmosphere and maintained in its original and hermetic container in order to low the absorbed humidity.

To verify that the alumina did not contribute with any impurity, especially uranium, which could interfere or cause error in the determination of the U isotopic composition, a blank pellet was analyzed. Several washes with distilled water and NO_3H 1M, as is applied to the recovery of the UO_2F_2, were carried out. The blank solutions were measured using the Total Reflection X Ray Fluorescence (TXRF) technique. The impurities detected by TXRF in the blank were the following:

- Iron: 0,15 µg/ml, equivalent to 1.8 µg/g in the alumina;
- Potassium and Calcium: 0.5 µg/ml, equivalent to 6 µg/g in the alumina;
- Uranium was not detected, being 0.02 µg/ml in the blank, equivalent to 0.2 µg/g in the alumina, the detection limit of the method.

Due to the presence of HF generated during the hydrolysis, the alumina presents certain solubility that increases with time and heating. Under the conditions selected for UO_2F_2 recovery, it was determined that the total alumina dissolution amounts to 0.05%. Such a low quantity does not cause any problem to the isotopic analysis by mass spectrometer.

2. Experimental setup

Figure 2 shows the equipment setup scheme used for the UF_6 sampling with alumina pellets at the Laboratorio de Control Químico y Físico – Combustibles Nucleares – Centro Atómico Constituyentes – Comisión Nacional de Energía Atómica - Argentina.

The UF_6 cylinder and the fluorothene tube loaded with the alumina pellets are connected to the manifold. The loaded fluorothene tube, with its plug and nuts, are tare before its connection to the system in order to estimate the quantity of uranium retained in each experiment.

The manifold is dried out before starting each test by applying vacuum and heating (80-90°C) during 30 minutes. Then, the UF_6 cylinder valve is opened in order to obtain the desired pressure and valve 2 is opened to allow that the alumina pellets enter in contact with the UF_6. After having elapsed the elected time for the test, valve 1 and 2 are closed. To remove the UF_6 from the system, valve 3 is opened, being UF_6 retained by the cold trap with liquid nitrogen. Valve 2 is also opened to be sure that there are no detectable gases in the fluorothene tube. Valve 4 is then opened to allow the entrance of nitrogen gas for equalizing the internal pressure to the atmospheric pressure. Finally valve 2 is closed and the fluorothene tube is disconnected from the manifold. It is closed with the respective plug and nuts and weighted to know the uranium mass retained in the alumina. In general, the procedure described above was applied on all experiments, with some variants according to the kind of test being done.

3. Experiments

Various experiments with fluorothene tube containing alumina pellets were carried out using UF_6 samples, which were obtained from ABACC´s inspections, having U enrichments between 0.31 to 4.05wt%. The first 5 experiments were carried out to set up the system. During these experiences some smaller losses took place, and the data was not reliable, but gave evidence that the uranium was retained by the alumina. Then the experiments were carried out at several constant pressures in the system to evaluate the quantity of uranium retained at a fixed time. Data were also collected when the UF_6 tubes were becoming empty, giving knowledge about the alumina behavior. In all the experiments, the fluorothene tube was loaded with 1g of alumina pellets without any previous treatment. Some representative experiments are described below.

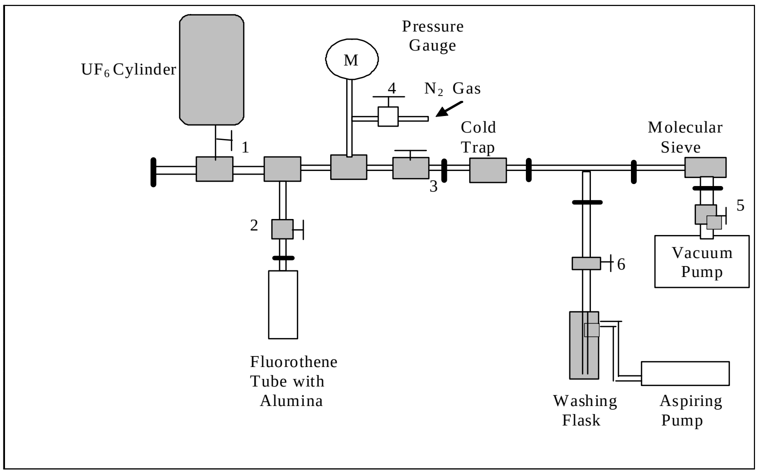

Figure 2: *equipment setup for UF_6 sampling with alumina pellets*

3.1. Experiments carried out at decreasing pressure

Experiments with decreasing pressure in the experimental setup are presented in Table 1. Figure 3 shows the evolution of pressure versus time for one specific test.

Test Number	***Alumina Mass (g)***	***Initial Pressure (mb)***	***Final Pressure (mb)***	***Contact Time (min)***	***Retained UF_6 Mass (mg)***	***Retained U Mass (mg)***	***U Mass / Al_2O_3 Mass Ratio***
#14	1.072	30	2.9	30	285	193	0.18
#18	1.033	15	2.4	12	111	75	0.07
#20	1.028	108	26.1	80	688	465	0.45

Table 1: *experiments carried out at decreasing pressure*

Test #18 showed a smaller U retention than the test #14, but the contact time was 12 minutes compared to 30 minutes in Test #14 and the pressure was also lower. Test #20 showed higher U retention for 80 minutes, but the final pressure of the system was 10 times higher than the other experiments because the alumina was coming closer to its loading limit.

According to Schultz [2] the maximum saturation load, expressed as the uranium to alumina mass ratio is between 0.4 and 0.5. The maximum values obtained in this work were something superior (up to 0.6 for all tests).

It is necessary to highlight that in Test #18, with an initial pressure as low as 15 mb, the pressure had a quickly decreasing because the tube of UF_6 was almost empty, but in only 12 minutes 75 mg of uranium were retained by the alumina pellets. This quantity of uranium is more than enough to carry out an isotopic analysis. This is an indicative that it is possible to sample UF_6 from almost empty containers or plant pipes that have very low pressure.

3.2. Experiments carried out at constant pressure

Several constant pressures in the system were set to evaluate the amount of uranium retained in a fixed time and the maximum uranium load for the alumina saturation as well. Table 2 presents some relevant data of the tests performed and Figures 4 and 5 show the pressure evolution as function of time. The pressure of the system was maintained as much as possible constant by regulating the UF$_6$ Hoke tube valve. After 60 minutes, the valve was closed but the pressure recording continued for 20 minutes more. It is clearly observed that the pressure keeps falling during the following 20 minutes in the case where the alumina is less loaded (Test #12, Figure 4), indicating a continuous UF$_6$ absorption. In opposite, Test #16 (Figure 5) shows that the alumina pellets seem to be practically saturated, with a very low decrease of the system pressure, and uranium to alumina mass ratio of 0.62.

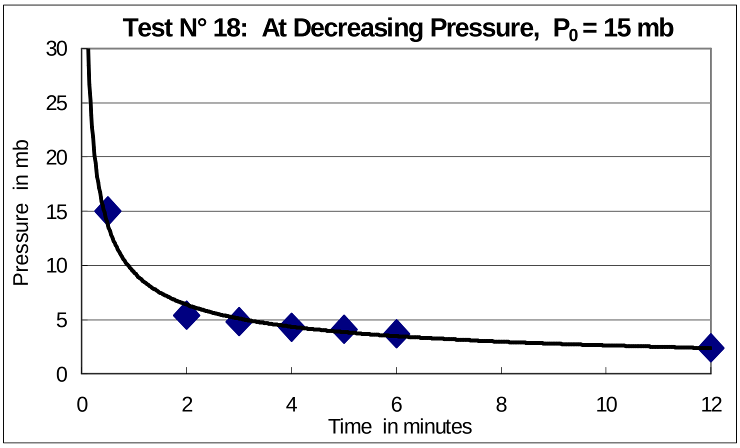

Figure 3: *experiment at Decreasing Pressure*

Test Number	***Alumina Mass (g)***	***Initial Pressure (mb)***	***Final Pressure (mb)***	***Contact Time (min)***	***Retained UF$_6$ Mass (mg)***	***Retained U Mass (mg)***	***U Mass / Al$_2$O$_3$ Mass Ratio***
#12	1.031	10	3.1	60 + 20	315	213	0.21
#17	1.067	25	17.1	60 + 20	662	447	0.42
#13	1.018	50	42.3	60 + 20	773	523	0.51
#16	1.040	100	95.3	60 + 20	947	640	0.62

Table 2: *Experiments carried out at constant pressure*

It is evident that the reaction is quite quick despite of the several steps that are involved in this kind of gas-solid reactions: diffusion of the UF$_6$ molecule from the bulk gas stream to the external pellet surface; diffusion into the porous structure; adsorption on the interior surfaces; reaction with the absorbing material; and diffusion of the UF$_6$ molecule through the complex layers to unreacted absorbers.

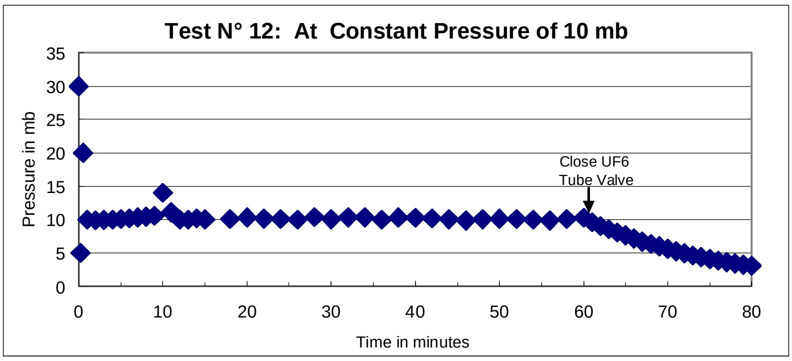

Figure 4: *experiment at constant pressure test#12*

In Test #12 at a very low pressure of only 10 mb, within 60 minutes, 213 mg of uranium were retained. The fourth part of this U mass is more than enough to perform an isotopic analysis. Therefore, 15 to 30 minutes seems to be an appropriate time interval for sampling lines with UF$_6$ pressures among 10-100 mb, and using only 1gram of alumina pellets as specified by this method.

3.3. Evaluation of the uranium mass retained as function of the system pressure

Figure 6 shows the uranium mass retained by 1 gram of alumina versus the UF_6 pressure inside the system. In this graph the value obtained at constant pressure tests were used (see Table 2). A similar curve can be obtained plotting the U/Al_2O_3 mass ratio versus the UF_6 pressure. The retained uranium was determined by the weight difference of the fluorothene tube loaded with the alumina pellets, before and after each test. Some data were also checked by measuring the uranium content by Davies & Gray Method.

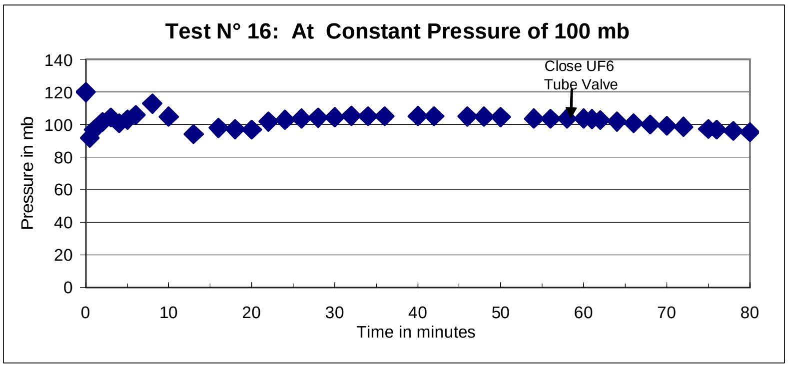

Figure 5: experiment at constant pressure test#16

The saturation value of U/Al_2O_3 mass ratio seems to be next to 0.62, which is the highest value obtained by Test #16, carried out at 100 mb of pressure during 80 minutes.

This is a high uranium retention value obtained with the alumina pellets used. This value is superior to the one obtained by Schulz [2], where values of 0.6-0.7 are consigned for the UF_6/Al_2O_3 mass ratio saturation, which are equivalent to 0.4-0.5 for the U/Al_2O_3 mass ratio.

3.4 Recovery of the uranium retained in the alumina

As the uranyl fluoride (UO_2F_2) is a very soluble salt, the uranium retained in the alumina pellets can be removed with distilled water without any effort. However, due to the high material porosity, several washes with small water volumes and even some washes with 1M nitric acid are necessary for complete uranium dissolution. A high solution acidity, intense heating or prolonged contact times are not recommended, because the alumina is partially dissolved and the final solution will have a high aluminum content that shall affect the isotopic analysis procedure.

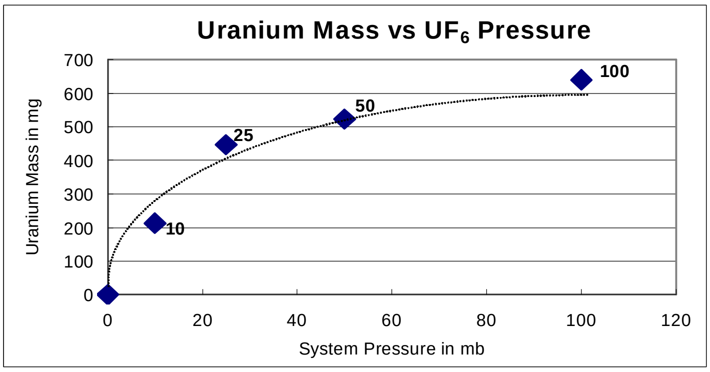

***Figure 6:** uranium mass retained in function of the system pressure*

After some tests, the uranium recovery procedure adopted for its simplicity and acceptable efficiency is the following:

- the pellets loaded with the UO_2F_2 are placed in an Erlenmeyer, added 5 ml of distilled water, stirred during 3 minutes and then left to settle other 5 minutes;
- the solution so far obtained is separated and the extraction process is repeated 3 times more, the first one with distilled water and the two remaining with 1M NO_3H;
- with these 4 serial washing it is possible to recover around 85% of the original uranium, without dissolving an appreciable quantity of alumina. As the solution has certain turbidity due to the presence of very fine alumina in suspension, it is necessary to centrifuge the solution to separate the alumina.

This solution or an aliquot of it is evaporated to eliminate the fluoride that interferes in the isotopic analysis, and finally the dried product is dissolved in 1M NO_3H to obtain a solution containing around 5 mg U/ml for the isotopic analysis.

3.5. Comparison of the isotopic analysis data

UF_6 standard samples were sub-sampled [3,4] in order to hydrolyze them directly for isotopic analysis. The isotopic analysis from the solution obtained by the UF_6 direct hydrolysis method is compared to the isotopic analysis obtained from the alumina pellet method. Table 3 present the result of this comparison.

No significant differences in the isotopic analysis by mass spectrometer were found between the direct hydrolysis method and the alumina pellet method. This is a logical result as the blank alumina pellet analysis by TXRF did not detect the presence of uranium. The presence of small quantities of alumina dissolved in the solution did not generate any difficulty in the isotopic analysis as well.

Sample	**U isotopic results actual method (UF_6 direct hydrolysis) (wt %)**	**U isotopic results new method (UF_6 alumina pellets sampling) (wt %)**	**Difference in the U-235 (wt%)**
IRMM 020	**U-235 = 0.210 ± 0.001** U-234 < 0.003 U-236 = 0.029 ± 0.001	**U-235 = 0.209 ± 0.001** U-234 < 0.003 U-236 = 0.029 ± 0.001	**-0.001**
IRMM 022	**U-235 = 0.720 ± 0.002** U-234 = 0.005 ± 0.001 U-236 < 0.003	**U-235 = 0.720 ± 0.003** U-234 = 0.005 ± 0.001 U-236 < 0.003	**0**
IRMM 023	**U-235 = 3.274 ± 0.004** U-234 = 0.033 ± 0,001 U-236 < 0.003	**U-235 = 3.268 ± 0.003** U-234 = 0.033 ± 0,001 U-236 < 0.003	**-0.006**
IRMM 029	**U-235 = 4.173 ± 0.006** U-234 = 0.080 ± 0.001 U-236 = 0.989 ± 0.001	**U-235 = 4.165 ± 0.004** U-234 = 0,079 ± 0,001 U-236 = 0.989 ± 0.002	**-0.008**

***Table 3:** Isotopic analysis data comparison for UF_6 standards*

As a routine procedure, UF_6 samples taken during safeguard inspections had the enrichment determined by mass spectrometry both from the solution obtained by the UF_6 direct hydrolysis method and from the solution obtained by the alumina pellet method. The differences obtained in the enrichment value are less than the precision obtained in the spectrometry analysis, as can be seen in figure 7.

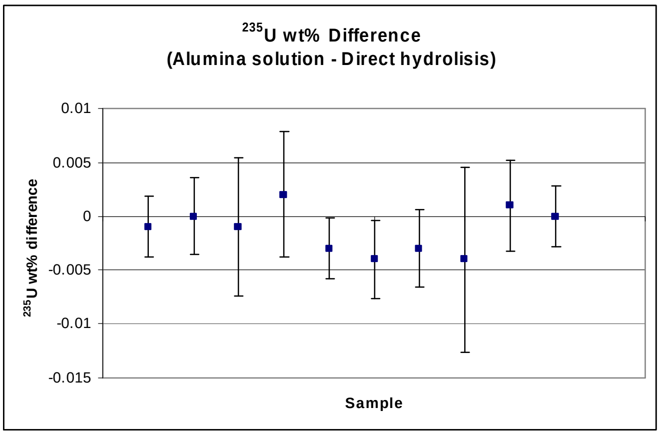

***Figure 7:** Enrichment difference from alumina pellet solution and direct hydrolysis solution.*

4. Qualification Step

As demonstrated in the previous section, the UF_6 sampling method using alumina pellets improves the safeguard measurement procedure applied to enrichment facilities.

Before implementing the new method as a routine procedure the following steps were foreseen as necessary:

- to perform a demonstration exercise at the enrichment facility in order to the operator evaluate its impact to the systems and operation;

- to certify the method by an independent international laboratory;

The first step was done at one of the enrichment facility laboratories in Brazil. The preliminary results reported by the laboratory indicate that the operator is comfortable with the method and is reproducing the positive results obtained previously at laboratory development reported in this paper.

The second step was asked to New Brunswick Laboratory. This work is performed under ABACC-DOE cooperation agreement.

The IAEA has also established a task under a project on destructive analysis of nuclear materials for safeguard to demonstrate the ABACC-Cristallini Method.

5. Conclusion

ABACC proposed a new method of sampling UF_6 for enrichment determination (ABACC-Cristallini Method) using a fluorothene tube containing alumina pellets that absorb and hydrolyze UF_6 directly during the sampling process.

The method was demonstrated at laboratory where an experimental system was set up.

The alumina pellets used are commercial catalyst support, and one gram of these pellets without any previous treatment was determined as enough for sampling UF_6 for enrichment determination.

The experimental results show that 10 to 30 minutes of contact of the UF6 with the pellets would retain enough quantities of uranium for isotopic analysis, even for system pressures lower than 10 mb.

The recovery of the uranium is simple and quick. It does not require any special equipment and it can be done in a radiochemical hood as well as in a laboratory bench, since no gas is liberated when the fluorothene tube is open.

The method shall be further qualified by the enrichment facility operator, and certified by an international independent laboratory. IAEA is also testing the method.

The method responds appropriately and its implementation as routine procedure to enrichment facility safeguard does not present any foreseen difficulty.

It is evident the advantages that the new method presents compared to the actual method as: the UF_6 sample content left at the installation (archive sample) will be lower and less reactive, the laboratory procedures for manipulating the sample will be much easier, the residual uranium retained at the laboratory will be much lower, the sampling device is less expensive, there will be saves in transport cost as well, and it is relatively safer concerning radiological protection aspects during transportation.

6. References

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[3] ISO 9884; *Subsampling Uranium Hexafluoride in Liquid Phase.*

[4] ASTM C 761-96; *Standard Test Methods for Chemical, Mass Spectrometric, Spectrochemical and Radiochemical Analysis of Uranium Hexafluoride.*