VANDELLOS 1 GRAPHITE SOLUBILISATION AND ACTIVITY DETERMINATION OF ^{36}Cl, ^{99}Tc AND ^{129}I

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Abstract

During the characterization processes of irradiate graphite performed in the dismantlig of the UNGG NPP of Vandellós 1, and as a consecuence of the sample treatment carried out for measuring the main radionuclides of interest included in the El Cabril inventory, it was no possible to measure the activity of ^{99}Tc, ^{129}I and ^{36}Cl. Further R&D projects have been developed to solve this issue and finally a proper sample treatment has been accomplished.

1. INTRODUCTION

When solubilising radioactive graphite, which has previously been ground to powder-grain size, if very energetic reagents used and it is performed in an open atmosphere, volatile radionuclides ^{36}C1, ^{99}Tc and ^{129}I are not present in the final solution. Therefore, it has been necessary to develop a graphite solubilisation process that avoids the loss of these volatile radionuclides. This method is based on acid digestion using a microwave system.

More dvanced technics are being developed for ^{129}I and ^{36}Cl, by using Accelerator Mass Spectrometry techncs, AMS, that are being currently implemented.

2. FINE-TUNING A METHOD FOR SOLUBILISING GRAPHITE POWDER SAMPLES USING A MICROWAVE SYSTEM

When carrying out a process of solubilising any matrix using a microwave system, it should be noted that perchloric acid is totally incompatible with the system. Therefore the reagent mixture (HNO_3, H_2SO_4 and $HClO_4$) normally employed to solubilise graphite powder cannot be used. During the initial tests the procedure of doubling the reagent volumes was adopted as the sample quantities to be dissolved were greater than 0.05 g. The process was implemented using 0.05 g; 0.17 g; 0.25 g; 0.55 g and 0.92 g of powdered graphite sample. The reagents used in the process and the temperature ramp used are described below:

- 10 mL H_2SO_4 98% + 2 mL HCl 37% + 2 mL H_2F_2 40%+ 2 mL HNO_3 65%
- 3 minutes to reach 150 °C
- 3 minutes to reach 230 ℃
- 3 minutes to reach 260 ℃

- 30 minutes at 260 °C

After cooling the vessels to room temperature, they were opened to reveal a totally black centrifuged solution. After centrifugation, a black precipitate was obtained indicating that there the graphite had not been completely solubilised. Therefore, the solubilisation process described in the microwave manual was discarded.

In general, HNO_3 and H_2SO_4 mixtures are very effective for solubilising organic matrices and therefore an attempt was made to dissolve different amounts of graphite (between 0.30 and 0.40 g) using different ratios of the nitric/sulphuric acid mixture. The process for each ratio was conducted four times in order to check its reproducibility. The results obtained are shown in Table 1.

Table 1

Weight (g)	V (mL) HNO_3	V (mL) H_2SO_4	Dissolved?
[0.3-0.4]	10	25	No
[0.3-0.4]	10	30	No
[0.3-0.4]	10	35	No
[0.3-0.4]	10	40	**Yes**

Although a volume of 10 mL HNO_3 and 40 mL H_2SO_4 resulted in complete solubilisation of between 0.3 and 0.4 g of graphite, an attempt was made to reduce the volume of sulphuric acid used in the process because it is a highly corrosive reagent and it causes very significant degradation of the vessels used, to the extent that after the third process they are deformed, and can no longer be used.

The presence of a catalyst such as vanadium oxide might help to solubilise graphite with decreased use of sulphuric acid. Therefore, several tests were carried out maintaining HNO_3 constant and varying the volumes of H_2SO_4 (between 5 and 20 mL) and V205 (between 0.01 and 0.07 g) without any improvement in solubilisation being observed. Therefore the use of this catalyst was rejected.

As it was necessary to decrease the quantity of H_2S0_4 used in the process, various tests were conducted reducing the amount of dissolved graphite, and the volumes of HNO_3 and H_2SO_4, while maintaining the ratio between them. Five trials were performed for each process and the results obtained are shown in Table 2.

Table 2

Weight (g)	V (mL) HNO_3	V (mL) H_2SO_4	Dissolved?
[0.20-0.25]	2.5	10	No
[0.20-0.25]	5	20	**Yes**

For complete solubilisation of the graphite powder sample under these conditions, only two vessels can be used simultaneously in the microwave. The use of three or four vessels requires the processing time to be increased to 60 minutes.

To summarise, the final procedure to enable the solubilisation of graphite powder is detailed below:

- Weigh between 0.20-0.25 g of graphite in a microwave vessel. Repeat the process
- Add 5 mL HNO_3 65% + 20 mL H_2SO_4 98%
- Programme the temperature ramp
- 3 minutes to reach 150 °C
- 3 minutes to reach 230 °C

- 3 minutes to reach 260 °C
- 30 minutes at 260 °C
- Collect the contents of the two vessels in a 50 mL flask and top-up the volume with HNO_3

After developing the solubilisation method it is necessary to confirm that the method is valid for determining ^{99}Tc and ^{129}I, ie. that these radionuclides are present in the final solution obtained. $^{36}C1$ is not studied in the same way because a specific reflux dissolution method using ^{12}C gas sampling has been developed.

3. ^{99}TC RECOVERY IN THE SOLUBILISATION PROCESS AND MEASUREMENT

To study the ^{99}Tc recovery obtained in the final dissolution, 10 virgin graphite samples set using the ^{99}Tc standard were prepared and analysed.

To determine the ^{99}Tc recovered an aliquot fraction of the solution obtained in the microwave was taken, mixed with Instagel and analysed using the liquid scintillation technique with its corresponding calibration curve.

The values obtained are shown in Table 3 demonstrating an average recovery of 100%.

Table 3

Ref.	Added Tc-99 (dpm)	Measured Tc-99 LSC±U (dpm)	% Recovery ±U
Tc-1	1042	1025 ± 15	0,98 ± 2%
Tc-2	1042	1116 ± 67	1,07 ± 6%
Tc-3	1042	1004 ± 15	0,96 ± 2%
Tc-4	1042	1062 ± 21	1,02 ± 2%
Tc-5	879,5	878 ± 26	1,00 ± 3%
Tc-6	562,8	557 ± 8	0,99 ± 2%
Tc-7	562,8	575 ± 12	1,02 ± 2%
Tc-8	562,8	540 ± 8	0,96 ± 2%
Tc-9	562,8	539 ± 12	0,96 ± 2%
Tc-10	562,8	580 ± 17	1,03 ± 3%
		Mean Value	**1,00 ± 4%**

The uncertainty expressed in the results is the overall uncertainty, evaluated using the expression:

$U = k\sqrt{V_c}$ K=2, Vc: combined variance

$$U' = k\sqrt{\left(\frac{U_{Ap}}{Ap}\right)^2 + \left(\frac{U}{2Aenc.}\right)^2}$$

Ap: Activity of the standard
Aenc: measured activity by liquid scintillating

The separation of Tc basically consists on a solvent extraction using a crown-ether as extractant, therefore the Tc as a pernectate (Tc(VII) is extracting from sulphuric media.

Once the ^{99}Tc is extracted, it is reduced with ascorbic acid to Tc(IV), finally from this oxidation state the ^{99}Tc is re-extracting in acidic media and the pH is adjusted to 11 in order to stabilize the cation.

Chemical Yield of 93% is calculated from the recovery percentage of ^{99}Tc standard added to an aliquot separately (all the separations are performed by quadruplicate).

The radiological measurement has to be performed by dual label method due to ^{3}H being in the sample as an unavoidable interfering.

From an aliquot of 1 mg of the original sample it is obtained a MDA of 40 Bq/g.

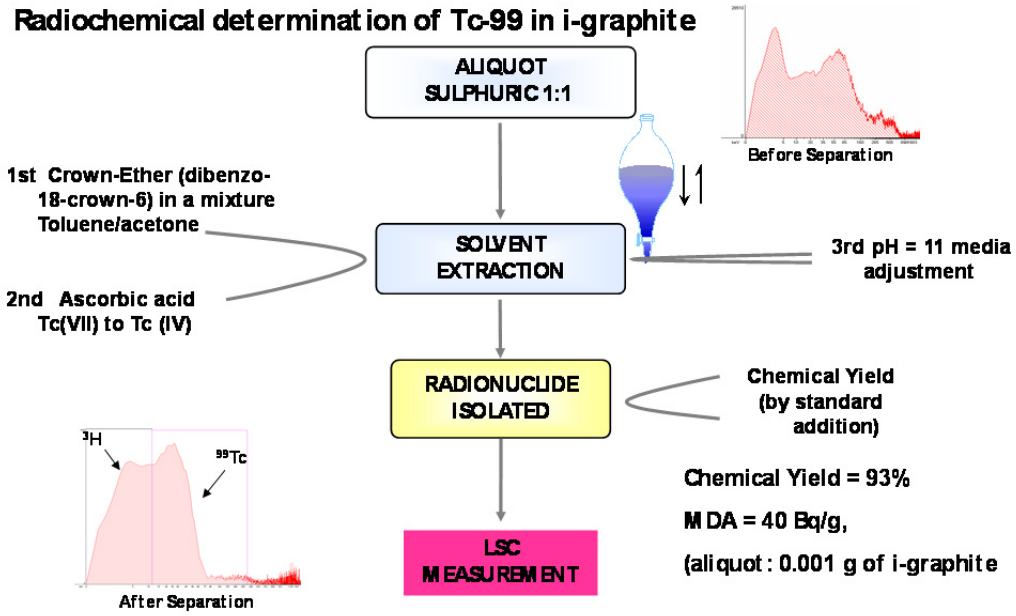

FIG. 1. Schematic of ^{99}Tc radiochemical determination.

Radiochemical measurements performed on i-graphite from the Vandellos 1 sleeves had the following results

Table 4

	Tc-99
Sample ID	Bq/g
GC-1 MEDIANO	< 3,62E+01
GC-2 GRUESO	< 3,85E+01
GC-3 FINO	< 4,01E+01
GC-4 MUY FINO	< 5,03E+01

4. ^{129}I RECOVERY IN THE SOLUBILISATION PROCESS AND MEASUREMENT

To study the recovery of ^{129}I, 3 virgin graphite samples set using the ^{129}I standard were prepared and analysed

The ^{129}1 present after the solubilisation was analyzed using low energy gamma spectrometry. As the measuring equipment does not have an efficiency calibration curve for this radionuclide, it is necessary to prepare a standard with the same geometry (volume and density) to determine the detector's counting efficiency.

The values obtained are shown in Table 5 which demonstrates an average recovery of 97%.

Table 5

Ref.	Added I-129 (dpm)	Measured I-129 LSC±U (dpm)	% Recovery ±U
I-1	2,30	2,28 ± 0,02	0,99 ± 1%
I-2	2,33	2,17 ± 0,02	0,93 ± 2%
I-3	2,64	2,58 ± 0,02	0,98 ± 1%
		Mean Value	0,97 ± 3%

The separation of ^{129}I is firstly performed by precipitation of main interferences (Fe, Co, Zn and other divalent cations) which are separated as hydroxides in alkaline media (Ph >8).

A posterior change of pH has to be done to a weak acidic value of approximately 4, and by this way and by using a specific reactant (phospho-wolframic ácid), the Cs is separated from the sample to avoid the interference of the X-rays in the specectrum, owing to the measurement is going to be performed By LEGe detector.

As in the case of ^{99}Tc, chemical yield is calculated by addition of ^{129}I standard to one aliquots out of four (quadriplicate) measured.

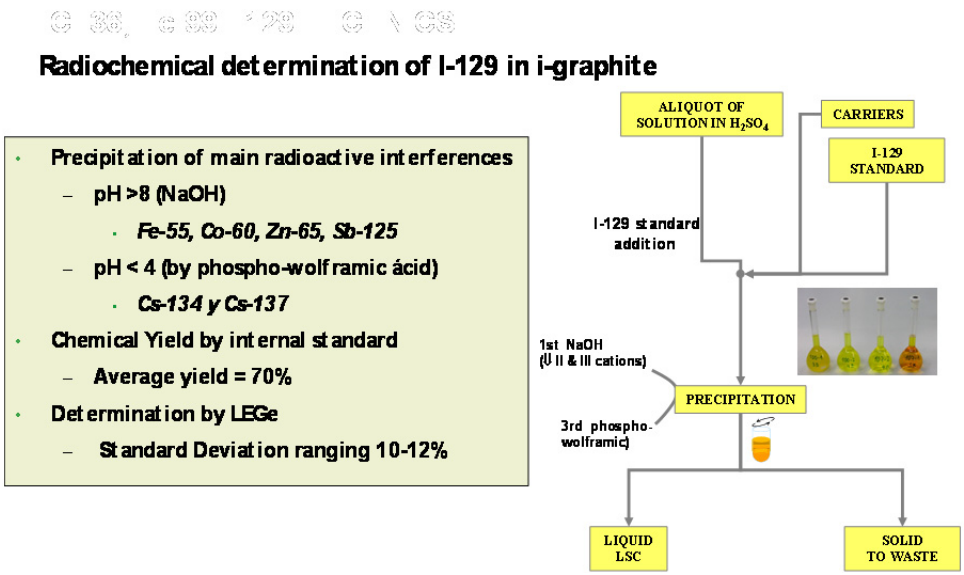

FIG. 2. Schematic of ^{129}I radiochemical determination.

Radiochemical measurements performed on i-graphite from the Vandellos 1 sleeves had the following results.

Table 6

	I-129
Sample ID	Bq/g
GC-1 MEDIANO	< 6,89E+00
GC-2 GRUESO	< 8,62E+00
GC-3 FINO	< 6,31E+00
GC-4 MUY FINO	< 4,85E+00

Further analysis of ^{129}I by using AMS technics performed in 2012 showed the following results.

Table 7

Sample	Description	^{129}I conc. (at/g)	Error (at/g)	Error (%)	^{129}I A (uBq/g)	Error (uBq/g)
CNAI-581	GC-1 MEDIANO	8,67E+08	1,94E+07	2,24	1,213	0,027
CNAI-582	GC-2 GRUESO	1,32E+10	2,28E+08	1,73	18,45	0,32
CNAI-583	GC-3 FINO	1,80E+10	2,79E+08	1,55	25,16	0,39
CNAI-584	GC-4 MUY FINO	8,63E+08	2,48E+07	2,87	1,208	0,035

Due to the very low level of ^{129}I measured, a new set of samples were taken from the same kind of i-graphite, performing experiments of Iodine chemical extraction and final AMS measurements, giving the following results, in agreement with the previous ones in magnitude and variability. The order of magnitude for the ^{129}I concentratiom in the background due to reprocessing activities is between 1E-01-1E-02 µBq/g indicating that the ^{129}I detected in i-graphite is due to contamination processes in Vandellos 1 NPP.

Table 8

Sample	Description	^{129}I A (uBq/g)	Error (uBq/g)
CNAI-748	GC-1	**2,62**	**0,31**
CNAI-749	GC-2	**19,41**	**0,34**
CNAI-750	GC-3	**1,99**	**0,26**
CNAI-751	GC-4	**5,92**	**0,97**

The scheme of radiochemical separation of ^{129}I carried out in the AMS centre of Seville is depicted below.

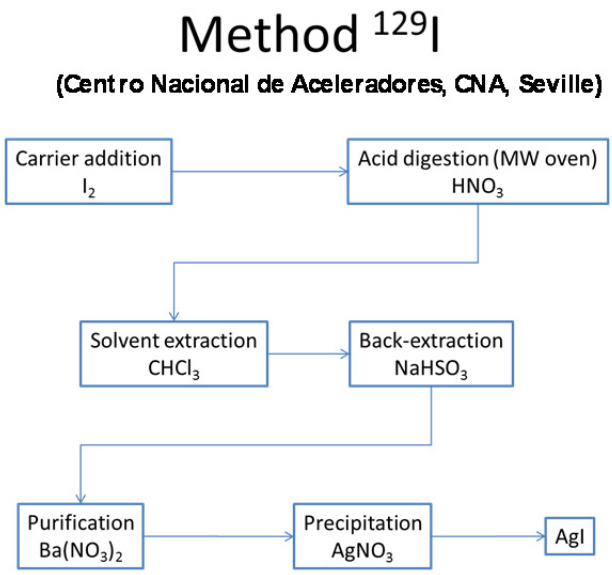

FIG 3. Schematic of ^{129}I chemical separation for AMS

5. ^{36}Cl SEPARATION PROCESS AND MEASUREMENT

The separation of ^{36}Cl requires a special performance of a classic reflux acidic treatment of the sample with reflux of condensed gases. The recovery basically consists on a NaOH trapping reactant; namely ^{36}Cl is extracting from alanine media and the volatilized chlorine is dissolved as sodium chloride. This process of dissolving, separation and trapping is made in only one step.

The radiological measurement has to be performed by dual label method due to C-14 being in the sample as an unavoidable interfering (dissolution of $^{14}CO_2$ as carbonate)

From an aliquot of 6 mg of the original sample is obteined a MDA of 4 Bq/g.

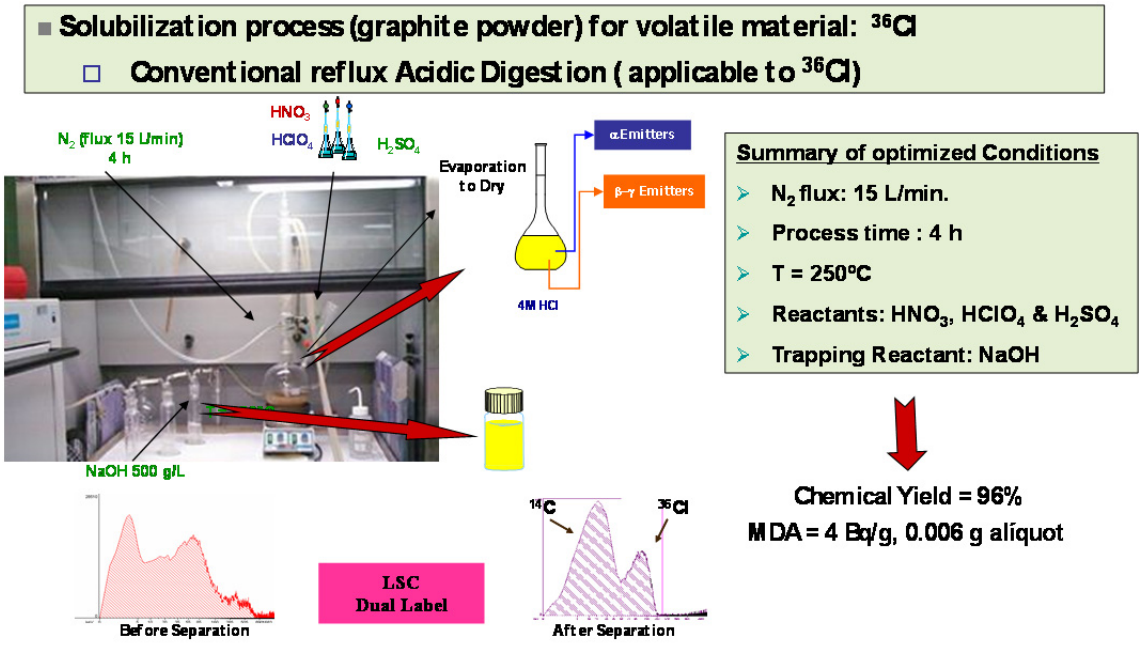

FIG. 4. Schematic of ^{129}I radiochemical determination.

Radiochemical measurements performed on i-graphite from the Vandellos 1 sleeves had the following results

Table VII

	Cl-36	Uncertainty
Sample ID	Bq/g	(%)
GC-1 MEDIANO	1,72E+01	1,50E+01
GC-2 GRUESO	1,47E+01	1,60E+01
GC-3 FINO	2,51E+01	1,10E+01
GC-4 MUY FINO	1,61E+01	1,40E+01

At the moment AMS technics for ^{36}Cl measurements did not succeed due to the low energy of the accelerator (Tamdem Cockcroft-Walton of 1 MV), and therefore more refine chemical separation processes have to be implemented for avoiding noise from ^{36}S, that is also present in the measurements.

6. CONCLUSIONS

A rapid method for solubilising graphite using a microwave digestion system has been developed that enables the volatile radionuclides ^{99}Tc and ^{129}I to be analysed. A mixture of acids is used for the solubilisation, specifically sulphuric and nitric acid, and 100% ^{99}Tc recovery and 97% ^{129}I recovery was demonstrated.

Measurements of ^{36}Cl and ^{129}I above detection limits have been achieved by using radiochemical measurements and AMS technics, whereas non measurementes above that limit have been obtained for ^{99}Tc.

REFERENCES

[1] [Ethos, 2000] ETHOS PLUS APPLICATION NOTES. Milestones Microwave Laboratory Systems. Junio 2000

[2] [Gaines, 2009] GAINES, P; "Dissolving Graphite to Measure by ICP". Inorganic Ventures (inorganicventures.com). 2009

[3] [Suárez, 1993] SUÁREZ GONZÁLEZ DEL REY, J.A; "Procedimiento para la solubilización de grafito en polvo" TN-TR-52. 1993