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ANALYTICAL METHOD DEVELOPMENT AND VALIDATION FOR QUANTIFICATION OF URANIUM BY FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR) FOR ROUTINE QUALITY CONTROL ANALYSIS

Elaine Pereira[1,2], Iêda de S. Silva[1], Ricardo G. Gomide[1], Maria Aparecida F. Pires[2]

[1]Centro Tecnológico da Marinha em São Paulo (CTMSP – SP)
Centro Experimental ARAMAR (CEA)
Estrada Sorocaba – Iperó, Km 12,5
18560-000 Iperó, SP
elaine.pereira@ctmsp.mar.mil.br

[2]Instituto de Pesquisas Energéticas e Nucleares (IPEN – CNEN/SP)
Av. Professor Lineu Prestes, 2242
05508-000 São Paulo, SP
mapires@ipen.br

ABSTRACT

This work presents a low cost, simple and new methodology for direct determination uranium in different matrices uranium: organic phase ($UO_2(NO_3)_2$.2TBP – uranyl nitrate complex) and aqueous phase ($UO_2(NO_3)_2$ – NTU – uranyl nitrate), based on Fourier Transform Infrared spectroscopy (FTIR) using KBr pellets technique. The analytical validation is essential to define if a developed methodology is completely adjusted to the objectives that it is destined and is considered one of the main instruments of quality control. The parameters used in the validation process were: selectivity, linearity, limits of detection (LD) and quantitation (LQ), precision (repeatability and intermediate precision), accuracy and robustness. The method for uranium in organic phase ($UO_2(NO_3)_2$.2TBP in hexane/embedded in KBr) was linear (r=0.9989) over the range of 1.0 g L^{-1}a 14.3 g L^{-1}, LD were 92.1 mg L^{-1} and LQ 113.1 mg L^{-1}, precision (RSD < 1.6% and p-value < 0.05), accurate (recovery of 100.1% - 102.9%). The method for uranium aqueous phase ($UO_2(NO_3)_2$/embedded in KBr) was linear (r=0.9964) over the range of 5.4 g L^{-1} a 51.2 g L^{-1}, LD were 835 mg L^{-1} and LQ 958 mg L^{-1}, precision (RSD < 1.0% and p-value < 0.05), accurate (recovery of 99.1% - 102.0%). The FTIR method is robust regarding most of the variables analyzed, as the difference between results obtained under nominal and modified conditions were lower than the critical value for all analytical parameters studied. Some process samples were analyzed in FTIR and compared with gravimetric and x ray fluorescence (XRF) analyses showing similar results in all three methods. The statistical tests (Student-t and Fischer) showed that the techniques are equivalent.

1. INTRODUCTION

The main objective of the Brazilian Navy´s Program Nuclear, which is being developed by the Centro Tecnológico da Marinha em São Paulo (CTMSP), is to establish the technical competence to design and build reactors of the type "Pressurized Water Reactor" (PWR) as well as produce their own nuclear fuel, in order to employ this technology to generate energy for ship propulsion [1].

Isotopically enriched uranium dioxide powder ($^{235}UO_2$) is the starting material for the manufacture of pellets which is the fuel in nuclear reactors and its obtainment involves a set of steps called the nuclear fuel cycle. At each stage of this nuclear cycle, there are chemical and

physical analyses to establish the composition and nuclear grade of the produced uranium compounds [2].

The quantification of uranium compounds traces can be performed by many analytical techniques, such as: fluorimetry [3-5], phosphorimetry (KPA - Kinetic Phosphorescence Analyzer) [6], UV-Vis spectrophotometry [7], Flame Atomic Absorption Spectromety (FAAS) [8], Graphite Furnace Atomic Absorption Spectrometry (GFAAS) [9], Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) [9], Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [9] and even by potentiometry [10,11].

However, as regards the measurement of elevated levels of uranium, there are limited available analytical techniques, including: Davies and Gray´s volumetry [11], gravimetry [13], UV-Vis spectrophotometry [5,7], fluorimetry [4] and x ray fluorescence analyses [12] (XRF). Each one this analytical techniques possesses advantages and disadvantages and a choice of a specific method depends on the nature of sample being analyzed and amount of uranium in it.

Infrared vibrational techniques are non-destructive techniques, with minimum generation of chemistry analytical waste, in some cases do not require sampling and its processes are suitable for "on-line" control. Thus, vibrational spectroscopy analytical offers almost unlimited opportunities for control systems for industrial processes and quality control [14,15].

The infrared spectrum can be divided into three regions: the far infrared (400 – 0 cm^{-1}), the mid-infrared (4000 – 400 cm^{-1}) and the near infrared (14285 – 4000 cm^{-1}). Most infrared analytical applications employ the mid-infrared region [20].

The infrared spectrum of a chemical compound is considered one of its physical-chemical properties therefore mid-infrared spectroscopy has wide application in the identification of compounds. Another important application of FTIR, but still less explored, is the quantitative analysis of compounds. As the intensity of an absorption band is directly proportional to the concentration of the component which provided this band, according to the Lambert–Beer's law [21], the concentration of an analyte in a sample can be determined through a calibration curve (band intensity versus concentration) constructed from analytical standards [22-24].

A growing interest of many academics groups, government and industrial research to develop sensitive methods, fast and highly specific to a variety of chemical compounds. Vibrational spectroscopy is an appropriate analytical technique for this need, therefore, within this perspective, the development of this work is extremely important to optimize the routine analysis in nuclear laboratories, which are improving their methods for direct determination uranium in different matrices (Organic Phase - OP or Aqueous Phase - AP).

2. EXPERIMENTAL

2.1. Materials and Reagents

The certified reference material NBL CRM 123-7 (U_3O_8) from New Brunswick Laboratory (NBL) was used for calibration standards preparation. N-hexane, nitric acid (HNO_3 65%) and Tri butyl phosphate (TBP 99%) were used of analytical grade. For FTIR samples were used potassium bromide (KBr) for IR spectroscopy Uvasol® from MERCK.

2.2. Instrumentation and infrared spectroscopic conditions

The method developed at this work was studied using Fourier Transform Infrared Spectrophotometer (FTIR-8400 Shimadzu) with spectral resolution of 4 cm^{-1}, 16 scans, spectral range from 4000 to 400 cm^{-1} and absorption mode. The FTIR samples were prepared by KBr technique.

2.3. Preparation of solutions

2.3.1. Aqueous standard solution – Uranyl nitrate $UO_2(NO_3)_2$

The certified reference material (11.7925 g of U_3O_8 accurately weighed - 0.848 g U per gram U_3O_8 according certificate of analysis) was digested with concentrated nitric acid 65%, boiled for 20 – 25 min to get a yellow solution of uranyl nitrate ($UO_2(NO_3)_2$) and transferred to 100 mL volumetric flask. The solution final concentration is 86.06 g L^{-1} in 4.0 mol L^{-1} nitric acid. Subsequently, aliquots of the solution were diluted in 4.0 mol L^{-1} nitric acid solution to obtain the uranium concentrations of 5.36, 10.44, 20.97, 31.50, 41.61 and 51.24 g L^{-1}.

2.3.2. Organic standard solution - $UO_2(NO_3)_2$.2TBP complex

The standard solution of uranyl nitrate (86.06 g L^{-1}) was used to prepare organic standard solution ($UO_2(NO_3)_2$.2TBP complex) using the extraction process. Organic solution containing 35% TBP/n-hexane (equilibrated by 4.0 mol L^{-1} nitric acid solution) were contacted with equal volume of 86,06 g L^{-1} standard solution of uranyl nitrate, under the following conditions: mixed time 15 minutes for each 5 repetition and phase ratio 1:1. The uranium in the organic phase (OP) was transferred to a 250 mL volumetric flask. The solution final uranium concentration is 17.21 g L^{-1} in 35% TBP/n-hexane. Subsequently, aliquots of the solution were diluted in 35% TBP/n-hexane organic solution to obtain the uranium concentrations of 1.01, 5.02, 7.68, 10.15, 11.61 and 14.35g L^{-1}.

2.3.3. Standard FTIR in KBr pellets

Approximately 100 mg of dry KBr for IR spectroscopy were accurately weighed in a watch glass. With an Eppendorf micropipettor, 20 µL (Organic standard $UO_2(NO_3)_2$.2TBP complex: 1.01, 5.02, 7.68, 10.15, 11.61 and 14.35 g L^{-1}) or 25 µL (Aqueous standard $UO_2(NO_3)_2$: 5.36, 10.44, 20.97, 31.50, 41.61 and 51.24 g L^{-1}) were embedded in KBr. The mixture was placed in a drying oven (105 ºC/24 h) and cooled in a vacuum desiccator. After that, the standard embedded in KBr was grinded and mixed with an agate mortar using the pestle and subjected to a pressure of approximately 23 tons for a pressing time of 5 min to form a KBr pellet.

2.4. Method validation

The methodology of the validation procedure was based on the analytical parameters INMETRO [25], such as: selectivity, calibration curve, quantitation and detection limits (LQ and LD), precision (intermediate precision and repeatability), accuracy and robustness.

2.5. Uranium process samples

The Uranium Hexafluoride Department of CTMSP to provide the samples used in statistical evaluation at this work: yellow cake, NTU in organic phase ($UO_2(NO_3)_2$.2TBP complex) and NTU in aqueous phase ($UO_2(NO_3)_2$).

3. RESULTS AND DISCUSSION

3.1. Method validation

3.1.1. Selectivity

The selectivity of the method by mid-infrared spectroscopy has been demonstrated by the presence of U=O vibration band which occurs between 970-910 cm^{-1} and the lack of any analytic signal in this region of absorption spectrum of the blank sample, as can be observed in the overlap of the spectra (Fig. 1 and 2).

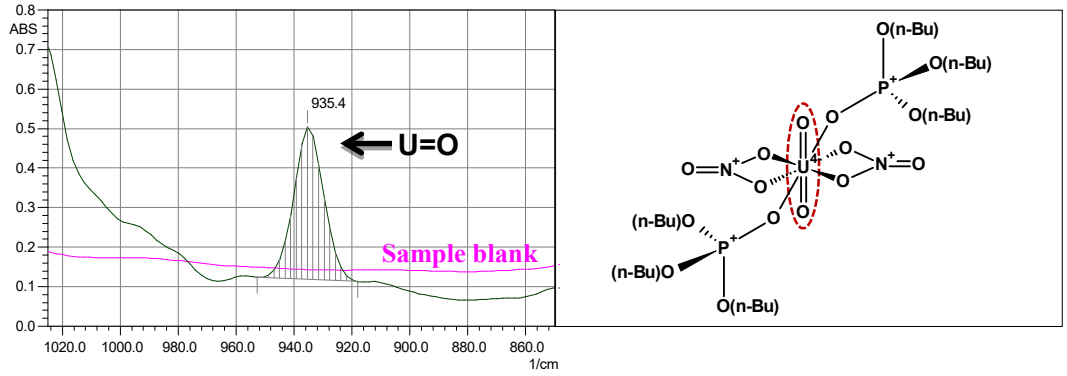

Figure 1: Infrared spectra of the organic standard solution – $UO_2(NO_3)_2$.2TBP complex (U=O stretching vibration which occurs at 935.4 cm^{-1}) and blank sample.

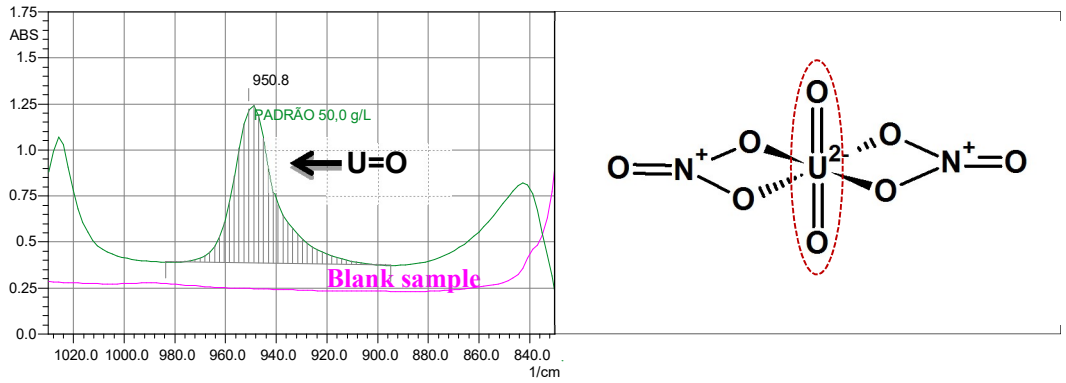

Figure 2: Infrared spectra of the aqueous standard solution – $UO_2(NO_3)_2$ (U=O stretching vibration which occurs at 950.8 cm^{-1}) and blank sample.

3.1.2. Calibration curves

The calibration curves were obtained using six reference standard concentrations in KBr pellets (uranium in OP: 0.20, 1.00, 1.53, 2.02, 2.31, 2.85 % U/KBr pellet and uranium in AP: 0.14, 0.26, 0.53, 0.79, 1.06, 1.29 % U/KBr pellet) in 3 independent replicates run in random order. The calibration curves constructed were assessed using residue analysis and linear regression analysis was done by the ordinal least squares method. In both cases, the linear model proved to be adequate as it could be shown that the residues followed a normal distribution pattern and were independent while homoscedasticity was evident and lack of fit was not significant. The calibration curves were constructed (Figure 3 and 4) presented a correlation coefficient (r) higher than 0.99.

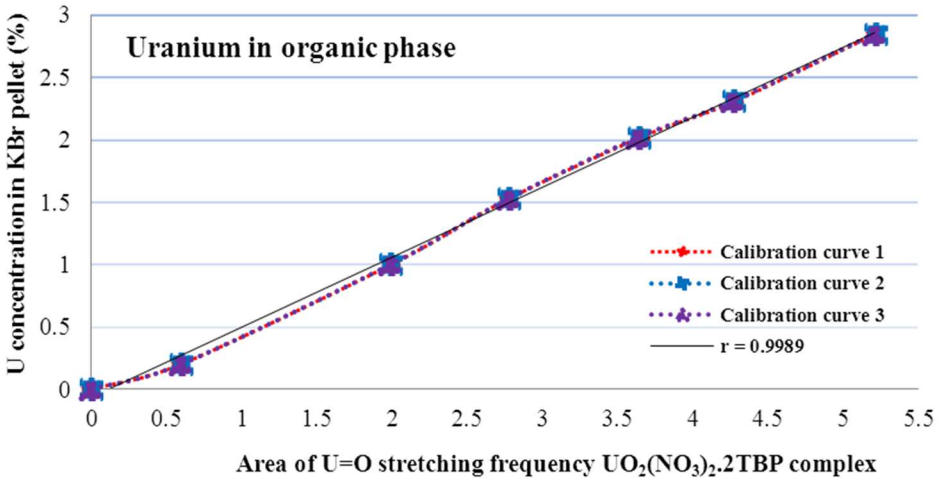

Figure 3: Calibration curves for uranium in organic phase (OP) within the range of 0.20 to 2.85 % U in KBr pellet (1.01 to 14.35 g L^{-1})

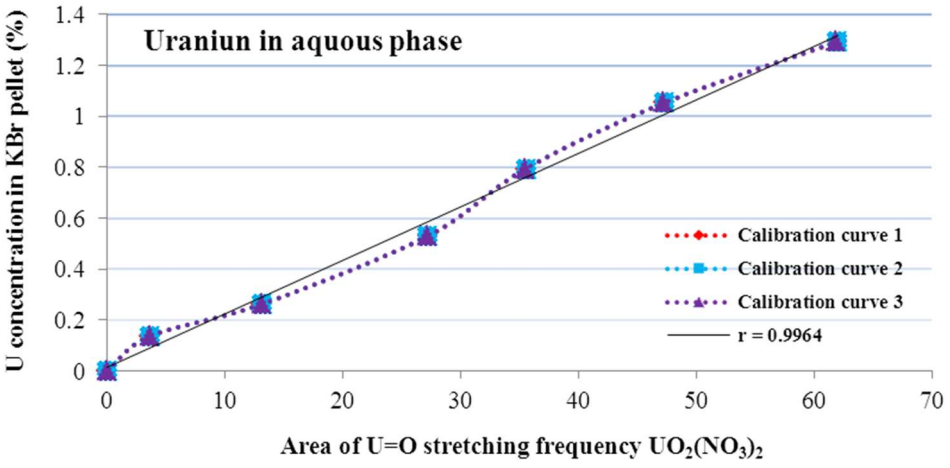

Figure 4: Calibration curves for uranium in aqueous phase (AP) within the range of 0.14 to 1.29 % U in KBr pellet (5.36 to 51.24 g L^{-1})

3.1.3. Quantitation and detection limits

The limit of detection value (LD) is defined as the lowest concentration that can be detected by equipment (Tab. 1). The LD can be calculated as:

$$\mathbf{LQ} = \overline{\mathbf{X}} + \mathbf{10s} \quad (1)$$

Where, $\overline{\mathbf{X}}$ is the sample blank average values (spectral region 970 - 910 cm^{-1}) and **s** is the standard deviation of sample blank.

The limit of quantitation value (LQ) is defined as the lowest concentration that can be quantitatively determined with suitable precision and accuracy. The LQ can be calculated as:

$$\mathbf{LD} = \overline{\mathbf{X}} + \mathbf{ts} \quad (2)$$

Where, $\overline{\mathbf{X}}$ is the sample blank average values (spectral region 970 - 910 cm^{-1}), **t** is Student distribution for 99% confidence level and n-1 = 9 and **s** is standard deviation of sample blank.

Table 1: LD and LQ for quantification uranium in organic and aqueous phase by FTIR

Matrix	LD (mg L^{-1})	LQ (mg L^{-1})
Uranium in organic phase	92	113
Uranium in aqueous phase	835	958

3.1.4. Accuracy

An accuracy was determined using a recovery test of uranium in standard KBr pellets. The results are shown Tab. 2 and 3.

Table 2: Results of the recovery test of uranium in standard KBr pellets (uranium in organic phase)

Day	Level [U] in KBr pellet (%)	Mean recovery [U] ± RSD (%)
1	1.00	100.3 ± 0.2
	1.05	100.1 ± 0.1
	1.02	101.5 ± 0.1
2	2.10	101.5 ± 0.1
	1.98	100.1 ± 0.1
	2.15	101.5 ± 0.1
3	3.21	102.9 ± 0.1
	3.08	102.8 ± 0.1
	3.00	102.2 ± 0.1

Table 3: Results of the recovery test of uranium in standard KBr pellets (uranium in aqueous phase)

Day	Level [U] in KBr pellet (%)	Mean recovery [U] ± RSD (%)
1	0.27	99.1 ± 0.2
	0.27	100.2 ± 1.1
	0.26	98.8 ± 0.2
2	0.79	102.0± 0.1
	0.80	100.1 ± 0.1
	0.80	100.7 ± 0.2
3	1.32	101.4 ± 0.6
	1.26	99.7 ± 0.2
	1.27	99.8 ± 0.4

3.1.5. Precision - Repeatability (intra-assay)

Repeatability was determined by the 10 standard samples analyses performed under the same measurement conditions (same day, same analyst, same equipment and same environmental conditions). The results of successive measurements are shown in Tab. 4 and 5.

Table 4: Results of the repeatability test – uranium in organic phase

REPEATABILITY – $UO_2(NO_3)_2.2TBP$										
Number of measurements (n)	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Level [U] in KBr pellet (%)	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Mean recovery [U] (%)	98.3	102.1	99.9	102.6	101.0	99.2	102.9	99.9	98.8	100.3
Mean [U] (%)	**100.5**									
DPR (%)	**1.6**									
DPR Horwitz (%)	**2.1**									

The mean recovery between 10 standard samples (uranium in organic phase - $UO_2(NO_3)_2.2TBP$) analyzed was 100.5% and RSD value were 1.6%. The value RSD by FTIR method (1.6%) was lower than the RSD Horwitz (2.1%) [26], therefore, the FTIR method has demonstrated repeatability of the readings in the same analytical conditions.

Table 5: Results of the repeatability test – uranium in aqueous phase

REPEATABILITY – $UO_2(NO_3)_2$										
Number of measurements (n)	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Level [U] in KBr pellet (%)	2.02	2.11	1.99	2.14	2.04	2.10	2.10	1.96	2.12	2.13
Mean recovery [U] (%)	101.4	99.7	99.2	101.3	101.3	99.8	99.7	99.9	99.6	101.8
Mean [U] (%)	**100.4**									
DPR (%)	**1.0**									
DPR Horwitz (%)	**1.8**									

In the same way, the mean recovery between 10 standard samples (uranium in aqueous phase - $UO_2(NO_3)_2$) analyzed was 100.4% and RSD value were 1.0 %. The RSD value by FTIR method (1.6%) was lower than the RSD Horwitz (1.8%) [26], therefore, the FTIR method has demonstrated repeatability of the readings in the same analytical conditions.

3.1.6. Precision–Intermediate precision (Inter-assay)

Intermediate precision was calculated from the samples used in the testing accuracy that were performed on 3 different days and in 3 different concentration levels. The results of the measures and analysis of variance (ANOVA) are shown in Tab. 6.

Table 6: Results of the intermediate precision

INTERMEDIATE PRECISION		
Day	**Mean recovery [U] ± RSD (%)**	**Mean recovery [U] ± RSD (%)**
	Uranium in organic phase	**Uranium in aqueous phase**
1	101.6 ± 1.3	100.8 ± 1.5
2	101.0 ± 1.6	100.0 ± 0.3
3	101.7 ± 0.4	99.8 ± 1.0
$F_{calculated}$	0.31	0.85
$F_{critical}$	5.14	5.14
p-value	0.74	0.85

The analyses of variance (ANOVA) will indicate also the existence of a significant difference between the percentage recovery. As Tab. 6, the calculated F value (F= 0.31 - uranium in organic phase and F = 0.85 - uranium in aqueous phase) was below the critical F_{value} ($F_{critical}$ = 5.14), indicating that with 95% confidence the recovery inter-day presented no significant differences. By analysis of the p-value (0.74 – uranium in OP and 0.85 – uranium in aqueous phase), which the value is above p-value 0.05, demonstrated again, that there are no significant differences between values of recovery in concentration ranges analyzed on different days [27].

3.1.7. Robustness

The method proposed by Youden and Steiner [28] was carried out to evaluate robustness. In this work, six parameters were selected and investigated at two levels as indicated by capital letters (nominal values) and lowercase letters (conditions with small variation in nominal values), as shown in Tab. 7. Eight runs were performed following the experimental design of Youden and Steinerin order to determine the influence of each parameter.

Table 7: Parameters, variation and factorial combination for robustness test

Analytical Parameter	Nominal condition	Altered condition	Factorial combination							
			1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Scan number	A=16	a=32	A	A	A	A	a	a	a	a
Resolution (cm^{-1})	B=4	b=8	B	B	b	b	B	B	b	b
KBr mass (mg)	C=100	c=120	C	c	C	c	C	c	C	c
volume pipetted (µL)	D=20 (OP) D= 25 (AP)	d=16 (OP) d=18 (AP)	D	D	d	d	d	d	D	D
Pressure KBr pellet (tons)	E=23	e=20	E	e	E	e	e	E	e	E
Time for formation KBr pellet (min)	F=5	f=3	F	f	f	F	F	f	f	F
Results			**s**	**t**	**u**	**v**	**w**	**x**	**y**	**z**

The results of each experiment were represented by letters ranging from s to z (Tab. 7). The difference between the mean of the four values corresponding to the capital letters (nominal conditions) and the mean of the values corresponding to the lowercase letters (altered conditions) was calculated (Tab. 8) to estimate the effect of each variable on the final result. The effect of the analytical parameter was considered to be significant if the value of the difference was greater ($s\sqrt{2}$ – reference value [28]), where S is the standard deviation of the 8 results (s to z).

Table 8: Effects of the analytical parameters

Analytical Parameter	Nominal condition	Altered condition	Effect X/x	Effect results	
				Uranium in OP	**Uranium in AP**
Scan number	A=16	a=32	A/a	0.21	-1.92
Resolution (cm^{-1})	B=4	b=8	B/b	1.25	-1.24
KBr mass (mg)	C=100	c=120	C/c	0.51	-0.16
volume pipetted (µL)	D=20 (OP) D= 25 (AP)	d=16 (OP) d=18 (AP)	D/d	1.94	0.37
Pressure KBr pellet (tons)	E=23	e=20	E/e	-1.31	-0.12
Time for formation KBr pellet (min)	F=5	f=3	F/f	-1.59	-0.44
Reference value ($s\sqrt{2}$)				**2.45**	**1.94**

The FTIR method seems to be robust regarding most of the variables analyzed, as the difference between results obtained under nominal and modified conditions were lower than the reference value for all analytical parameters studied.

3.1.8. Process samples results and statistical tests

The values of mean concentrations, number of measurements, standard deviations (SD), and relative standard deviations (RSD %) for gravimetric, XRF and FTIR techniques were also calculated and summarized in Tab. 9 and 10. For NTU samples in organic and aqueous phase the Tab. 9 shows similar values in uranium determination obtained in FTIR technique compared to XRF with RSD values in both methods are lower than 5%. These results are an indicative of the good application of FTIR for direct determination of uranium in this two process samples.

Table 9: Results for uranium determination in NTU samples (organic phase and aqueous phase) with FTIR (direct determination) and XRF

Process sample	NTU in organic phase		NTU in aqueous phase	
Method	**FTIR**	**XRF**	**FTIR**	**XRF**
Mean [U] (g L^{-1})	99.46	99.56	32.15	32.06
Number of measurements (n)	7	7	7	7
SD (standard deviation)	0.19	0.52	0.23	0.12
RSD (%)	0.002	0.005	0.73	0.38

In the case of yellow cake sample the Tab. 10 shows a similar values in uranium determination obtained in FTIR technique compared to gravimetric analyses with RSD values in both methods are lower than 5%. These results are an indicative of the good application of FTIR for direct determination of uranium in this process sample.

Table 10: Results for uranium determination in yellow cake sample with FTIR (digestion sample procedure) and gravimetry

Process sample	Yellow cake	
Method	**FTIR**	**GRAVIMETRY**
Mean [U] (%)	75.56	75.31
Number of measurements (n)	7	3
SD (standard deviation)	0.24	0.03
RSD (%)	0.32	0.04

The t-Student (accuracy) and F (Fischer) value (precision) [25], two statistical tests were applied to compare the means obtained for the uranium determined in process samples the XRF/gravimetric method and direct determination of sample in FTIR method. The

experimental values calculated results are less than to theorical data (Tab. 11), indicating the between the results of uranium levels obtained by XRF/FTIR and gravimetric/FTIR methods amounts to techniques used in this study arrived similar results. The x ray fluorescence (XRF) and gravimetry are analytical techniques usually used in nuclear laboratories for uranium quantification and the results obtained are comparable at the FTIR new method at the 95% confidence level.

Table 11: Theorical and experimental values of statistical tests t-Student and Fischer for 95% confidence

TESTS		PROCESS SAMPLES		
		NTU in organic phase	NTU in aqueous phase	Yellow cake
t-Student	Experimental	-0.45	0.96	1.73
	Theorical	2.18	2.18	2.31
F-Fischer	Experimental	0.20	0.96	2.98
	Theorical	4.75	4.75	5.32

4. CONCLUSIONS

The selectivity, linearity, accuracy, precision, robustness, simplicity, freedom from matrix effects, no separation steps and minimum generation of radioactive analytical waste have demonstrated the technical feasibility of the application of FTIR method as a new analytical tool in quality control for direct determination of uranium in compounds of the nuclear fuel cycle.

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