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Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste

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Topical Report on Characterization Methods (T-3.1.6)

Author(s): **G. Piña (CIEMAT), M. Rodriguez (CIEMAT), D. Vulpius (FZJ), J. Comte (CEA), R. Brennetot (CEA), A. Dodaro (ENEA), G. Duskeas (FTMC), C. Brune (INR), E, 'Visser - Tynova (NRG), K. Van Hecke (SCK·CEN), C. Landesman (SUBATECH), A. Jones (UOM)**

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Topical Report on Characterization Methods

Executive summary

The present document is the CW-Cooking-book with the compilation of the analytical methods applied as routine and developed within the project for radiological characterization of irradiated graphite.

The CW-Cooking book try to be a guide for implementation of Inventory determination of i-graphite for the main radionuclides (Tritium, Radiocarbon, Cobalt-60 and other high energy (>50 keV) gamma emitters, Nickel-63 and Strontium-89/90) present in i-graphite and to find improvement lines in the routine operation of lab's that leads to harmonization of methods. .

Also the Cooking book could be use as reference document for making standardization efforts within EU and as a base of laboratories accreditation to improve the confidence of the final users of data and in the public opinion.

Revisions

Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
00	20/02/2012	Issue	G. Piña, CIEMAT	M. Rodriguez, CIEMAT	G. Piña, CIEMAT	G. Piña, CIEMAT
01	07/01/2013	First issue	G. Piña, CIEMAT	M. Rodriguez, CIEMAT	G. Piña, CIEMAT	G. Piña, CIEMAT
02	06/03/2013	Second issue	G. Piña, CIEMAT	M. Rodriguez, CIEMAT	G. Piña, CIEMAT	G. Piña, CIEMAT
03	22/04/2013	Third issue	G. Piña, CIEMAT	M. Rodriguez, CIEMAT	G. Piña, CIEMAT	G. Piña, CIEMAT

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1. OBJECTIVES

This document compiles the analytical procedures development and apply within IP-CARBOWASTE in order to both have a reference in the inventory characterisation of irradiated graphite within the EU experts labs and on the other hand to give a reference document on the application of radio-analytical methodologies for this waste stream.

Knowing and understand the weak and strong points of each method submitted as well as the complexity , beyond the results obtained with each one, help to harmonise the response of the EU labs within the proper accuracy deal with in each case and the confidence in the lab results.

Procedures reported are mainly devoted to the following determination methods:

- Dissolution of powder i-graphite
- Determination of tritium
- Determination of radiocarbon
- Determination of Cobalt-60 and other high energy gamma emitters
- Determination of Chlorine-36
- Determination of Nickel-63
- Determination of Strontium-90

2. REPORTING ANALYTICAL PROCEDURES

The template used in this document is a way of organise the information managed in the application and the quality assurance and control to be address in the lab work.

The main subject are:

- GENERAL INFORMATION
  - Reference
  - Scope & Range of Application
  - Principle
  - Instrumentation
- OPERATING PROCEDURE
  - Separation Method
  - Flow chart
  - Chemical Yield
  - Calibration
  - Measurement geometry
- EXPRESION OF MEASUREMENT RESULTS
  - Chemical Yield
  - Activity
  - Efficiency

- Uncertainty
- MDA

- GLOSSARY
- REFERENCES

2.1. Template

TITLE: Determination of "X-A" in "matrix"

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
CW Reference	A CW reference is assigned to all procedures. The reference must content: CWAP-B-N, Where: B is the beneficiary number N is a correlative natural number starting by 1 for each beneficiary.
Scope & Range of Application	In this field Should have to be included: The propose of the method, type of matrix or matrices for applying, Range of relative masses or volume, Activity range, aggregation state, Physical form, etc……
Principle	The analytical principle of chemical methodology or separation method and basis of the instrumentation to be used.
Instrumentation	Apparatus to be used & their Model or main characteristics

OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Separation Method	Step 1.	Detailed Description of the first step and its propose
	Step 2.	Subsequent step description
	…..	
	Step n.	
Flow chart	Bock diagram illustrating the method	
Chemical Yield	Description of Methodology to be apply for Chemical yield determination	
Calibration	Description of Calibration methodology	
Measurement	Description of preparation of proper measurement geometry.	

geometry	

EXPRESION OF MEASUREMENT RESULTS	
SUBJETC	**DESCRIPTION**
Chemical Yield	Equation for chemical Yied Calculation
Activity	Equation for Specific Activity Calculation
Efficiency	Equation for Efficiency Calculation
Uncertainty	Equation for Activity uncertainty Calculation
MDA	Equation for Minimum Detectable Specific Activity Calculation

GLOSSARY	
SUBJETC	**DESCRIPTION**
Term 1	Description of acronyms, special terms and symbols within the procedure
….	
Term n	

References

3. PROCEDURES

3.1. Procedures from Lab #1 FZJ

3.1.1. TITLE: Determination of High Energy gamma emitters from i-graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
Reference	CWAP-1-1
Scope & Range of Application	The procedure is used for the determination of gamma emitters directly in the graphite samples without pre-treatment.
Principle	Measurement by multi-channel gamma spectrometry
Instrumentation	HPGe detector Type PGC 2018

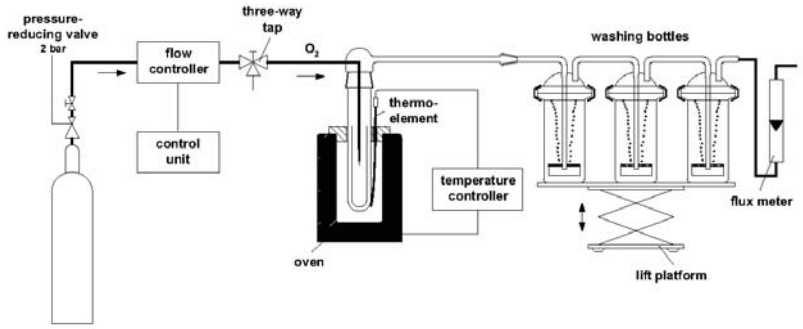
OPERATING PROCEDURE	
SUBJETC	**DESCRIPTION**
Separation Method	N/A
Flow chart	N/A
Chemical Yield	N/A
Calibration	Graphite powder with ^{152}Eu standard solution in the same geometry and distance from the detector as the sample

Measurement geometry	Samples (solid and powdered) were measured in PE LSC vials. The vials were placed directly on the detector in a fixed coaxial position (15 cm).

3.1.2. TITLE: Determination of Tritium and carbon-14 from i-graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
Reference	CWAP-1-2
Scope & Range of Application	The procedure is used for the determination of ^{3}H and ^{14}C directly in the graphite samples without pre-treatment.
Principle	The procedure is based on the oxidation of graphite to CO_2 in pure O_2 at 800 °C. The off-gases are trapped in gas washing bottles filled with 0.1 M HNO_3 for ^{3}H and with 4 M NaOH for ^{14}C. The content of ^{3}H und ^{14}C is determined by measuring an aliquot of the solutions using liquid scintillation counting.
Instrumentation	Liquid Scintillation Analyser Tri-Carb 2770 TR/SL

OPERATING PROCEDURE	
SUBJETC	**DESCRIPTION**
Separation Method	Trapping the off-gases in gas washing bottles filled with 0.1 M HNO_3 for ^{3}H and with 4 M NaOH for ^{14}C

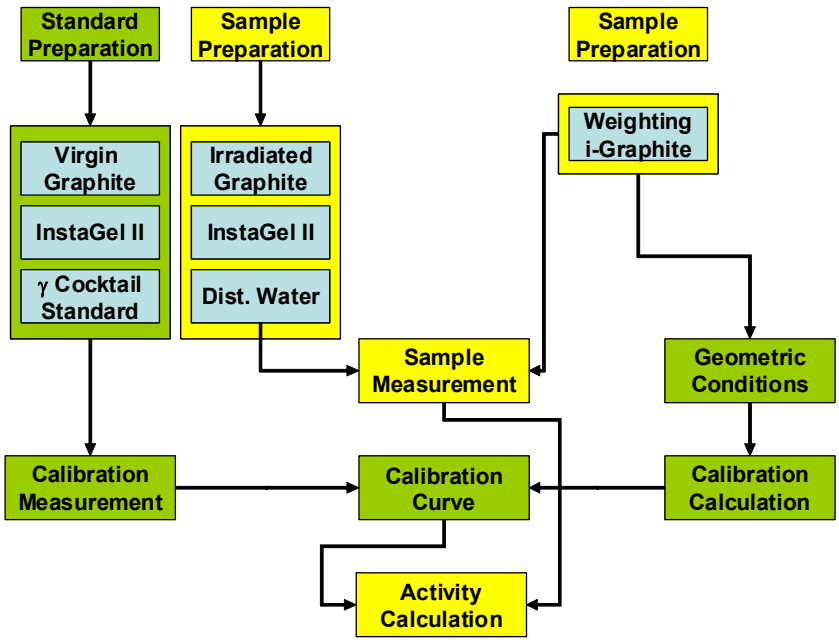
Flow chart	
Chemical Yield	Determined by incineration of solid standards of ^{3}H and ^{14}C
Calibration	By reference standards of ^{3}H and ^{14}C supplied by the device manufacturer
Measurement geometry	N/A

3.2. Procedures from Lab #7 CIEMAT

3.2.1. TITLE: Determination of High Energy gamma emitters from i-graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
Reference	CWAP-7-1
Scope & Range of Application	The procedure is used in the determination of gamma emitters directly in the samples of powder i-graphite, without pre-treatment and by direct measurement after dissolution.
Principle	The procedure is based in experimental and/or numerical calibration in the range 50-1500 keV of a gamma spectrometry systems with GeHP detectors.
Instrumentation	• HPGe detector and electronics • Acquisition and analysis gamma spectrometry software (Genie2000) • Numerical calibration software.(Labsocs)

OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Standard Sample preparation Method	Step 1.I	Weigh virgin graphite powder in amounts of approximately 0.03, 0.05, 0.08 and 0.10 g
	Step 2.I	Prepare amounts (equal amount per standard sample) of multienergetic gamma standard in a volume of 1 ml in acidic media.
	Step 3.I	Mix by shaking the weight virgin graphite in a LSC glass vial with 10 ml of of InstaGel II Plus liquid scintillation cocktail and 8 ml of distilled water
	Step 4.I	Repeat steps 1-3 for others replicates
	Step 5.I	Acquire gamma spectra enough time to ensure statistical uncertainty arond 1% in each gamma line used for calibrate.
Sample preparation Method-I	Step 6.I	Weigh i-graphite powder in amounts of approximately 0.03, 0.05, 0.08 or 0.10 g
	Step 7.I	Mix by shaking the i- graphite in a LSC glass vial with 10 ml of of InstaGel II Plus liquid scintillation cocktail and 8 ml of distilled water

	Step 8.I	Repeat steps 1-2 for others replicates
Sample preparation Method-II	Step -1.II	Weigh i-graphite powder in amounts ranging 0.5-5 g
	Step 2.II	Put into a LSC glass vial
	Step 3.II	Repeat steps 1-2 for others replicates
Measurement	Step 9.I Step 4.II	Acquire gamma spectra enough time to ensure statistical uncertainty according with the assessment desired and dead-time lower than 5%.
Flow chart		
Calibration Method I	With the spectra acquired give the data to the software Genie 2000 for performing calibration curve in the range of standard energy lines and with updated calibration data from standard certificate	
Calibration Method II	Prepare the template for LABSOCs software with the geometrical and physical conditions of sample and perform the calculation of the calibration curve with the converged uncertainty required by the method.	

EXPRESION OF MEASUREMENT RESULTS	
SUBJETC	**DESCRIPTION**
Chemical Yield	The relative mass or volumen can be from the direct measuremnt o fan aliquot of the original simple or comming from a process in which the recovery factor has to be calculate $V = V_o \cdot \frac{m_f}{m_o}$

Activity	$${}^{X}A_i = \frac{N_i}{V \cdot \varepsilon_i \cdot TL \cdot {}^{X}\eta_i}$$
Efficiency	The efficiency is calculated from the efficiency curve as function of energy. $$\log Eff = a + b\log E + c(\log E)^2 + d(\log E)^3$$ The curve is fitting from the individual calibration points coming from experimental measurement of the certified standards. $$\varepsilon_i = \frac{N_i}{V \cdot A \cdot TL \cdot \eta_i}$$
Uncertainty	Identification of uncertainty sources: ♦ m: • u from mass determination $$\frac{U_V}{V} = \sqrt{\left(\frac{U_{V_o}}{V_o}\right)^2 + \left(\frac{U_{mf}}{m_f}\right)^2 + \left(\frac{U_{mo}}{m_o}\right)^2}$$ ♦ Area: u from net area (N) from the equation: **N= Area**$_{Sample}$**-Area**$_{background}$ $$\sigma(N) = \sqrt{u^2_{dpm_{sample}} + u^2_{dpm_{background}}}$$ $$\sigma_N = \sqrt{\sigma_I^2 + \sigma_F^2 + \sigma_{NB}^2}$$ **Ilustración 1** Quasi-variance if n replicates are measured: $$\sigma(sample) = \sqrt{\frac{\sum(Area_{sample} - \overline{Area_{sample}})^2}{n-1}}; \sigma(B) = \sqrt{\frac{\sum(Area_{background} - \overline{Area_{backgr}}}{n-1}}$$ $$\sigma(N) = \sqrt{\sigma(sample)^2 + \sigma(B)^2}$$ **Note:** Uncertainty regarding efficiency is taking into account directly into uncertainty of Activity given by the software. $$\left[\frac{U_\varepsilon}{\varepsilon}\right]_i = \sqrt{\left(\frac{\sigma_N}{N}\right)_i^2 + \left(\frac{U_A}{A_{mr}}\right)^2 + \left(\frac{U_\eta}{\eta}\right)_i^2}$$ Expression of activity uncertainty in relative terms is given by:

	$${}^{X}\left[\frac{U_A}{A}\right]_i = \sqrt{\left(\frac{\sigma_N}{N}\right)_i^2 + \left(\frac{U_V}{V}\right)^2 + \left(\frac{\sigma_\varepsilon}{\varepsilon}\right)_i^2 + \left(\frac{U_\eta}{\eta}\right)_i^{2\,2}}$$ The established coverage factor (**k**) is 2 for a confidence level of 95 % given the result expression: $$A \pm 2 \cdot U(A)$$
MDA	The minimum detectable activity is calculated according to the Currie equation shown in the equation: $$L_C = k_\alpha \cdot \sigma_0$$ $$L_D = L_C + k_\beta \cdot \sigma_D$$ $${}^{X}MDA_i = \frac{L_D}{V \cdot \varepsilon_i \cdot TL \cdot {}^{X}\eta_i}$$ $$L_D = k^2 + 2L_C$$ $${}^{X}MDA_i = \frac{4.66 \times \sqrt{B/T}}{V \cdot \varepsilon_i \cdot TL \cdot {}^{X}\eta_i}$$

GLOSSARY	
SUBJETC	**DESCRIPTION**
V	Volume or mass measured from original sample
V_0	Volume or mass from original sample taken to prepare the measurement item.
m_f	Tracer activity or carrier mass added after sample preparation process.
m_0	Tracer activity or carrier mass added before sample preparation process.
${}^{X}A_i$	Specific activity of nuclide X measured in the peak of energy i
N_i	Net counts Ander the peak of energy i (under the peak of the standard used in case of efficiency calculation)
TL	Live time of the simple (or reference sample)
${}^{X}\eta_i$	Emission probability of nuclide X at energy i
ε_i	Efficiency at energy i for the measurement pair Detector-Geometry.
A	Activity of the reference used for calculate efficiency (standard)
η_i	Emission probability of the line at energy I of the reference nuclide
L_C	Critical level

L_D	Decision level
σ_0	Deviation at signal 0 (backaground/blank measurement)
$^{X}MDA_i$	Minimum Detectable Activity for nuclide X at energy i

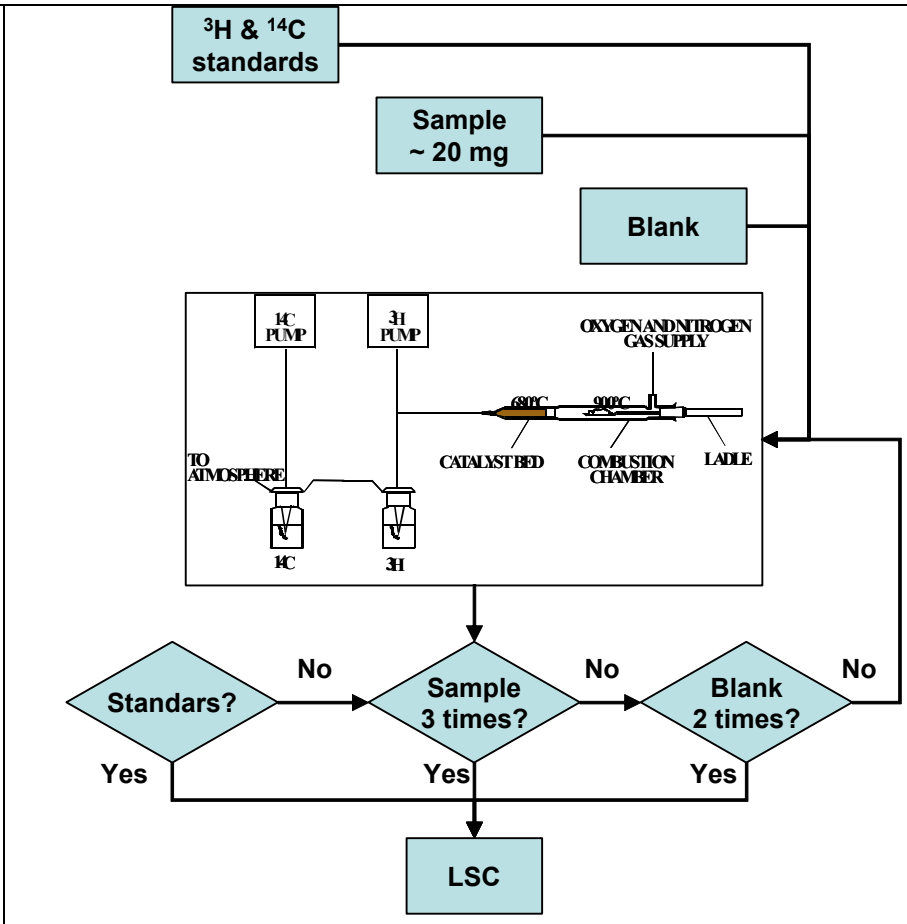
References

[1]. L.A. Currie, "Limits o Qualitative Detection and Quantitative Determination", Analytical Chemistry, 40. 1968

3.2.2. TITLE: Determination of Tritium and carbon-14 from i-graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
Reference	CWAP-7-2
Scope & Range of Application	The procedure is used in the determination of ^{3}H and ^{14}C directly in the samples of graphite, without pre-treatment.
Principle	The procedure is based on the oxidation of any burnable materials (wet and dry) and conversion of the sample to a gaseous state. When the sample burned at 900ºC in an oxygen stream, the bulk of the material is converted to carbon dioxide and steam. Metals, salts, oxides and materials with very high melting points remain without react. ^{3}H and ^{14}C is determined by the measured of its beta emission once the possible gamma interferences are checked by gamma spectrometry.
Instrumentation	• Harvey OX-500 Biological Material Oxidizer • Liquid Scintillation Analyzer Tri-Carb 2750 TR/LL • Ge-HP or Ge-Li detectors associated with 8K channels-spectrometers and analysis software

OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Separation Method	Step 1.	Burning and trapping of standards of ^{3}H and ^{14}C at 900º C
	Step 2.	Three times burning of a sample (~20mg)
	Step 3.	2 Blank burning once (holder empty) for clean up system
	Step 4.	Next replicate or sample

Flow chart	
Chemical Yield	To determine the chemical yield is prepared a vial is prepared with ^{3}H standard, which has been oxidised in the combustion furnance, and another vial with the same amount of ^{3}H standard directly added to the trapping solution (Harvey OX-161 model). Both vials are measuring by liquid scintillation counting. The same procedure is apply for ^{14}C chemical yield determination
Calibration	As ^{3}H in some cases can pass to the carbon vial and the ^{14}C to the tritium vial, it is necessary to use the dual technique (^{3}H/^{14}C) in the determination of the activity. Therefore the efficiency is calculated from a tSIE value with quenching curves established with ^{3}H and ^{14}C reference standards. For performing these quenching curves Cl_4C was added in increasing amounts to ten vials containing the same activity of the ^{3}H standard solutions and the scintillation cocktail Harvey OX-162, and Cl_4C in increasing amounts to ten vials containing the same activity of the ^{14}C standard and the scintillation cocktail Harvey OX-161. The windows settings optimised are: 0-7.0 keV 7.0-35.0 keV for ^{14}C and 0-12.0 keV 12.0 – 156 keV for ^{3}H

Measurement geometry	The samples are directly ready from the Oxidizer to be measured by liquid scintillation counting.

EXPRESION OF MEASUREMENT RESULTS	
SUBJETC	**DESCRIPTION**
Chemical Yield	$CY = \frac{dpm_{Combustion}}{dpm_{direct}}$
Activity	The activity of ^{14}C is calculated in Bq per volume or mass of the original sample. The formula for the calculation is: $A = \frac{dpm_{sample} - dpm_{backgound}}{60 \times CY} \times DF$ $DF = \frac{1}{m_{al}}$
Efficiency	As ^{3}H in some cases can pass to the carbon vial it is necessary to use the dual technique ($^{3}H/^{14}C$) in the determination of the activity. Therefore the efficiency is calculated from a tSIE value with quenching curves established with ^{3}H and ^{14}C reference standards. For performing these quenching curves Cl_4C was added in increasing amounts to ten vials containing the same activity of the ^{3}H standard solutions and the scintillation cocktail Harvey OX-162, and Cl_4C in increasing amounts to ten vials containing the same activity of the ^{14}C standard and the scintillation cocktail Harvey OX-161. The windows settings optimised are: 0-7.0 keV and 7.0-35.0 keV.
Uncertainty	Identification of uncertainty sources: ♦ DF: • u from mass determination • u from volume of aliquots ♦ CY: • σ from counting of ^{3}H or ^{14}C standard direct measurement (dpm_{direct}) • σ from counting of ^{3}H or ^{14}C standard after combustion ($dpm_{combustion}$) ♦ N: u from net dpm (N) from the equation: **N=** dpm_{sample}-$dpm_{background}$ if single measurement if done absolute uncertainty is obtained by propagation of absolute uncertainties from sample and background measurements. $\sigma(N) = \sqrt{u^2_{dpm_{sample}} + u^2_{dpm_{background}}}$ Quasi-variance if n replicants are calculated:

	$\sigma(\text{sample}) = \sqrt{\frac{\sum(\text{dpm}_{\text{sample}} - \overline{\text{dpm}_{\text{sample}}})^2}{n-1}}; \sigma(B) = \sqrt{\frac{\sum(\text{dpm}_{\text{background}} - \overline{\text{dpm}_{\text{background}}})^2}{n-1}}$ $\sigma(N) = \sqrt{\sigma(\text{sample})^2 + \sigma(B)^2}$ **Note:** Uncertainty regarding efficiency is taking into account directly into uncertainty of dpm given by the equipment. Expression of activity uncertainty in relative terms is given by: $\frac{U(A)}{A} = \sqrt{\left(\frac{\sigma(N)}{N}\right)^2 + \left(\frac{u(CY)}{CY}\right)^2 + \left(\frac{u(DF)}{DF}\right)^2}$ where: $\frac{u(DF)}{DF} = \sqrt{\left(\frac{u(m_{al})}{m_{al}}\right)^2}$ $\frac{u(CY)}{CY} = \sqrt{\left(\frac{\sigma(\text{dpm}_{\text{combustion}})}{\text{dpm}_{\text{combustion}}}\right)^2 + \left(\frac{\sigma(\text{dpm}_{\text{direct}})}{\text{dpm}_{\text{direct}}}\right)^2}$ The established coverage factor (**k**) is 2 for a confidence level of 95 % given the result expression: $A \pm 2 \cdot U(A)$
MDA	The minimum detectable activity is calculated according to the Currie equation shown in the equation: $\text{MDA} = \frac{4.66 \times \sqrt{\text{cpm}_{\text{background}}/t}}{60} \times \text{DF} \times \frac{\text{cpm}_{\text{background}}}{\text{dpm}_{\text{background}}}$

GLOSSARY	
SUBJETC	**DESCRIPTION**
CY	Chemical yield of the procedure
$\text{dpm}_{\text{Combustion}}$	dpm obtained in the measured of the standard sample oxidised
$\text{dpm}_{\text{direct}}$	dpm obtained in the direct measured of the standard sample
$\text{dpm}_{\text{sample}}$	Average activity of sample
$\text{dpm}_{\text{background}}$	Average activity of background (blank)
$\text{cpm}_{\text{background}}$	Average count rate of background (blank)
m_{al}	Mass of the aliquot taken
DF	Dilution factor Factor of aliquot taken

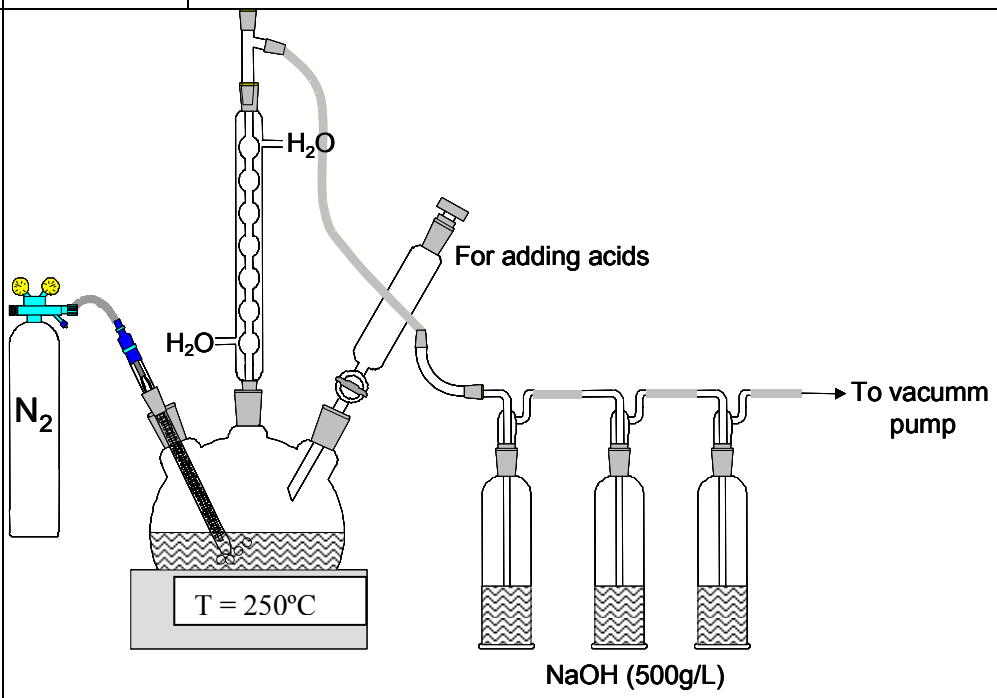
References

[2]. M. Rodríguez, G. Piña and A.G. Espartero, "Procedimiento para la preparación de muestras donde analizar ^{99}Tc and ^{129}I presentes en resinas cambiadoras de ión". TN-TR-42.1992
[3]. M. Rodríguez and G. Piña, "Procedimiento para la determinación de tritio procedente de resinas cambiadoras de ión". TN-TR-31.1992
[4]. A.G. Espartero, G. Piña and M. Rodríguez, "Procedimiento para la separación de ^{3}H y ^{14}C en alícuotas procedentes de residuos radiactivos de diversa naturaleza, mediante horno de combustión automático". TN-TR-47.1992
[5]. R.J. Harvey Instrument Corporation, "Biological material oxidizer OX-500 operating and service manual".
[6]. L.A. Currie, "Limits o Qualitative Detection and Quantitative Determination", Analytical Chemistry, 40. 1968

3.2.3. TITLE: Determination of Cl-36 from i-graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
Reference	CWAP-7-3
Scope & Range of Application	The procedure is used in the determination of ^{36}Cl in i-graphite samples.
Principle	The separation method proposed is based on an oxidation technique where chlorine is trapped by NaOH. ^{36}Cl beta emissions are measured by liquid scintillation counting by the dual label technique for graphite samples in order to avoid the contamination produced by ^{14}C which is also trapped by NaOH and which is the main contaminant present in these samples.
Instrumentation	Liquid Scintillation Analyzer

OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
	Step 1.	The graphite sample (approximately 1 gram) is put into a flask and mixed with 40 mL HNO_3, 40 mL $HClO_4$ and 160 mL H_2SO_4 conc. Addition of known amounts of stable chlorine as carrier
	Step 2.	Nitrogen gas is bubbled through the solution (15 L/min).
	Step 3.	Refluxed is performed during four hours
	Step 4.	^{36}Cl presents in the sample is oxidised to Cl_2 at high temperature and trapped in three washing bottles that contain, in total, 150 cm^3 alkaline solutions (500 g/L NaOH). Due to the corrosive atmosphere produced in the reactor, the connections employed in the digestion system have to be acid resistant in order to avoid losses of the gases produced.
	Step 5.	The solutions in the washing bottles are combined in a 250 cm^3 beaker and one millilitre of the solution is transferred to a 20 cm^3 liquid scintillation counting vial. This solution has to be prepared for measuring by liquid scintillation counter and therefore drops of HNO_3 conc. have to be added to the vial in order to neutralise the solution and distilled water has to be added to reach a volume of 10

		cm^3. Finally, 11 cm^3 of Instagel cocktail is added to the vial and the gel solution obtained is mixed.
	Step 6.	^{36}Cl is analysed in a liquid scintillation counter by the dual label technique.
Flow chart		
Chemical Yield	The final solutions obtained from different standard samples show a constant chemical yield ranging from 98 to 99% and therefore this value will be used in the calculation of the activity in all analysis performed.	
Calibration	The efficiency is calculated with quenching curves established with ^{14}C and ^{36}Cl reference standards. For performing these quenching curves ten vials of each radionuclide containing the same activity of the standard solution are prepared. Then the scintillation cocktail Instagel is added to each vial and finally before counting Cl_4C is added in increasing amounts. It is used a ^{14}C (or low-energy beta nuclides) window (0-50 keV) and ^{36}Cl (or high-energy beta nuclides) window (50-300 keV) for the measurement of ^{14}C and ^{36}Cl, respectively. The quench level was measured by the external standard method tSIE, and the counting efficiency calculated using standards at different quench levels.	

Measurement geometry	First, it is prepared a vial with a blank sample prepared according step 5 described in the procedure. Then and in the same conditions three vials are prepared from the final solution.

EXPRESION OF MEASUREMENT RESULTS	
SUBJETC	**DESCRIPTION**
Chemical Yield	$CY = 0.985$
Activity	The activity of ^{36}Cl is calculated in Bq per volume or mass of the original sample. The formula for the calculation is: $A = \left(\frac{N}{60 \times CY} \right) \times DF$ $N = dpm_{Cl36} = dpm_{sample} - dpm_{background}$
Efficiency	The counting efficiencies are calculated from the quenching curves performed with ^{14}C and ^{36}Cl reference standards and established as a function of a quench index parameter (tSIE).
Uncertainty	Identification of uncertainty sources: ♦ DF: • u from mass determination • u from volume of aliquots ♦ CY: • Quasi-variance of n replicants measured at determination of CY while process setting-up ♦ N: u from net dpm (N) from the equation if single measurement if done absolute uncertainty is obtained by propagation of absolute uncertainties from sample and background measurements. $\sigma(N) = \sqrt{u^2_{dpm_{sample}} + u^2_{dpm_{background}}}$ Quasi-variance if n replicants are calculated:

	$\sigma(\text{sample}) = \sqrt{\frac{\sum(\text{dpm}_{\text{sample}} - \overline{\text{dpm}_{\text{sample}}})^2}{n-1}};$ $\sigma(\text{B}) = \sqrt{\frac{\sum(\text{dpm}_{\text{background}} - \overline{\text{dpm}_{\text{background}}})^2}{n-1}}; \Rightarrow$ $\sigma(\text{N}) = \sqrt{\sigma(\text{sample})^2 + \sigma(\text{B})^2}$ **Note:** Uncertainty regarding efficiency is taking into account directly into uncertainty of dpm given by the equipment. Expression of activity uncertainty in relative terms is given by: $\frac{u(A)}{A} = \sqrt{\left(\frac{\sigma(N)}{N}\right)^2 + \left(\frac{u(CY)}{CY}\right)^2 + \left(\frac{u(DF)}{DF}\right)^2}$ where: $\frac{u(DF)}{DF} = \sqrt{\left(\frac{u(m_{al})}{m_{al}}\right)^2 + \sum_i \left[\left(\frac{u(V_i)}{V_i}\right)^2\right]}$ $\frac{u(CY)}{CY} = 0.04$ The established coverage factor (**k**) is 2 for a confidence level of 95 % given the result expression: $\mathbf{A \pm 2 \cdot u(A)}$
MDA	The minimum detectable activity is calculated in Bq per volume or mass of the original sample: $\text{MDA} = \frac{4.66 \times \sqrt{\text{N}/t}}{60 \times \text{Eff} \times \text{CY}} \times \text{DF}$

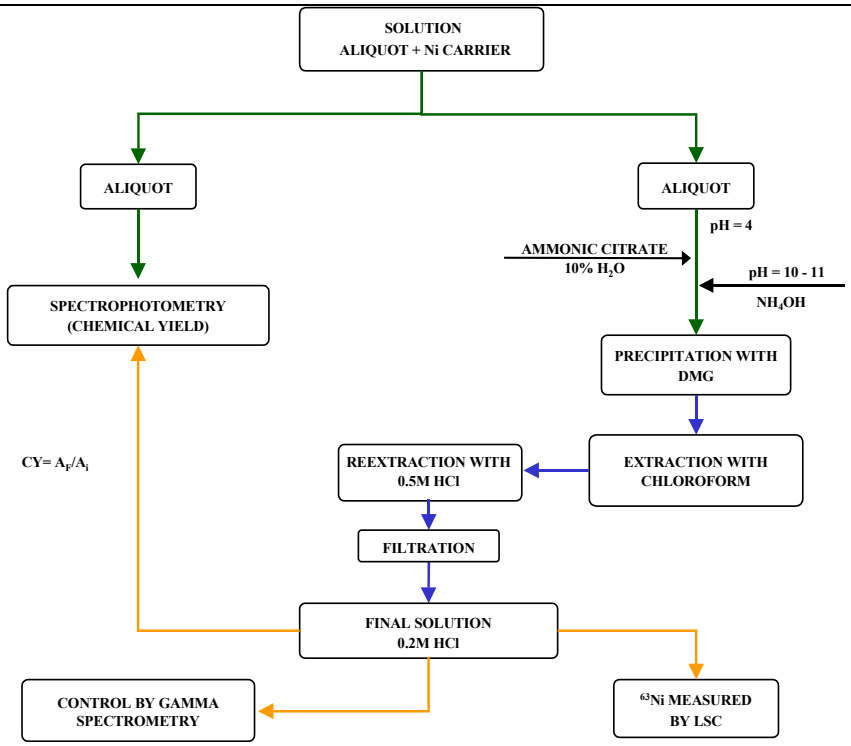
GLOSSARY	
SUBJETC	**DESCRIPTION**
CY	Chemical yield of the procedure
Eff	Efficiency obtain from quenching curve
N	Net count Rate
DF	Dilution Factor
t	Measurement time

References

3.2.4. TITLE: Determination of nickel-63 from dissolved i-graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
Reference	CWAP-7-4
Scope & Range of Application	The procedure is used in the determination of ^{63}Ni in solutions coming from solubilisation of graphite radioactive wastes.
Principle	The procedure is performed in aliquots from the solution obtained in 4M HCl such. The procedure to analyse ^{63}Ni is based on the selective liquid-liquid extraction of the complex nickel-dimethylglyoxime. ^{63}Ni is determined by the measured of its beta emission by liquid scintillation counting once the possible gamma interferences are checked by gamma spectrometry. The chemical yield is determined by spectrophotometry.
Instrumentation	• Liquid Scintillation Analyzer Tri-Carb 2750 TR/LL • UV-Visible Spectrophotometer, Shimadzu S-1203 • Ge-HP or Ge-Li detectors associated with 8K channels-spectrometers and analysis software

OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Separation Method	Step 1a.	Addition of known amounts of stable nickel as carrier
	Step 1b.	Aliquot is measured by Spectrophotometry to obtain initial Ni concentration.
	Step 2.	Precipitation of Ni with specific reactant (DMG) with previous adjustment at pH = 4 for the adition of ammonic nitrate and adjustment at ph = [10,11] with ammonic hydroxide.
	Step 3.	Liquid-liquid extraction of nickel with chloroform
	Step 4.	Re-extraction with 0.5M HCl to obtain the 0.2M HCl final solution.
	Step 5a.	Aliquots are taken for Activity measurement by LSC
	Step 5b.	Aliquot is taken for measuring final Ni concentration by Spectro-photometry.

Flow chart	
Chemical Yield	Nickel as carrier is added to the aliquot of the initial solution in order to determine the chemical yield by spectrophotometry. It is used the ratio between the absorbance value obtained in the final aliquot, once the procedure has finished and the spectrophotometry method has been performed, and the absorbance value obtained with the spectrophotometry method in the aliquot taken before performing the procedure.
Calibration	The efficiency is calculated with quenching curves established with ^{63}Ni reference standard. For performing these quenching curves ten vials containing the same activity of the standard solution are prepared. Then the scintillation cocktail Instagel is added to each vial and finally before counting Cl_4C is added in increasing amounts. The window settings optimised is: 0-60 keV.
Measurement geometry	First, it is prepared a vial with a blank sample that contains 1 ml of 0.2M HCl and 10 ml of liquid scintillation cocktail Instagel. Then, three vials are prepared containing each one 1 ml from the final solution (0.2M HCl) and 10 ml of Instagel.

EXPRESION OF MEASUREMENT RESULTS	
SUBJETC	**DESCRIPTION**
Chemical Yield	$CY = \frac{A_F}{A_I} \times F$
Activity	The activity of ^{63}Ni is calculated in Bq per volume or mass of the original sample. The formula for the calculation is: $A = \left(\frac{N/Eff}{60 \times CY} \right) \times DF$
Efficiency	The counting efficiencies are calculated from the quenching curves performed with ^{63}Ni reference standard and established as a function of a quench index parameter (tSIE).
Uncertainty	Identification of uncertainty sources: ♦ DF: • u from mass determination • u from volume of aliquots ♦ CY: • σ from counting of ^{63}Ni standard (N) • σ from counting of ^{63}Ni standard after separation (N') ♦ Eff: • u from standard counting • u from calibration curve fitting (Eff vs TSIE) • u from standard activity ♦ N: u from net count rate (N) from the equation: **N= R-B** where R is the sample count rate and B is the background count rate: • Poisson determination if single measurement if done $\sigma(N) = \sqrt{R/t + B/t}$ Quasi-variance if n replicants are calculated: • Quasi-variance if n repetitions are done: $\sigma = \sqrt{\frac{\sum (R - \bar{R})}{n-1}}; \sigma_B = \sqrt{\frac{\sum (B - \bar{B})}{n-1}}; \Rightarrow \quad \sigma(N) = \sqrt{\sigma(R)^2 + \sigma(B)^2}$ Expression of activity uncertainty in relative terms is given by: $\frac{u(A)}{A} = \sqrt{\left(\frac{\sigma(N)}{N}\right)^2 + \left(\frac{u(Eff)}{Eff}\right)^2 + \left(\frac{u(CY)}{CY}\right)^2 + \left(\frac{u(DF)}{DF}\right)^2}$

	where: $\frac{u(DF)}{DF} = \sqrt{\left(\frac{u(m_{al})}{m_{al}}\right)^2 + \sum_i \left[\left(\frac{u(V_i)}{V_i}\right)^2\right]}$ $\frac{u(CY)}{CY} = \sqrt{\left(\frac{\sigma(A_F)}{A_F}\right)^2 + \left(\frac{\sigma(A_I)}{A_I}\right)^2 + \left(\frac{u(F)}{F}\right)^2}$ $\frac{u(Eff)}{Eff} = \sqrt{\left(\frac{\sigma(N_s)}{N_s}\right)^2 + (u(Eff - tSIE))^2 + \left(\frac{u(A_s)}{A_s}\right)^2}$ The established coverage factor (**k**) is 2 for a confidence level of 95 % given the result expression: $A \pm 2 \cdot u(A)$
MDA	The minimum detectable activity is calculated in Bq per volume or mass of the original sample: $MDA = \frac{4.66 \times \sqrt{N/t}}{60 \times Eff \times CY} \times DF$

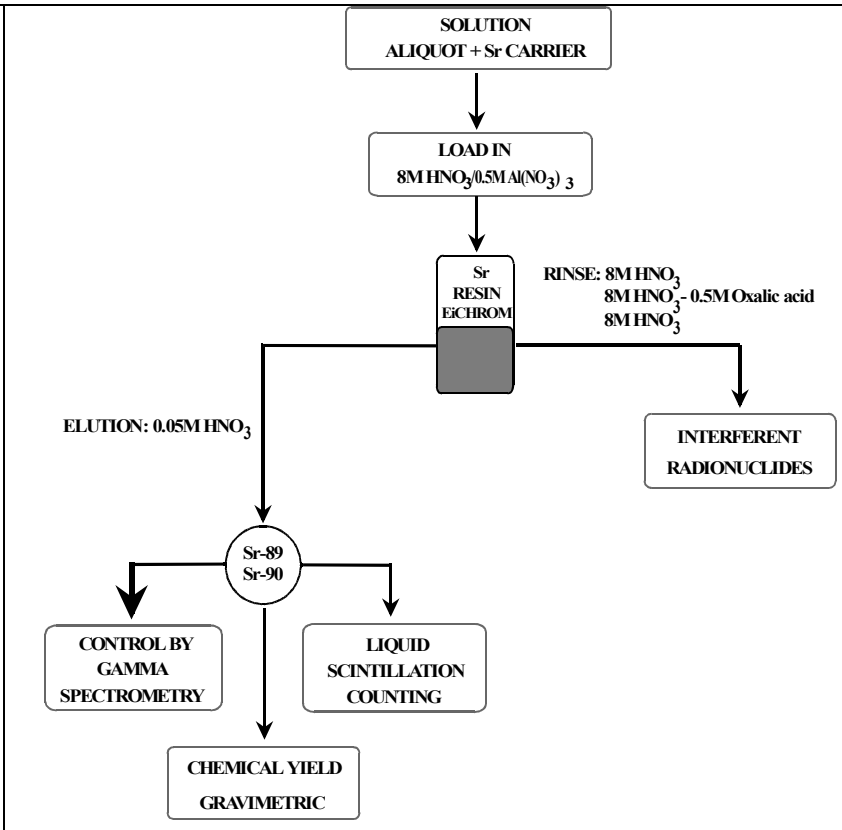
GLOSSARY	
SUBJETC	**DESCRIPTION**
CY	Chemical yield of the procedure
A_F	Absorbance measured in the aliquot from the final solution
A_I	Absorbance measured in the aliquot from the initial solution
F	Factor of aliquot taken to the spectrophotometric analysis
Eff	Efficiency obtain from quenching curve
N	Net count Rate
DF	Dilution Factor
t	Measurement time

References

3.2.5. TITLE: Determination of strontium-89 and strontium-90 from dissolved i-graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
CW Reference	CWAP-7-5
Scope & Range of Application	The procedure is used in the determination of $^{89/90}$Sr in solutions coming from the mineralization of irradiated graphite and another liquid radioactive wastes.
Principle	The procedure is performed in aliquots from the solution obtained in 4M HCl (CWAP-7-1,). The procedure to analyse $^{89/90}$Sr is based on the strontium adsorption on an "Eichrom Sr"-Resin specific column after conversion of the solution to the nitrate form. $^{89/90}$Sr is determined by the measured of its beta emission by liquid scintillation counting once the possible gamma interferences are checked by gamma spectrometry. Two counting are made, one immediately after the separation and the other one with a minimum time interval of 8-10 days to correct the influence of ^{89}Sr. The chemical yield is determined by gravimetry.
Instrumentation	• Liquid Scintillation Analyzer Tri-Carb 2750 TR/LL • Ge-HP or Ge-Li detectors associated with 8K channels-spectrometers and a microcomputer

OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Separation Method	Step 1.	Addition of known amounts of stable strontium as carrier and after conversion of the solution to the nitrate form.
	Step 2.	Strontium is separated by adsorption on an Eichrom Sr-Resin column
	Step 3.	The rinse are performed with 8M HNO_3, 8M HNO_3-0.5M oxalic acid and 8M HNO_3
	Step 4.	The elution of strontium is carried out with 0.05M HNO_3.

Flow chart	
Chemical Yield	The solution obtained in the separation procedure is evaporated to dry, then it is added HNO_3 and again is evaporated to dry in order to be sure that all sample is in the nitrate form. Finally the residue is weighted and the weigh corresponding to $Sr(NO_3)_2$ form is obtained.
Calibration	The efficiency is calculated with a ^{89}Sr and $^{90}Sr/^{90}Y$ reference standards. The efficiency obtained is practically 100% to the different quenching values analysed The window settings optimised is: 0-2000 keV.
Measurement geometry	First, it is prepared a vial with a blank sample that contains 1 ml of 0.05M HNO_3 and 10 ml of liquid scintillation cocktail Instagel. Then, three vials are prepared dissolving the evaporated residue obtained in the determination of the chemical yield, by the addition of 1 ml of 0.05M HNO_3 and 10 ml of Instagel.

EXPRESION OF MEASUREMENT RESULTS	
SUBJETC	**DESCRIPTION**
Chemical Yield	$CY = \frac{m_F}{m_I}$
Activity	$A_{Sr90} = \left(\frac{E_{Sr90}}{60 \times CY}\right) \times DF \qquad A_{Sr89} = \left(\frac{E_{Sr89}}{60 \times CY}\right) \times DF$ $N(t_1) = E_{Sr90} \times Eff_{Rr90} + E_{Sr90} \times \left(1 - e^{-\lambda_{Y90} t_1}\right) \times Eff_{y90} + E_{Sr89} \times Eff_{Sr89}$ $N(t_2) = E_{Sr90} \times Eff_{Rr90} + E_{Sr90} \times \left(1 - e^{-\lambda_{Y90} t_2}\right) \times Eff_{y90} + E_{Sr89} \times Eff_{Sr89} e^{-\lambda_{Sr89}(t_2 - t_1)}$
Efficiency	The counting efficiencies are considered 100% both ^{90}Sr and ^{89}Sr $Eff_{Sr90} = Eff_{Sr89} = Eff_{Y90} = 1$
Uncertainty	$\sigma = \sqrt{\frac{\sum (R - \bar{R})}{n-1}}; \sigma_B = \sqrt{\frac{\sum (B - \bar{B})}{n-1}}; \Rightarrow \quad \sigma(N) = \sqrt{\sigma(R)^2 + \sigma(B)^2}$ or $\sigma(N) = \sqrt{R/t + B/t}$ $\frac{u(CY)}{CY} = \sqrt{\left(\frac{\sigma(m_f)}{m_f}\right)^2 + \left(\frac{\sigma(m_i)}{m_i}\right)^2} \qquad \frac{u(Eff)}{Eff} = \sqrt{\left(\frac{\sigma(N_s)}{N_s}\right)^2 + \left(\frac{u(A_s)}{A_s}\right)^2}$ Re-defining: $N(t_1) = N_1;$ $N(t_1) = N_1$ $Eff_{Sr90} = Eff_{Sr89} = Eff_1;$ $Eff_{y90} \cdot \left(1 - e^{-\lambda_{Y90} t_1}\right) = Eff_2$ $Eff_{y90} \cdot \left(1 - e^{-\lambda_{Y90} t_2}\right) = Eff_3;$ $Eff_{Sr89} \cdot \left(e^{-\lambda_{Sr89}(t_2 - t_1)}\right) = Eff_4$

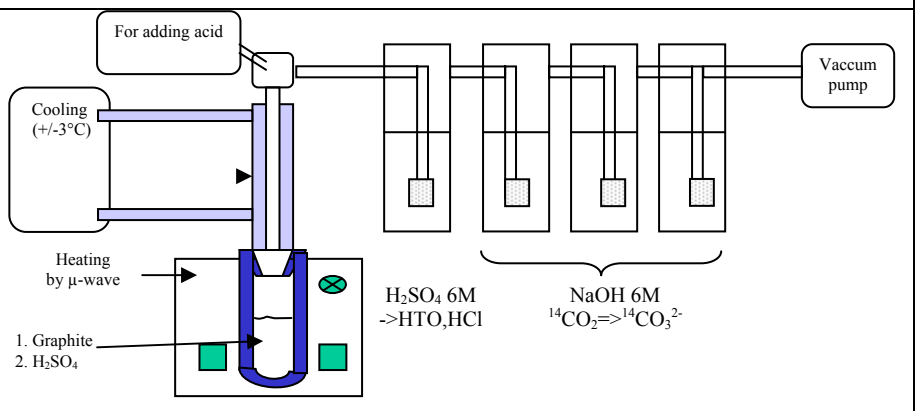
	$$\frac{u(E_1)}{E_1}=\sqrt{\left(\frac{\sigma(N_2)}{[N_2+E_2Eff_4]}\right)^2+\left(\frac{u(E_2)}{[N_2+E_2Eff_4]}\right)^2\cdot Eff_4^{\,2}+\left(\frac{u(Eff)}{[N_2+E_2Eff_4]}\right)^2\cdot\frac{E_2^{\,2}+2N_2^{\,2}+2E_2^{\,2}\cdot Eff_4^{\,2}}{(Eff_1+Eff_3)^2}}$$ $$\frac{u(E_2)}{E_2}=\sqrt{\left(\frac{\sigma(N_1)}{[N_1+E_1(Eff_1+Eff_2)]}\right)^2+\left(\frac{u(E_1)}{[N_1+E_1(Eff_1+Eff_2)]}\right)^2\cdot(Eff_1^{\,2}+Eff_2^{\,2})+\left(\frac{u(Eff)}{[N_1+E_1(Eff_1+Eff_2)]}\right)^2\cdot\frac{N_1^{\,2}+E_1^{\,2}\cdot(Eff_1^{\,2}+Eff_2^{\,2})}{Eff_1^{\,2}}}$$ $$\frac{u(A)}{A}=\sqrt{\left(\frac{u(E)}{E}\right)^2+\left(\frac{u(Eff)}{Eff}\right)^2+\left(\frac{u(CY)}{CY}\right)^2}$$
MDA	$$MDA=\frac{4.66\times\sqrt{N/t}}{60\times Eff\times CY}\times DF$$

GLOSSARY	
SUBJETC	**DESCRIPTION**
CY	Chemical yield of the procedure
m_F	weight of $Sr(NO_3)_2$ obtained in the final solution (g)
m_I	weight of $Sr(NO_3)_2$ added to the initial solution (g)
DF	Dilution factor
Eff	Efficiency
$N(t_1)/N_1$	Net count Rate in the first counting
$N(t_2)/N_2$	Net count Rate in the second counting
λ_{Y90}	0.0108
λ_{Sr89}	$5.55*10^{-4}$
t_1	hours from the radiochemical separation up to the first counting
t_2	hours from the radiochemical separation up to the second counting

References

3.3. Procedures from Lab #8C CEA-LARC

3.3.1. TITLE: Mineralisation of i-grafite

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
CW Reference	CWAP-8C-1
Scope & Range of Application	The procedure is used for the mineralisation of i-graphite by acid wet process with recovery of the elements and radionuclides volatile for radiochemical analysis.
Principle	About 1 to 2 g of powder i-graphite is placed in a digestion vessel. Concentrated sulphuric acid are carefully added and head at refluxed during 6H. After cooling, $HClO_4$ was introduced in the digestion vessel to made oxidation into CO_2 of the graphite. During this step additional nitric acid or H_2O_2 solution can be made to accelerate/finish the dissolution.
Instrumentation	• Open microwave digester • Usual glass and pipet of laboratory • Balance
Reagent	• Water purified (18 mohm;cm) • Nitric acid • Perchlorohydric acid ($HClO_4$) • Sulfuric acid ($H2SO_4$) • H_2O_2 solution •
Scheme	

OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Separation Method	Step 1.	All the digestion vessels must be cleaned before use
	Step 2.	Carry out the assembly following the scheme
	Step 3.	Check the vacuum pump, the cooling…
	Step 4	Introduced the sulphuric acid (50 ml/g of graphite) and after the graphite Heat during 6 Hours
	Step 5	After cooling add the perchloric acid (30 ml/ g of graphite) After reaction an heating (115°C) must be done to accelerate the oxidation
	Step 6	If still graphite in solution add carefully H2O2 or HNO3 solution to achieve the dissolution
	Step 7	The alkaline solutions in the washing bottles are combined in a 250 cm^3 beaker The acid solutions in the washing bottle and in the digestion vessel are combined in a 250 ml breaker All the digestion vessels must be rinsed with acid or alkaline solution
	Sept 8	Volume the acid and base phase to have the rate of digestion
Remarks		Due to the corrosive atmosphere produced in the reactor, the connections employed in the digestion system have to be acid resistant in order to avoid losses of the gases produced and all the mineralisation system must be in depression (assured by the vacuum pump) If analyse of 14C contain

References

CEA LARC MO 037

3.3.2. TITLE: Determination of Nickel 63 from dissolved i-graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
CW Reference	CWAP-8C-2
Scope & Range of Application	The procedure is used in the determination of ^{63}Ni in solutions coming from the mineralization of irradiated graphite
Principle	The procedure is performed on an aliquots provided from the solution obtained after mineralization of graphite. The procedure to analyse ^{63}Ni is based on the formation of Nickel-Dimethylglyoxime complex at pH under 8 up to 10 after adding a stable tracer and it's extraction on chloroform solvent. The ^{63}Ni is measured by liquid scintillation through an ultra low background noise analyser. The counting time is 3600 seconds. The chemical efficiency is approximately 85 %.
Instrumentation	pH meter Liquid Scintillation Analyzer Ge-HP
Reagent	Water purified (18 mohm;cm) Chloroform ($CHCl_3$) Dimethylglyoxime(C4H8N2O2) PA Standard solution for pH meter calibration Solution of sodium citrate (100mg/l) freshly prepared Nitric acid Chlorohydric acid (HCL) Ammonium solution Certified solution of Ni carrier

OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Separation Method	Step 1.	Addition of known amounts of stable Ni as carrier (after having checking the concentration of the sample)
	Step 2.	Adjust to pH=5 by adding ammoniac solution
	Step 3.	Add 5 ml of solution of citrate sodium
	Step 4.	Adjust th pH=8,5 by adding ammoniac solution under agitation
	Step 5	Add 2 ml of dimethylglyoxime solution and shake the solution

	Step 6	Add 3ml of Chloroform ($CHCl_3$) - shake the solution 5 minutes Extract the organic layer Repeat this step 4 time gather together the organic layer Eliminate the aqueous phase (contain the others gamma/beta emitters)
	Step 7	Wash by 5 ml of ammoniac solution the organic layer Repeat twice
	Sept 8	Back extraction of Ni using 5 ml of HCl 1Mol/l Repeat twice gather together the HCl 1M layer Check by gamma measurement the selectivity of the chemical separation before sampling the solution for scintillation liquid measurement and chemical yield
Flow chart	Sampling+1 ml of Ni solution at 100mg/l Adjusting at pH5 with ammoniac Adding 5 ml of Na citrate Adjusting at pH 8.5 under agitation by adding ammoniac Adding of Diméthylglyoxime (Keep in contact 10mn) Extraction 4 times by 3 ml of chloroform (organic layer) Wash the organic layer by 5 ml of ammoniac solution(0,3mol/l) Desextraction of Ni with HCl solution	
Chemical Yield	The solution obtained at the end of the separation procedure is analysed by AAS ou ICP/AES to determine the Ni yield	
Calibration	The efficiency curve is realized and calculated with a ^{63}Ni reference standards .	
Measurement geometry	Solution were prepared in the same geometry and ratio aqueous phase/liquid scintillation cocktail as the calibration curve	

References:

- CEA LARC MA 0054 -CETAMA-374

3.3.3. TITLE: Determination of chlore36 in i-graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
CW Reference	CWAP-8C-3
Scope & Range of Application	Description of a method of separation and measurement of chlorine 36 by liquid scintillation in irradiated graphite after mineralization in bomb of Parr. Application on 0,5 g of graphite Detection limit is 0,2 Bq/g
Principle	About 0,5g of the graphite powder sample is introduced into a little quartz vessel. For the determination of the chemical yield, $CoCl_2$ is added and mixed to the graphite powder. Then, mineralisation is carried out under pressure in a closed system and the halogen is trapped into a solution. This solution is purified through the formation of AgCl induced by adding silver nitrate. The solid phase is then dissolved and a chromatographic extraction step is performed in order to purify the ^{36}Cl solution. The solution obtained at the end of the separation procedure is analysed by anion chromatography to determine the Cl yield and the ^{36}Cl is determined by liquid scintillation counting. Quenching is corrected by referring to a quenching calibration curve realized in the same sample geometry and the same counting scintillation cocktail**.**
Instrumentation	• Liquid Scintillation Analyzer • Ionic chromatography for chemical yield • Usual glass and pipet of laboratory • Chromatographic column out of glass (10 X 0.5 cm) • Peristaltic pump • Balance • System of mineralization IKA AOD1 • Centrifugal machine -
Reagent	• (1) Acid nitric 7 M • (2) Silver nitrate • (3) Sodium thiosulfate • (4) Ultrapure water presenting a content chlorides lower than 0,1 µg/l. • (5) Cobalt chloride (CoCl2, 6:2 O).

	• (6) Exchanging resin of anions Dowex 1X8 200-400 Mesh (7) Chlorine 36 standard solution

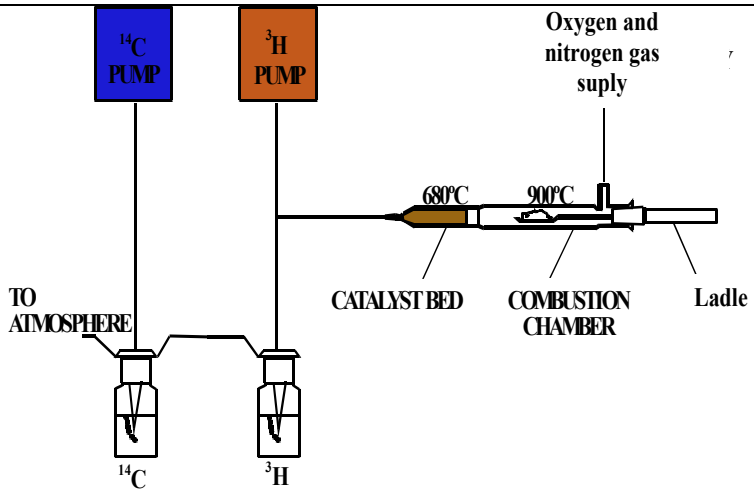
OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Separation Method	Step 1. Mineralization	**Sample preparation** In a crucible for mineralization (quartz) 1°) Weigh exactly approximately 500 mg of irradiated graphite 2°) add exactly 25 mg of $CoCl_2$ ($6H_2O$) as chemical tracer. **Solution in decomposition vessel** Add 10 ml of HNO3 0.1 M to the decomposition vessel **Mineralization** Carry out the mineralization following the operating instructions for decomposition vessel AOD 1.1 **After mineralization** The decomposition vessel must be vented following the operating instructions for decomposition vessel AOD 1.1 Open the decomposition vessel and check the crucible and decomposition vessel wall for signs of incomplete combustion. If you find evidence of incomplete combustion, reject the results of that test, and repeat it. Transfer the absorption solution carefully to a flask adapted to centrifugation with distilled water. All components of the decomposition vessel must be thoroughly rinsed
	Step 2. Chemical separation by precipitation	Add 1 ml ofHNO3 7 M Add 1.5 ml of AgNO3 0.2 M (8). Check the solution (minimum 1/4 hours). Wait the precipitation of AgCl (1 hours) Centrifuge 5 min Eliminate the surnageant Wash the AgCl solid with 5 ml of water (twice)

		Dissolve the precipitate in 2 ml of $Na_2S_2O_3$ 0.2 Mol/l
	Step 3. chromatographic extraction	Prepare à column with 4 cm of resin DOWEX 1×8 200-400 Mesh (6) Equilibrate with $Na_2S_2O_3$ # 0.2 M Regulate the flow at 1ml/min using a peristaltic pump. – Wash the column with 30ml of $Na_2S_2O_3$ 0.2M Load sample (the solution of dissolved AgCl) and rinse the column with 20 mL of $Na_2S_2O_3$0.2 M Eliminate the 5 first ml (corresponding to the dead volume of the chromatographic system) Recover the chlorine fraction in a 15 ml following in a graduated tube. (around 12-15 ml) Homogenize this solution before sampling for liquid scintillation measurement and chemical yield.
Chemical Yield	The solution obtained at the end of the separation procedure is analysed by ionic chromatography to determine the Cl yield	
Calibration	The efficiency curve is realized and calculated with a ^{36}Cl standard solution.	
Measurement geometry	Solutions were prepared in the same geometry and ratio aqueous phase/liquid scintillation cocktail as the calibration curve.	

References :

- CEA LARC MA 040
- Brevet FR2940470B1

3.3.4. TITLE: Determination of 14C in i-graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
CW Reference	CWAP-8C-4
Scope & Range of Application	The procedure is used in the determination of ^{14}C directly in the samples of graphite, without pre-treatment by thermal combustion of the graphite.
Principle	A complete combustion of the sample is carried out under oxygen current in a furnace at a temperature about 900°C. The produced gases are treated in an oven with catalyst (Pt and CuO catalyst) in order to make sure of the total conversion of carbon in form CO_2 before trapping in a liquid scintillating specific to the ^{14}C. The device used also makes it possible to make sure of the separation of the ^{3}H in a vial before that of recovery of carbon-14. Metals, salts, oxides with very high melting points stay in the combustion ladle.
Instrumentation	• Liquid Scintillation Analyzer • Harvey OX-500 Biological Material Oxidizer • Usual glass and pipet of laboratory • Balance
	
Reagent	• (1) Carbon 14 standard solution • (2) Scintillation liquid for carbon (Zinsser analytical Oxysolve C400) • (3) Scintillation liquid for 3H (Zinsser analytical Oxysolve-T)

OPERATING PROCEDURE	
SUBJETC	**DESCRIPTION**

Separation Method	Setp 1	**Determination of the chemical Yield** Burning and trapping of standards of ^{3}H and ^{14}C at 900º C For cheeking the combustion yield
	Step 2	**Combustion of graphite sample** Introduce the sample in the combustion boat (around 20 to 25 mg) Put the combustion boat in the ladle and introduced in the oven Start the burning
	Step 3	Burring 5 times (4 min per burning)
	Step 4	Made a blank of the system (empty boat)
	Step 5	Next sample
	Step 6	Control the chemical yield after 5 sample
Chemical Yield	To determine the chemical yield, combustion of ^{14}C standard solution mixed in virgin graphite powder is made, the chemical yield was determined after measuring the vial by liquid scintillation by comparison to the theoretical value. Same procedure is applied with ^{3}H standard to estimate the rejection of ^{3}H in the vial for 14C measurement (selectivity) and to check the chemical yield for 3H.	
Calibration	The efficiency curve is realized and calculated with a ^{14}Cstandard solution.	
Measurement geometry	Solutions are prepared directly (mixed of CO2 gas and scintillated liquid) to be measured in the liquid scintillation counter	

References

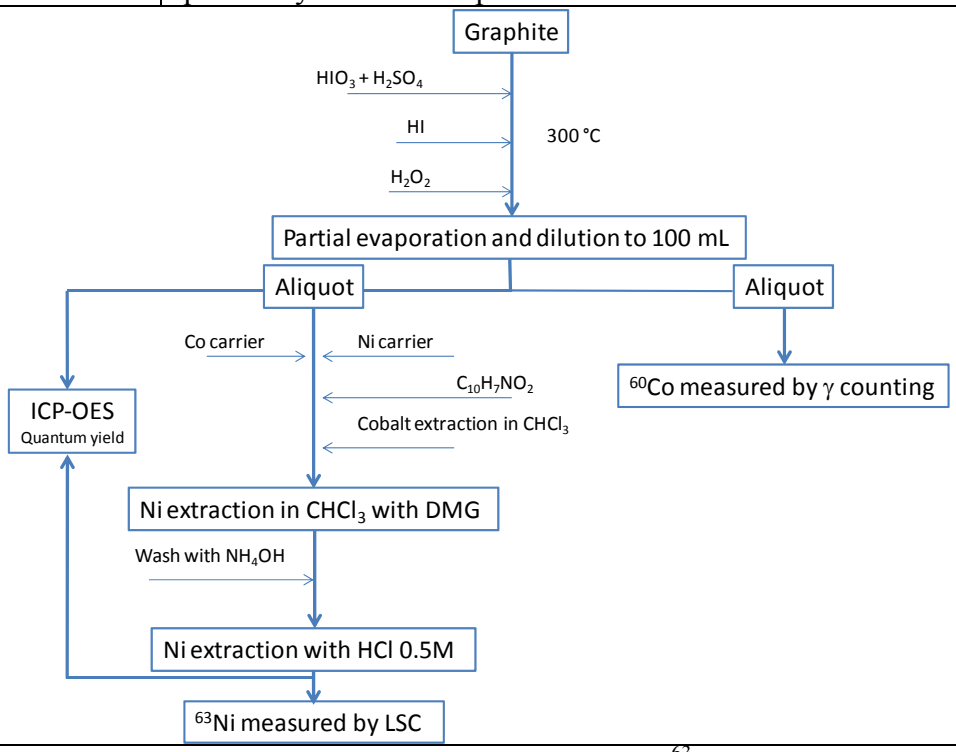
- CEA LARC MA 001 –CETAMA 377

3.4. Procedures from Lab #8S CEA-SACLAY

3.4.1. TITLE: Determination of nickel-63 and cobalt-60 from dissolved i-graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
CW Reference	CWAP-8S-1
Scope & Range of Application	The procedure is used in the determination of ^{63}Ni and ^{60}Co in solutions coming from the mineralization of irradiated graphite.
Principle	The procedure is performed in aliquots from the solution obtained after acid attack (H_2SO_4/HIO_3). From this solution, one aliquot is taken to measure directly ^{60}Co by gamma spectrometry. Another aliquot is used to analyse ^{63}Ni by a selective extraction of the complex nickel-dimethylglyoxime after cobalt elimination. ^{63}Ni is determined by the measurement of its beta emission by liquid scintillation counting. The chemical yield is determined by ICP-OES.
Instrumentation	• Liquid Scintillation Analyzer Tri-Carb A2900 TR • ICP-OES Jobin Yvon ACTIVA M. • GC 3018 Canberra

OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Separation Method	Step 1.	Addition of known amounts of stable cobalt and nickel as carrier.
	Step 2a.	Mineralization of the graphite with stable nickel and cobalt Oxidation of graphite into CO_2 on hotplate at 300°C
		$4H^+ + 4IO_3^- + 5C \rightarrow 2I_{2(g)} + 2H_2O + 5CO_{2(g)}$
		Reduction of iodate in excess on hotplate
		$6H^+ + IO_3^- + 5I^- \rightarrow 3I_{2(g)} + 3H_2O$
		Oxidation of residual iohydric acid on hotplate
		$2HI + H_2O_2 \rightarrow I_{2(g)} + 2H_2O$
		Partial evaporation of H_2SO_4 and dilution to 100 mL
	Step 2b	Aliquot is measured by ICP-OES to obtain initial nickel concentration.
	Step 2c	Aliquot is measured by gamma spectrometry to determine ^{60}Co
	Step 3.	Aliquot is taken and oxidation and extraction of Cobalt in

		organic phase is performed
		$2Co^{2+} + 2H^{+} + H_2O_2 \leftrightarrows 2Co^{3+} + 2H_2O$ $Co^{3+} + 2H_2O + 3C_{10}H_7NO_{2(org)} \rightarrow Co(C_{10}H_6NO_2)_3.2H_2O_{(org)} + 3H^{+}$
	Step 4.	Extraction of nickel in organic phase with dimethylglyoxime.
		$Ni^{2+} + C_4H_8N_2O_{2(org)} \rightarrow Ni(C_4H_6N_2O_2)_{(org)} + 2H^{+}$
	Step 5.	Organic Phase wash with NH_4OH
	Step 6.	Re extraction of nickel in aqueous phase with HCl 0.5M
	Step 7.	Measurement of ^{63}Ni by LSC and total nickel by ICP-OES for quantum yield of the separation.
Flow chart		
Chemical Yield	Natural nickel is added to aliquot used for ^{63}Ni determination after mineralization. An aliquot of the mineralization solution is measured by ICP-OES in order to determine the nickel concentration before separation. Quantum yield is calculated by ratio of the nickel concentration measured before and after separation.	
Calibration	The efficiency is calculated with quenching curves established with ^{63}Ni reference standard. To perform these quenching curves, ten vials containing the same activity of ^{63}Ni are prepared. Then, the scintillation cocktail, Ultimagold LLT is added to each vial and finally, before counting CCl_4 is added in increasing amounts.	

Measurement geometry	First, it is prepared a vial with a blank sample that contains 5 ml of 0.5M HCl and 15 ml of liquid scintillation cocktail Ultimagold LLT. Then, two vials are prepared with 5 mL of the final solution with 15 mL of liquid scintillation cocktail Ultimagold LLT.

EXPRESION OF MEASUREMENT RESULTS	
SUBJETC	**DESCRIPTION**
Chemical Yield	Chemical Yield for ^{63}Ni determination : $CY = \frac{C_{Ni} \times V_{sep}}{m_{Niaj} + m_{Niech}}$
Activity	**For ^{63}Ni activity :** $A_{Ni} = A_m \times \frac{F_d \times V_{sep} \times V_{\min}}{pe_{mesni} \times pe_{\min} \times CY \times pe_{sep}}$ $A_m = \frac{CPM_{Ni} - CPM_{blk}}{eff_{Ni} \times 60}$ **For ^{60}Co activity :** $A_{Co} = A \times \frac{F_d \times V_{\min}}{pe_{mesco} \times pe_{\min}}$
Efficiency	$eff_{Ni} = \frac{N_{rs}}{A_{rs}}$
Uncertainty	**Uncertainty on chemical yield u_{CY}** $u_{CY} = \sqrt{u^2_{C_{Ni}} + u^2_{v_{sep}} + \left(\frac{m_{Niaj} \times u_{m_{Niaj}} + m_{Niech} \times u_{m_{Niech}}}{m_{Niaj} + m_{Niech}} \right)^2}$ With $u_{m_{Niech}} = \sqrt{u^2_{pe_{esep}} + u^2_{C_{Ni\,\min}} + u^2_{FD}}$ and $u_{m_{Niaj}} = 1\%$ **Uncertainty on counting rate u_{Am}** $u_{A_m} = \sqrt{\left(\frac{\sqrt{CPM_{Ni} + CPM_{blk}}}{(CPM_{Ni} - CPM_{blk}) \times \sqrt{\frac{tps}{60}}} \right)^2 + u^2_{eff_{Ni}}}$ **with** $u_{eff} = 1.5\%$ **Global uncertainty for a confidence level of 95% : U_{Ani}** $U_{A_{Ni}} = 2 \times \sqrt{u^2_{A_m} + u^2_{CY} + u^2_{FD} + u^2_{Vsep} + u^2_{v\,\min} + u^2_{pesep} + u^2_{pe\,\min} + u^2_{pemes}}$ For V_{sep}, V_{min}, pe_{min}, pe_{sep}, pe_{mes}, uncertainty is 1% if it is done by volumetric or 0.04/weight if it is done by weight For ^{60}Co determination :

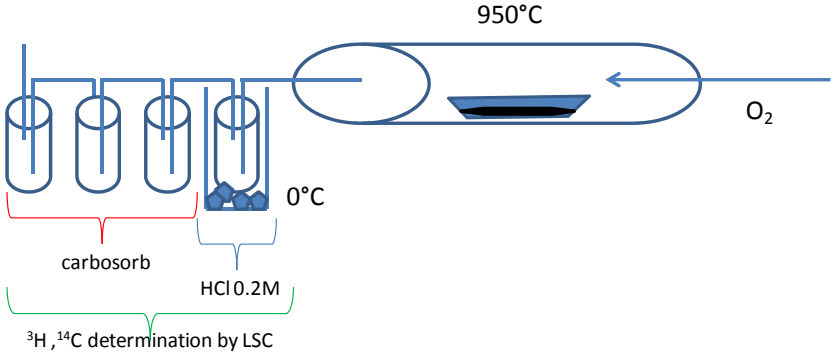
	$U_{A_{Co}} = 2 \times \sqrt{u_{A_m}^2 + u_{Fd}^2 + u_{v\min}^2 + u_{pe\min}^2 + u_{pemesco}^2}$
MDA	$LD = 4\left(1 + \sqrt{2 \times CPM_{Ni} \times tps/60 + 1}\right) \times \frac{Fd \times V_{sep} \times V_{\min}}{pe_{mes} \times pe_{\min} \times CY \times pe_{sep}}$

GLOSSARY	
SUBJETC	**DESCRIPTION**
CY	Chemical yield of the separation
C_{Ni}	Ni concentration after chemical separation (mg/L)
V_{sep}	Volume of the solution after chemical separation (L)
m_{Niaj}	Weight of Ni added to the initial solution (g)
m_{Niech}	Weight of Ni initially present in sample (g)
F_d	Dilution factor
A_m	Measured activity by LSC (Bq)
A	Measured activity by gamma spectrometry (Bq)
V_{min}	Volume of the solution after mineralization (L)
pe_{mes}	Sampling for LSC measurement (Ni) or for gamma counting (Co) (g)
pe_{sep}	Sampling for chemical separation (g)
pe_{min}	Sampling for mineralization (g)
CPM_{Ni}	Count rate for sample
CPM_{blk}	Count rate for blank
eff_{Ni}	Efficiency
N_{rs}	Activity of reference sample
A_{rs}	Net count rate of reference sample
Tps	Counting time (min)

References

3.4.2. TITLE: Determination of tritium and carbon-14 from i-graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
CW Reference	CWAP-8S-2
Scope & Range of Application	The procedure is used in the determination of ^{3}H and ^{14}C directly in the graphite sample without pre-treatment.
Principle	The procedure is based on the oxidation of any burnable material and conversion of the sample into gaseous state. The sample is burning at 950°C in an oxygen stream. Organic material is converted into carbon dioxide and steam. ^{3}H and ^{14}C is determined by the measurement of its beta emission by liquid scintillation counting.
Instrumentation	• Liquid Scintillation Analyzer Tri-Carb A2900 TR •

OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Separation Method	Step 1.	Oxidation of sample in a tube furnace at 950°C under an oxygen flow
	Step 2.	Trapping of ^{14}C in carbosorb and ^{3}H in HCl 0.2M
	Step 3.	Measurement of activity in ^{3}H and ^{14}C by liquid scintillation counting
Flow chart		
Chemical Yield	Chemical yield is verified periodically with reference material. Quantum yield obtained is 100% and this value is used in the calculation of the	

	activity of the sample.
Calibration	The efficiency is calculated with quenching curves established with both ^{3}H and ^{14}C.
Measurement geometry	Volumes in the trapped solutions are 5 mL each. 10 mL of Ultimagold LLT is added in each vial before counting by LSC. Before and after each sample, a blank is performed (empty porcelain vial in the oven).

EXPRESION OF MEASUREMENT RESULTS	
SUBJETC	**DESCRIPTION**
Chemical Yield	
Activity	$A = \sum A_i$ With $A_i = \frac{Fd \times (CPM_i - CPM_{blk})}{pe_{pyro} \times R \times eff \times 60}$
Efficiency	$eff = \frac{N_{rs}}{A_{rs}}$
Uncertainty	$u_{A_i} = 2 \times \sqrt{u_{Fd}^2 + u_R^2 + u_{CPM_i}^2 + u_{pe_{pyro}}^2 + u_{eff}^2}$ u_{Fd} = 1%, u_R = 3%, u_{pe} = 0.08/m if weight, 1% if volume, u_{eff} = 1.5% $u_{CPM_i} = \frac{100 \times \sqrt{CPM_i + CPM_{blk}}}{(CPM_i - CPM_{blk}) \times \sqrt{\frac{tps}{60}}}$ $u_A = \frac{\sum u_{A_i} \times A_i}{\sum A_i}$
MDA	$LD = Fd \times \frac{4(1 + \sqrt{2 \times CPM_{blk} \times \frac{tps}{60} + 1}}{pe_{pyro} \times R \times eff \times tps}$

GLOSSARY	
SUBJETC	**DESCRIPTION**
F_d	Dilution factor
A_i	Measured activity by LSC in bubbler i (Bq)

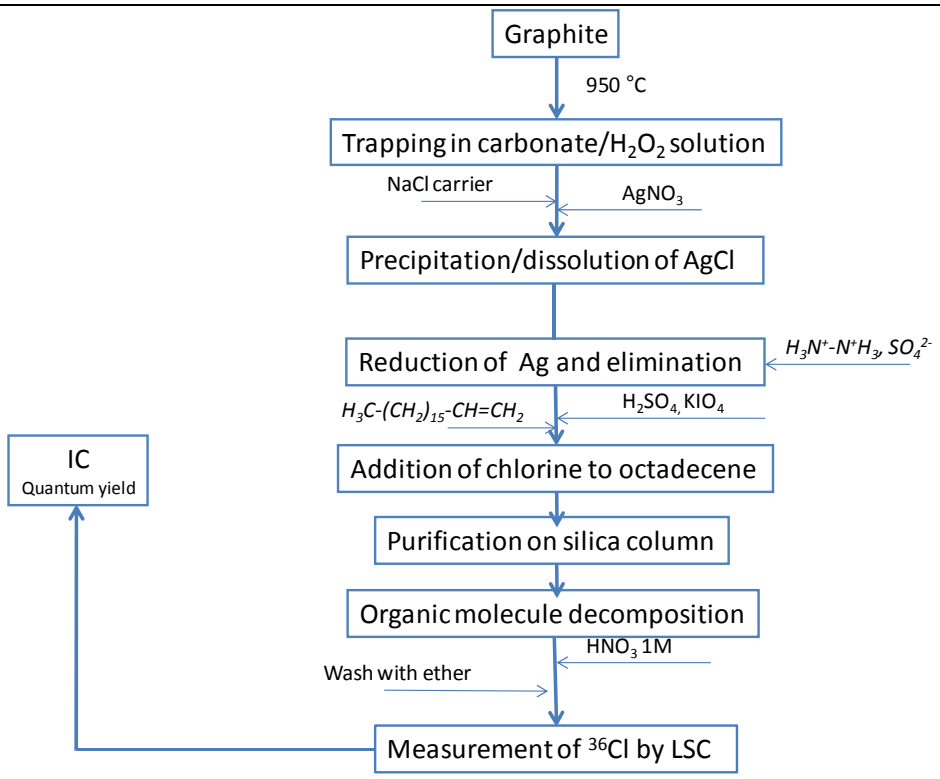
pe_{pyro}	Sampling for pyrolysis (g)
CPM_i	Count rate for bubbler i
CPM_{blk}	Count rate for blank
Eff	Efficiency
N_{rs}	Activity of reference sample
A_{rs}	Net count rate of reference sample
Tps	Counting time (min)
R	Oven yield

References

3.4.3. TITLE: Determination of chlorine-36 from i-graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
CW Reference	CWAP-8S-3
Scope & Range of Application	The procedure is used in the determination of ^{36}Cl in i-graphite sample
Principle	The procedure is based on the extraction of chlorine by oxidation of the sample into gaseous state. The sample is burning at 950°C in an oxygen stream. ^{36}Cl is trapped in a solution containing sodium carbonate/hydrogen peroxide/water. Specific radiochemical protocol is used to separate ^{36}Cl from others beta emitters. ^{36}Cl is determined by the measurement of its beta emission by liquid scintillation counting.
Instrumentation	• Liquid Scintillation Analyzer Tri-Carb A2900 TR • ICS 2000 Dionex

OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Separation Method	Step 1.	Oxidation of sample in a tube furnace at 950°C under an oxygen flow
	Step 2.	Trapping of ^{36}Cl in sodium carbonate/hydrogen/peroxide/water solution $Cl_{2(g)} + H_2O_2 + 2OH^- \rightarrow 2Cl^- + O_{2(g)} + 2H_2O$
	Step 3.	Precipitation of AgCl $AgNO_3 + Cl^- \rightarrow AgCl_{(s)} + NO_3^-$
	Step 4.	Dissolution of AgCl $(AgCl_{(s)} + H_2O + NH_{3(aq)} \rightarrow AgOH_{(aq)} + NH_4Cl)$
	Step 5	Ag reduction with hydrazinium sulphate and elimination by centrifugation $H_2N\text{-}NH_2 \rightarrow N_{2(g)} + 4H^+ + 4e^-$ et $Ag^+ + e^- \rightarrow Ag_{(s)}$
	Step 6	Oxidation of Chloride into Cl_2 with H_2SO_4 and KIO_4
		$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$ and $2Cl^- \rightarrow Cl_2 + 2e^-$
	Step 7	Formation of dichloro-octadecane $H_3C\text{-}(CH_2)_{15}\text{-}CH{=}CH_2 + Cl_2 \rightarrow H_3C\text{-}(CH_2)_{15}\text{-}CCl\text{-}CH_2Cl$
	Step 8	Purification on silica column
	Step 9	Isolation of chlorine in aqueous phase
	Step 10	^{36}Cl measurement by LSC

Flow chart	
Chemical Yield	Chemical yield is performed by measurement of chlorine concentration at the end of the separation procedure by ionic chromatography. For this, natural chlorine as NaCl is added to the solution obtained after pyrolysis of the sample. The tube and the porcelain plate are rinsed in order ensure a complete recovery of the total chlorine content in the sample.
Calibration	The efficiency is calculated with quenching curves established with ^{36}Cl reference standard. To perform these quenching curves, ten vials containing the same activity of ^{36}Cl are prepared. Then, the scintillation cocktail, Ultimagold LLT is added to each vial and finally, before counting CCl_4 is added in increasing amounts.
Measurement geometry	A blank sample is prepared. It consists in a solution of $NaNO_3$ 2M. This solution is used to make the blank measurement in LSC.

EXPRESION OF MEASUREMENT RESULTS	
SUBJETC	**DESCRIPTION**
Chemical Yield	$CY = \frac{C_{Cl} \times V_{sep}}{m_{Claj}}$
Activity	$A_{Cl} = A_m \times \frac{V_{sep} \times V_{\min}}{pe_{mes} \times pe_{\min} \times CY \times pe_{sep}}$

	$A_m = \frac{CPM_{Cl} - CPM_{blk}}{eff_{Cl} \times 60}$
Efficiency	$eff_{Cl} = \frac{N_{rs}}{A_{rs}}$
Uncertainty	**Uncertainty on chemical yield u_{CY}** $u_{CY} = \sqrt{u_{C_{Cl}}^2 + u_{v_{sep}}^2}$ **Uncertainty on counting rate u_{Am}** $u_{A_m} = \sqrt{\left(\frac{\sqrt{CPM_{Cl} + CPM_{blk}}}{(CPM_{Cl} - CPM_{blk}) \times \sqrt{\frac{tps}{60}}}\right)^2 + u_{eff_{Ni}}^2}$ **with** $u_{eff} = 1.5\%$ **Global uncertainty for a confidence level of 95% : U_{Ani}** $U_{A_{Cl}} = 2 \times \sqrt{u_{A_m}^2 + u_{CY}^2 + u_{Vsep}^2 + u_{v\min}^2 + u_{pesep}^2 + u_{pe\min}^2 + u_{pemes}^2}$ For V_{sep}, V_{min}, pe_{min}, pe_{sep}, pe_{mes}, uncertainty is 1% if it is done by volumetric or 0.04/weight if it is done by weight
MDA	$LD = 4\left(1 + \sqrt{2 \times CPM_{Cl} \times tps/60 + 1}\right) \times \frac{Fd \times V_{sep} \times V_{\min}}{pe_{mes} \times pe_{\min} \times CY \times pe_{sep}}$

GLOSSARY	
SUBJETC	**DESCRIPTION**
CY	Chemical yield of the separation
C_{Cl}	Cl concentration after chemical separation (mg/L)
V_{sep}	Volume of the solution after chemical separation (L)
m_{Claj}	Weight of Ni added to the initial solution (g)
A_m	Measured activity by LSC (Bq)
V_{min}	Volume of the solution after mineralization (L)
pe_{mes}	Sampling for LSC measurement (g)
pe_{sep}	Sampling for chemical separation (g)
pe_{min}	Sampling for mineralization (g)
CPM_{Cl}	Count rate for sample
CPM_{blk}	Count rate for blank
eff_{cl}	Efficiency
Tps	Counting time (min)

A_{rs}	Activity of reference sample
N_{rs}	Net count rate for reference sample

References

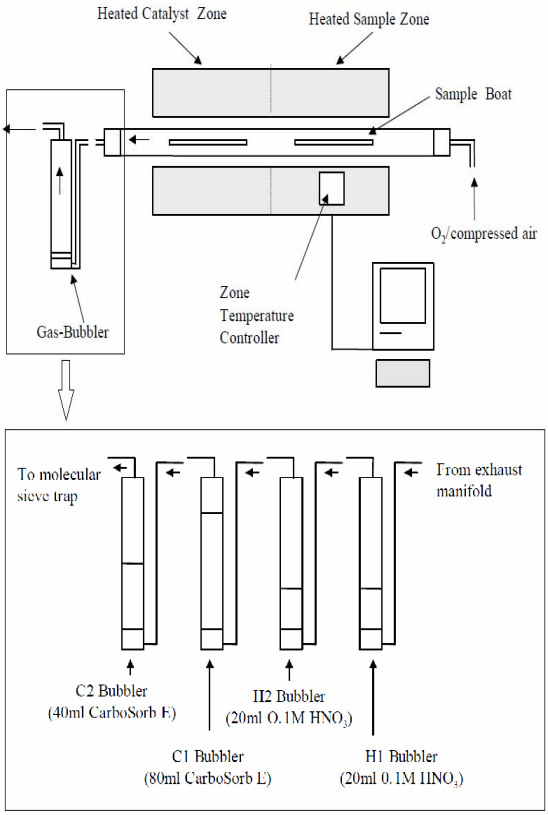
C. Frechou, J. P. Degros, J. Radioanal. Nucl. Chem., 263, 2005, 333.

3.5. Procedures from Lab #12 ENEA

3.5.1. TITLE: Determination of Tritium and carbon-14 from i-graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
Reference	CWAP-12-1
Scope & Range of Application	The procedure is used in the determination of ^{3}H and ^{14}C directly in the samples of graphite, without pre-treatment.
Principle	The technique involves the controlled combustion of a sample in air or oxygen to convert all the carbon and hydrogen species to carbon-dioxide gas and water vapour which are then selectively trapped. The water vapour (T_2O) is trapped through adsorption in 0.1M nitric acid contained in a gas bubbler. The ^{14}C is extracted by bubbling the carbon dioxide gas through an alkaline liquid trapping agent such as Carbosorb-E (ethanolamine). In order to ensure complete conversion of all thermal decomposition products produced by the sample combustion, the combustion products are swept over a catalyst such as copper oxide heated to a temperature of 850°C. Finally the carbon-14 or tritium content of the trapping medium is assessed by liquid scintillation counting, hence, with knowledge of the analytical recovery, ascertained through the controlled combustion, the ^{14}C and/or ^{3}H content of the sample can be assessed.
Instrumentation	• Carbolite-AEA Technology Combustion Furnace • Liquid Scintillation Analyser TDCR HIDEX 300 SL

OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Separation Method	Step 1.	Burning and trapping of standards of ^{3}H and ^{14}C at 850º C for 6 hours, for yields calculation
	Step 2.	Three replicates for each i-graphite sample of about 100 mg
	Step 3.	3 Blank burning
	Step 4.	Next sample: goto step 2

Flow chart	
Chemical Yield	To determine the chemical yield, a sample of virgin graphite has been spiked with a known quantity of ^{3}H standard. This sample has been then oxidised in the combustion furnace following the same combustion procedure yet described. The same procedure has been applied for ^{14}C chemical yield determination.
Calibration	The Hidex 300SL is a commercial liquid scintillation analyser based on the Triple to Double Coincidence Ratio counting method (TDCR). For pure beta-emitting radionuclides the ratio of triple to double (all) coincidences is directly proportional to the overall efficiency. The proportional factor is 1 (±15%). Hence, in TDCR the quench level is automatically included in the ratio of the triple to double coincidences (as different from systems with 2 PMT's at 180° facing the sample). Therefore, measuring TDCR enables the determination of activities for pure beta-emitting radionuclides with high accuracy and the level of

	quench is directly taken into account by TDCR. So the TDCR does not require an external source and does not require a vial of known activity, therefore it is an "absolute" measurement when constant quench is experienced. The TDCR value can also be used as an indicator of quench in standards and, in case of variable quench samples, a Double-label counting with external standard is performed.
Measurement geometry	The samples are directly ready from the Oxidizer to be measured by liquid scintillation counting.

EXPRESSION OF MEASUREMENT RESULTS	
SUBJETC	**DESCRIPTION**
Chemical Yield	$CY = \frac{\text{dpm}_{\text{Combustion}}}{\text{dpm}_{\text{direct}}}$
Activity	The activity of ^{3}H and/or ^{14}C is calculated in Bq per volume or mass of the original sample. The formula for the calculation is: $A = \frac{dpm_{sample} - dpm_{backgound}}{CY \times W}$ $dpm_{sample} = \frac{[(dpm_1 \times T_1) + (dpm_2 \times T_2)]}{60}$
Efficiency	The Hidex 300SL is a commercial liquid scintillation analyser based on the Triple to Double Coincidence Ratio counting method (TDCR). For pure beta-emitting radionuclides the ratio of triple to double (all) coincidences is directly proportional to the overall efficiency. The proportional factor is 1 (±15%). Hence, in TDCR the quench level is automatically included in the ratio of the triple to double coincidences (as different from systems with 2 PMT's at 180° facing the sample). Therefore, measuring TDCR enables the determination of activities for pure beta-emitting radionuclides with high accuracy and the level of quench is directly taken care of by TDCR. So the TDCR does not require an external source and does not require a vial of known activity, therefore it is an "absolute" measurement when constant quench is experienced. The TDCR value can also be used as an indicator of quench in standards and, in case of variable quench samples, a Double-label counting with external standard is performed.

Uncertainty	Identification of uncertainty sources: ♦ W: • u from mass determination ♦ CY: • σ from counting of ^{3}H or ^{14}C standard direct measurement (dpm_{direct}) • σ from counting of ^{3}H or ^{14}C standard after combustion ($dpm_{combustion}$) ♦ N: u from net dpm (N) from the equation: **N**= dpm_{sample}-$dpm_{background}$ if single measurement is done, absolute uncertainty is obtained by propagation of absolute uncertainties from sample and background measurements. $$\sigma(N) = \sqrt{u^2_{dpm_{sample}} + u^2_{dpm_{background}}}$$ Quasi-variance if n replicants are calculated: $$\sigma(sample) = \sqrt{\frac{\sum (dpm_{sample} - \overline{dpm_{sample}})^2}{n-1}};$$ $$\sigma(B) = \sqrt{\frac{\sum (dpm_{background} - \overline{dpm_{background}})^2}{n-1}};$$ $$\sigma(N) = \sqrt{\sigma(sample)^2 + \sigma(B)^2}$$ **Note:** Uncertainty regarding efficiency is taking into account directly into uncertainty of dpm given by the equipment. Expression of activity uncertainty in relative terms is given by: $$\frac{U(A)}{A} = \sqrt{\left(\frac{\sigma(N)}{N}\right)^2 + \left(\frac{u(CY)}{CY}\right)^2 + \left(\frac{u(W)}{W}\right)^2}$$ where: $$\frac{u(W)}{W} = \sqrt{\left(\frac{u(m_{al})}{m_{al}}\right)^2} \quad \frac{u(CY)}{CY} = \sqrt{\left(\frac{\sigma(dpm_{combustion})}{dpm_{combustion}}\right)^2 + \left(\frac{\sigma(dpm_{direct})}{dpm_{direct}}\right)^2}$$

	The established coverage factor (**k**) is 2 for a confidence level of 95 % given the result expression: $A \pm 2 \cdot U(A)$
MDA	The minimum detectable activity is calculated according to the Currie equation shown in the equation: $MDA = \frac{4.66 \times \sqrt{cpm_{background} / t}}{60 \times W} \times \frac{cpm_{background}}{dpm_{background}}$

GLOSSARY	
SUBJETC	**DESCRIPTION**
CY	Chemical yield of the procedure
$dpm_{Combustion}$	dpm obtained in the measured of the standard sample oxidised
dpm_{direct}	dpm obtained in the direct measured of the standard sample
dpm_{sample}	Average activity of sample
$dpm_{background}$	Average activity of background (blank)
$cpm_{background}$	Average count rate of background (blank)
W	Mass of the aliquot taken
T_1	Fraction between mass of the 1st bubbling bottle and the volume taken for the measure
T_2	Fraction between mass of the 2st bubbling bottle and the volume taken for the measure

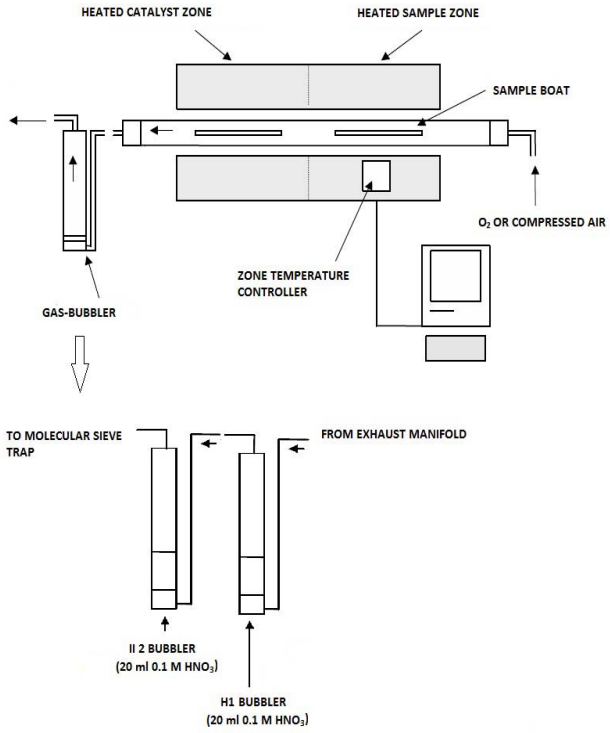
References

[7]. D.A. Wickenden, “Analysis of Tritium and Carbon-14 in Combustible Materials using the Carbolite/AEA Technology Combustion Furnace and associated apparatus”, Process Manual Carbolite, Barloworld Scientific, MF38PR, 20 September 2002.
[8]. L.A. Currie, "Limits o Qualitative Detection and Quantitative Determination", Analytical Chemistry, 40. 1968

3.5.2. TITLE: Determination of chlorine-36 from i-graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
Reference	CWAP-12-2
Scope & Range of Application	The procedure is used in the determination of ^{36}Cl in i-graphite samples without pre-treatment.
Principle	The actual method used for CARBOWASTE Round Robin Test involves the controlled combustion in oxygen of a sample of graphite in a Carbolite Tubular Furnace. The ^{36}Cl is extracted by bubbling the Cl_2 gas through 0.1M HNO_3 solution trapping. In order to ensure complete conversion of all thermal decomposition products produced by the sample combustion, the combustion products are swept over a catalyst such as copper oxide heated to a temperature of 850°C. Measurement by LSC
Instrumentation	• Carbolite-AEA Technology Combustion Furnace • Liquid Scintillation Analyser TDCR HIDEX 300 SL

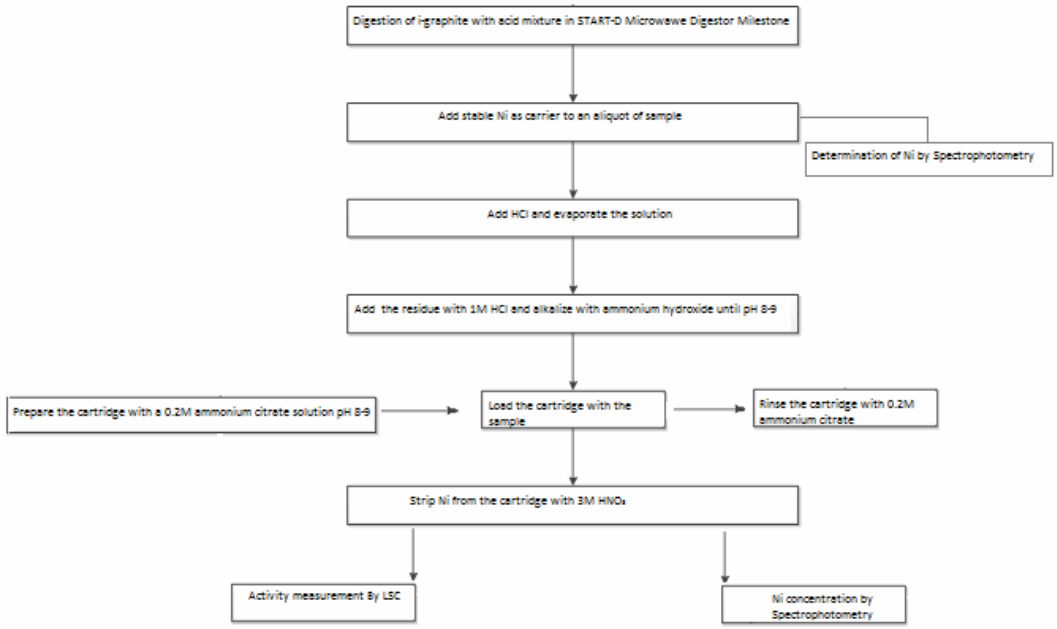
OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Separation Method	Step 1.	Burning and trapping of graphite samples with ^{36}Cl at 850º C for 6 hours, for yields calculation
	Step 2.	Three replicates for each i-graphite sample of about 100 mg
	Step 3.	3 Blank burning
	Step 4.	Next sample: goto step 2

Flow chart	
Chemical Yield	The chemical yield is calculated burning virgin graphite samples spiked with known amount of ^{36}Cl.
Measurement	^{36}Cl content of the trapping medium is assessed by liquid scintillation counting, hence, with knowledge of the analytical recovery, ascertained through the controlled combustion, the content of the sample can be assessed; beta emissions are measured by Liquid Scintillation Analyser TDCR HIDEX 300 SL: the added value of the TDCR is its purpose as an indicator of quench in standards and, in case of variable quench samples, a Double-label counting with external standard is performed to avoid tritium interferences.

3.5.3. TITLE: Determination of nickel-63 from i-graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
Reference	CWAP-12-3
Scope & Range of Application	The procedure describes a method for the measurement of ^{63}Ni in i-graphite samples.
Principle	^{63}Ni is precipitated as a ^{63}Ni/DMG complex on Eichrom (or similar) Nickel Resin cartridges from an acid solution of Microwave assisted digested i-graphite samples. The ^{63}Ni/DMG complex is then removed with 3M HNO_3. The strip solution is determined by liquid scintillation counting. The chemical yield is determined by ICP-OES or MS technique .
Instrumentation	• Liquid Scintillation Analyser TDCR HIDEX 300 SL • ICP-MS 7700x Agilent or ICP-OES Perkin Elmer

OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Separation Method	Step 1a.	Add 1 ml of stable nickel as carrier to an aliquot of 100 ml of mineralized solution sample.
	Step 1b.	An aliquot is measured by Spectrophotometry to obtain initial Ni concentration.
	Step 2.	Add 5 ml of concentrated HCl and evaporate to dryness.
	Step 3.	Dissolve the residue in 5 ml of 1M HCl
	Step 4.	Add 1 ml of 1M ammonium citrate to the sample and adjust to pH 8-9 with ammonium hydroxide.
	Step 5.	Pipet 5 ml of 0.2M ammonium citrate adjusted to pH 8-9 with ammonium hydroxide into the cartridge and discard eluent to waste.
	Step 6.	Load the sample on the Nickel cartridge. A red band will appear on the column. Discard the eluent to waste.
	Step 7.	Rinse the column with 20 ml of 0.2M ammonium citrate that have been adjusted to pH 8-9 with ammonium hydroxide. Discard eluent to waste.

	Step 8.	Strip Nickel from the column with a minimum amount of 3M HNO_3 required to completely dissolve and eluate the red band from the column.
	Step10a.	Aliquots are taken for Activity measurement by LSC
	Step10b.	Aliquot is taken for measuring final Ni concentration by Spectrophotometry.
Flow chart		
Chemical Yield	Nickel as carrier is added to the aliquot of the initial solution in order to determine the chemical yield by spectrophotometry ICP-MS or ICP-OES.	
Calibration	The Hidex 300SL is a commercial liquid scintillation analyser based on the Triple to Double Coincidence Ratio counting method (TDCR). For pure beta-emitting radionuclides the ratio of triple to double (all) coincidences is directly proportional to the overall efficiency. The proportional factor is 1 (±15%). Hence, in TDCR the quench level is automatically included in the ratio of the triple to double coincidences (as different from systems with 2 PMT's at 180° facing the sample). Therefore, measuring TDCR enables the determination of activities for pure beta-emitting radionuclides with high accuracy and the level of quench is directly taken care of by TDCR. So the TDCR does not require an external source and does not require a vial of known activity, therefore it is an "absolute" measurement when constant quench is experienced. The TDCR value can also be used as an indicator of quench in standards	

	and, in case of variable quench samples, a Double-label counting with external standard is performed.
Measurement geometry	The blank sample is prepared in a 20 ml vial with 2 ml of 0.2M HCl and 18 ml of liquid scintillation cocktail. Then, three vials are prepared containing each 2 ml of the final solution and 18 ml of liquid scintillation cocktail.

EXPRESSION OF MEASUREMENT RESULTS	
SUBJETC	**DESCRIPTION**
Chemical Yield	$CY = \frac{A_F}{A_I} \times F$
Activity	The activity of ^{63}Ni is calculated in Bq per volume or mass of the original sample. The formula for the calculation is: $A = \left(\frac{N/Eff}{60 \times CY} \right) \times DF$
Efficiency	The Hidex 300SL is a commercial liquid scintillation analyser based on the Triple to Double Coincidence Ratio counting method (TDCR). For pure beta-emitting radionuclides the ratio of triple to double (all) coincidences is directly proportional to the overall efficiency. The proportional factor is 1 (±15%). Hence, in TDCR the quench level is automatically included in the ratio of the triple to double coincidences (as different from systems with 2 PMT's at 180° facing the sample). Therefore, measuring TDCR enables the determination of activities for pure beta-emitting radionuclides with high accuracy and the level of quench is directly taken care of by TDCR. So the TDCR does not require an external source and does not require a vial of known activity, therefore it is an "absolute" measurement when constant quench is experienced. The TDCR value can also be used as an indicator of quench in standards and, in case of variable quench samples, a Double-label counting with external standard is performed.
Uncertainty	Identification of uncertainty sources: ♦ DF: • u from mass determination • u from volume of aliquots ♦ CY:

	• σ from counting of ^{63}Ni standard (N) • σ from counting of ^{63}Ni standard after separation (N') ♦ N: u from net count rate (N) from the equation: **N= R-B** where R is the sample count rate and B is the background count rate: • Poisson determination if single measurement if done $\sigma(N)=\sqrt{R/t+B/t}$ Quasi-variance if n replicates are calculated: • Quasi-variance if n repetitions are done: $\sigma=\sqrt{\frac{\sum(R-\overline{R})}{n-1}};\sigma_B=\sqrt{\frac{\sum(B-\overline{B})}{n-1}};\Rightarrow \quad \sigma(N)=\sqrt{\sigma(R)^2+\sigma(B)^2}$ Expression of activity uncertainty in relative terms is given by: $\frac{u(A)}{A}=\sqrt{\left(\frac{\sigma(N)}{N}\right)^2+\left(\frac{u(CY)}{CY}\right)^2+\left(\frac{u(DF)}{DF}\right)^2}$ where: $\frac{u(DF)}{DF}=\sqrt{\left(\frac{u(m_{al})}{m_{al}}\right)^2+\sum_i\left[\left(\frac{u(V_i)}{V_i}\right)^2\right]} \quad \frac{u(CY)}{CY}=\sqrt{\left(\frac{\sigma(A_F)}{A_F}\right)^2+\left(\frac{\sigma(A_I)}{A_I}\right)^2+\left(\frac{u(F)}{F}\right)^2}$ The established coverage factor (**k**) is 2 for a confidence level of 95 % given the result expression: $\mathbf{A\pm 2\cdot u(A)}$
MDA	The minimum detectable activity is calculated in Bq per volume or mass of the original sample: $\mathrm{MDA}=\frac{4.66\times\sqrt{N/t}}{60\times \mathrm{Eff}\times \mathrm{CY}}\times \mathrm{DF}$

GLOSSARY	
SUBJETC	**DESCRIPTION**
CY	Chemical yield of the procedure
A_F	Absorbance measured in the aliquot from the final solution
A_I	Absorbance measured in the aliquot from the initial solution
F	Factor of aliquot taken to the spectrophotometric analysis

Eff	Efficiency obtain from TDCR value
N	Net count Rate
DF	Dilution Factor
t	Measurement time

References

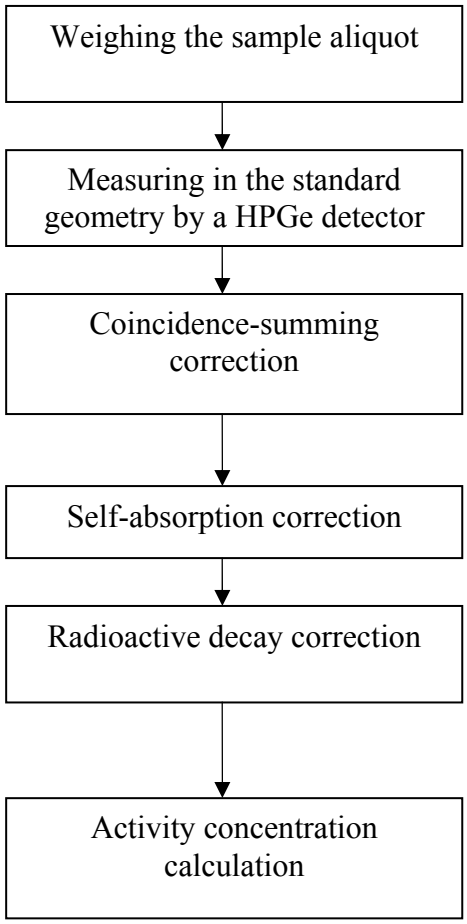
[1]. J. Lehto, X. Hou, “Chemistry and Analysis of Radionuclides”, Wiley-VCH, 2011.
[2]. Analytical Procedures, Eichrom Technologies Inc., February 25 2003.
[3]. L.A. Currie, "Limits o Qualitative Detection and Quantitative Determination", Analytical Chemistry, 40. 1968

3.6. Procedures from Lab #15 FTMC

3.6.1. TITLE: Determination of cobalt-60 from irradiated graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
CW Reference	CWAP-15-1
Scope & Range of Application	The procedure is used in the determination of ^{60}Co in irradiated graphite.
Principle	^{60}Co is determined by a non-destructive analysis method with the help of the gamma-ray spectrometry. An irradiated graphite sample is measured in the geometry for which the efficiency curve is determined. An apparent counting efficiency is corrected for the true coincidence-summing effect. Finally, the density correction is applied to get the precise value of ^{60}Co activity.
Instrumentation	• Gamma-ray spectrometer with a HPGe detector

OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Activity measurement method	Step 1.	An irradiated graphite sample aliquot is placed in the measuring container and weighed.
	Step 2.	A gamma-ray spectrum is acquired to reveal the presence of ^{60}Co and collect not less than 20,000 counts in each of the full energy absorption peaks at 1173.2 keV and 1332.5 keV.
	Step 3.	The counting efficiency obtained from the curve is corrected for the true coincidence-summing and the self-absorption effects, the activity is determined and corrected for the radioactive decay.
	Step 4.	The activity concentration is calculated.

Flow chart	
Coincidence-summing correction	The dependence of the counting efficiency on energy is assessed for the standard geometry using the set of nuclides in water matrix free of the coincidence-summing effect. The coincidence-summing correction factor is determined from calibrations using a reference standard solution of ^{60}Co.
Self-absorption correction	The counting efficiency obtained from calibrations is corrected for self-absorption in graphite matrix using the linear function constructed from responses covering the sample density range (0.4 – 1.7) g cm^{-3} (Gudelis et al., 2000).
Calculation of the activity concentration	The activity concentration of ^{60}Co in irradiate graphite is calculated as a ratio of the activity corrected for the radioactive decay at the reference date and the mass of aliquot of the original sample.

EXPRESSION OF MEASUREMENT RESULTS	
SUBJETC	**DESCRIPTION**
Counting efficiency	$\varepsilon = f(E_1, E_2, ..., E_n)$, where E_i (i=1, 2, ..., n) – energies of radionuclides free of the coincidence-summing effect. $\varepsilon_i = \frac{N_C}{t \times A_i \times \eta_i}$
Activity concentration	$C = \frac{N_{1332.5}}{t \times \varepsilon_{1332.5} \times m_0 \times \eta_{1332.5} \times F_c \times F_d}$
Coincidence-summing correction factor	$F_c = \frac{^{60Co}\varepsilon_{1332.5}}{\varepsilon_{1332.5}}$
Uncertainty	$\frac{u(A)}{A} = \sqrt{(\frac{u(N_{1332.5})}{N_{1332.5}})^2 + (\frac{u(\varepsilon_{1332.5})}{\varepsilon_{1332.5}})^2 + (\frac{u(\eta_{1332.5})}{\eta_{1332.5}})^2 + (\frac{u(F_c)}{F_c})^2 + (\frac{u(F_d)}{F_d})^2}$
Minimum detectable activity	$MDA = \frac{(2.71 + 4.65\sqrt{B})}{t \times \varepsilon_{1332.5} \times \eta_{1332.5} \times F_c \times F_d}$

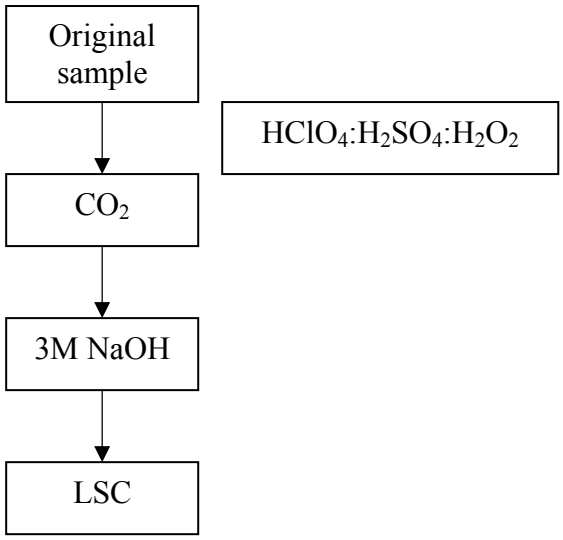
GLOSSARY	
SUBJETC	**DESCRIPTION**
ROI	Region of interest
HPGe	High purity germanium detector
MDA	Minimum detectable activity, Bq
$\eta_{1332.5}$	Emission probability of ^{60}Co at energy 1332.5 keV
η_i	Emission probabilities of radionuclides used for calibration
F_c	Coincidence-summing correction factor
F_d	Self-absorption correction factor
ε_i	Counting efficiency at the selected energy
m_0	Mass of a sample, g
C	Activity concentration, Bq g^{-1}
A_i	Activity of a reference standard solution, Bq
A	Activity of a sample, Bq
N_C	Number of net counts in the ROI when measuring a reference sample
$N_{1332.5}$	Number of net counts in the ROI when measuring a sample
B	Number of gross counts in the ROI when measuring background
t	Counting time, s

References

1. Gudelis, A., Remeikis, V., Plukis, A., Lukauskas, D. (2000) Efficiency calibration of HPGe detectors for measuring environmental samples. Environmental and Chemical Physics, 22, 3-4, 117-125.
2. Gudelis, A., Krivošein, K., Gvozdaitė, R., Druteikienė, R., Lukšienė, B., Lukoševičius, Š. (2009) Use of non-destructive and destructive analyses for radionuclide determination in aqueous samples from the Ignalina Nuclear Power Plant drainage system. In: Eikenberg, J., Jäggi, M., Beer, H., Baehrle, H., editors. LSC 2008, Advances in Liquid Scintillation Spectrometry. Tucson: Radiocarbon, p. p. 409-413.
3. Gudelis A., Druteikienė R., Lukšienė B., Gvozdaitė R., Nielsen S. P., Hou X., Mažeika J., Petrošius R. (2010) Assessing deposition levels of ^{55}Fe, ^{60}Co and ^{63}Ni in the Ignalina NPP environment. Journal of Environmental Radioactivity, 101, 6, 464–467.

3.6.2. TITLE: Determination of carbon-14 from irradiated graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
CW Reference	CWAP-15-2
Scope & Range of Application	The procedure is used in the determination of ^{14}C in irradiated graphite.
Principle	Radiocarbon is separated from the matrix in the form of $^{14}CO_2$, which reacts with 3M NaOH solution in two catches and forms Na_2CO_3. The liquid phase of sodium carbonate is measured by LSC.
Instrumentation	• Chemical separation system • Liquid scintillation counter Quantulus-1220

OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Separation Method	Step 1.	Sample destruction with strong reagents to form carbon dioxide.
	Step 2.	Reaction of carbon dioxide with sodium hydroxide to form $^{14}CO_3$.
Flow chart		
Chemical Yield	Using certified reference materials with ^{14}C the chemical yield of the procedure is determined as 94% for two catches filled with 3M NaOH.	

Calibration	The counting efficiency is calculated using a ^{14}C reference standard solution. The counting efficiency obtained is around 75% for usual quenching values analysed. The window settings optimised is: 100 - 500 channels.
Measurement geometry	The 4-mL samples are mixed with 16 mL of liquid scintillation cocktail OptiPhase HiSafe3 and measured by LSC.

EXPRESSION OF MEASUREMENT RESULTS	
SUBJETC	**DESCRIPTION**
Chemical yield	The chemical yield of 94% is determined for the procedure.
Activity concentration	$C = \frac{N_s - N_B}{60 \times \varepsilon_{^{14}C} \times m_0 \times \eta_{ch}} F_d$
Counting efficiency	$\varepsilon_{^{14}C} = \frac{N_C - N_b}{60 \times A_R}$
Uncertainty	$\frac{u(A)}{A} = \sqrt{(\frac{u(N)}{N})^2 + (\frac{u(\varepsilon_{^{14}C})}{\varepsilon_{^{14}C}})^2 + (\frac{u(\eta_{ch})}{\eta_{ch}})^2 + (\frac{u(F_d)}{F_d})^2}$
Minimum detectable activity	$MDA = \frac{(2.71 + 4.65\sqrt{B})}{t \times \varepsilon_{^{14}C} \times \eta_{ch}}$

GLOSSARY	
SUBJETC	**DESCRIPTION**
LSC	Liquid scintillation counting
MDA	Minimum detectable activity, Bq
η_{ch}	Chemical yield of the procedure
F_d	Dilution factor
$\varepsilon_{^{14}C}$	^{14}C counting efficiency
m_0	Mass of a sample, g
C	Activity concentration, Bq g^{-1}
A_R	Activity of a reference standard solution, Bq
A	Activity of a sample, Bq
N_S	Sample counting rate, cpm
N_B	Blank counting rate, cpm
N_C	Reference sample counting rate, cpm
N_b	Background counting rate, cpm
N	Number of counts when measuring a sample
B	Number of counts when measuring a blank

t	Blank counting time, s

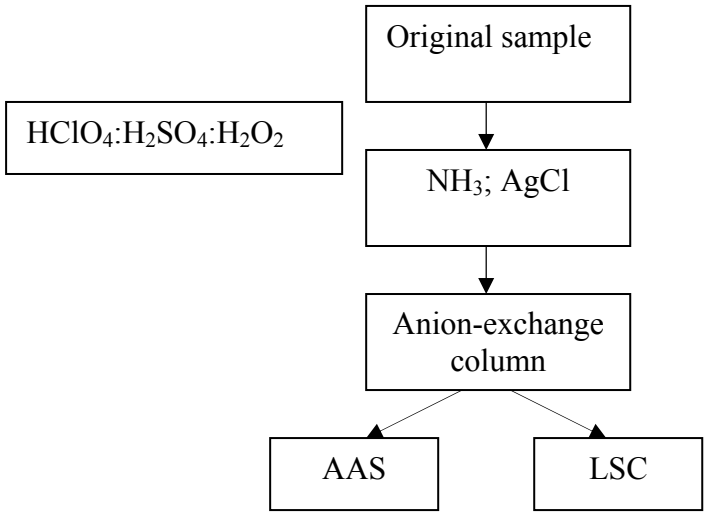
References

1. Gudelis, A., Gvozdaitė, R., Lukoševičius, Š. (2009) On determination of radiocarbon leakage from a shallow-land radioactive waste repository. In: Eikenberg, J., Jäggi, M., Beer, H., Baehrle, H., editors. LSC 2008, Advances in Liquid Scintillation Spectrometry. Tucson: Radiocarbon, p. p. 415-420.
2. Gudelis A., Gvozdaitė R., Kubarevičienė V., Druteikienė R., Lukoševičius Š., Šutas A. (2010) On radiocarbon and plutonium leakage to groundwater in the vicinity of a shallow-land radioactive waste repository. Journal of Environmental Radioactivity, 101, 6, 443–445.
3. Remeikis V., Plukis A., Plukienė R., Garbaras A., Barisevičiūtė R., Gudelis A., Gvozdaitė R., Duškesas G., Juodis L. (2010) Method based on isotope ratio mass spectrometry for evaluation of carbon activation in the reactor graphite. Nuclear Engineering and Design, 240, 10, 2697–2703.

3.6.3. TITLE: Determination of chlorine-36 from irradiated graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
CW Reference	CWAP-15-3
Scope & Range of Application	The procedure is used in the determination of ^{36}Cl in irradiated graphite.
Principle	Chlorine is released from the matrix using the destruction process with strong reagents. The following reaction with concentrated NH_3 leads to the formation of precipitate in the form of AgCl. Chlorine is separated by using the ion-exchange chromatography. ^{36}Cl activity is measured by LSC. Quantities of stable chlorine are controlled with the help of an atomic absorption spectrometer.
Instrumentation	• Chemical separation system • Liquid scintillation counter Quantulus-1220 • Atomic absorption spectrometer with a graphite atomizer (standard deviation 5-10%).

OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Separation Method	Step 1.	Addition of known amounts of stable chlorine as a carrier.
	Step 2.	Chlorine is released from the matrix in reactions with strong reagents.
	Step 3.	Chlorine precipitates in the form of AgCl after the reaction with NH_3.
	Step 4.	Chlorine is separated by adsorption on an anion-exchange column.

Flow chart	
Chemical Yield	The chemical yield of the procedure is determined with the help of AAS with grahite atomizer.
Calibration	The counting efficiency is calculated using a ^{36}Cl reference standard solution. The counting efficiency obtained is around 98% for usual quenching values analysed. The window settings optimised is: 100 - 950 channels.
Measurement geometry	The 2-mL samples are mixed with 16 mL of liquid scintillation cocktail OptiPhase HiSafe3 and measured by LSC.

EXPRESSION OF MEASUREMENT RESULTS	
SUBJETC	**DESCRIPTION**
Chemical yield	$\eta_{ch} = \frac{m_F}{m_I}$
Activity concentration	$C = \frac{N_s - N_B}{60 \times \varepsilon_{^{36}Cl} \times m_0 \times \eta_{ch}} F_d$
Counting efficiency	$\varepsilon_{^{36}Cl} = \frac{N_C - N_b}{60 \times A_R}$
Uncertainty	$\frac{u(A)}{A} = \sqrt{(\frac{u(N)}{N})^2 + (\frac{u(\varepsilon_{^{36}Cl})}{\varepsilon_{^{36}Cl}})^2 + (\frac{u(\eta_{ch})}{\eta_{ch}})^2 + (\frac{u(F_d)}{F_d})^2}$

Minimum detectable activity	$MDA = \frac{(2.71 + 4.65\sqrt{B})}{t \times \varepsilon_{^{36}Cl} \times \eta_{ch}}$

GLOSSARY	
SUBJETC	**DESCRIPTION**
AAS	Atomic absorption spectrometer
LSC	Liquid scintillation counting
MDA	Minimum detectable activity, Bq
η_{ch}	Chemical yield of the procedure
m_F	Mass of Cl obtained in the final solution, g
m_I	Mass of Cl added to the initial sample, g
F_d	Dilution factor
$\varepsilon_{^{36}Cl}$	^{36}Cl counting efficiency
m_0	Mass of a sample, g
C	Activity concentration, Bq g^{-1}
A_R	Activity of a reference standard solution, Bq
A	Activity of a sample, Bq
N_S	Sample counting rate, cpm
N_B	Blank counting rate, cpm
N_C	Reference sample counting rate, cpm
N_b	Background counting rate, cpm
N	Number of counts when measuring a sample
B	Number of counts when measuring a blank
t	Blank counting time, s

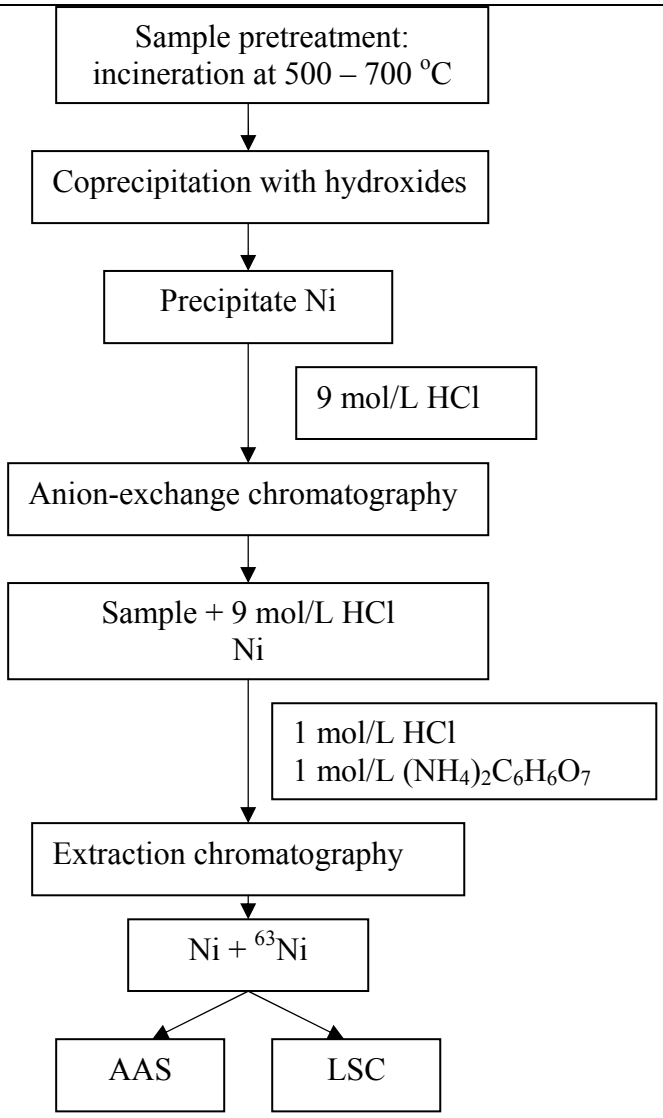
References

1. Hou, X., Østergaard, L.F., Nielsen, S.P. (2007) Determination of ^{36}Cl in nuclear waste from reactor decommissioning. Anal. Chem. 79, 3126-3134.

3.6.4. TITLE: Determination of nickel-63 from irradiated graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
CW Reference	CWAP-15-4
Scope & Range of Application	The procedure is used in the determination of ^{63}Ni in irradiated graphite.
Principle	Nickel pre-concentration is based on ferric hydroxide co-precipitation that enables Fe and Ni separation from Sr, Cs, C, Ba, Ca, Cl. Nickel is separated by adsorption on an Eichrom Ni Spec. column (Eichrom Technologies, Inc.). ^{63}Ni activity is measured by LSC. Quantities of stable nickel are controlled with the help of an atomic absorption spectrometer.
Instrumentation	• Chemical separation system • Liquid scintillation counter Quantulus-1220 • Atomic absorption spectrometer with a graphite atomizer (standard deviation 5-10%).

OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Separation Method	Step 1.	Addition of known amounts of stable nickel as a carrier.
	Step 2.	Nickel is transferred to precipitate with the following anion-exchange chromatography. The rinse is performed with 9M HCl while the elution with 1M HCl and 1M ammonium citrate.
	Step 3.	Nickel is separated by adsorption on an Eichrom Ni Spec. column.
	Step 4.	The elution of nickel is carried out with 3M HNO_3.

Flow chart	
Chemical Yield	The eluate is evaporated until dryness, the residue is dissolved in 2 mL of distilled water following ^{63}Ni measurement by LSC and stable Ni determination by the AAS.
Calibration	The counting efficiency is calculated using a ^{63}Ni reference standard solution. The counting efficiency obtained is around 70% for usual quenching values analysed. The window settings optimised is: 20 - 400 channels.
Measurement geometry	The 1-mL samples are mixed with 16 mL of liquid scintillation cocktail OptiPhase HiSafe3 and measured by LSC.

3.7. Procedures from Lab #16 INR

3.7.1. TITLE: Determination of Cobalt-60 in i-graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
Reference	CWAP-16-1
Scope & Range of Application	The procedure is used in the determination of ^{60}Co activity directly in the graphite samples, without pre-treatment.
Principle	Measurement by multi-channel gamma spectrometry on graphite powder
Instrumentation	Ge-HP detector (35%) associated with 4096 channels-spectrometer Analysis software: Genii 2000, version 3.1

OPERATING PROCEDURE	
SUBJETC	**DESCRIPTION**
Separation Method	N/A
Flow chart	-
Chemical Yield	No chemical yield has to be determined since there is no separation
Calibration	In house source prepared from standard solution containing Am-241, Ba-139, Cs-137 and Co-60
Measurement geometry	Small quantities of sample (powder) were measured in glass LSC vials. The vials were placed directly on the detector in a fixed coaxial position. The calibration source was prepared by using 1 ml standard solution. Apparently, the source and samples had the same volume.

	No self-absorption correction was applied.

EXPRESION OF MEASUREMENT RESULTS	
SUBJETC	**DESCRIPTION**
Chemical Yield	N/A
Specific Activity	C=A/m
Efficiency	$\varepsilon = M/A_s$
Uncertainty	$\sigma_A = A \cdot \sqrt{\frac{\sigma_G^2}{G^2} + \frac{\sigma_B^2}{B^2} + \frac{\sigma_{As}^2}{As^2}}$ $\sigma_G = \sqrt{G}$ $\sigma_B = \sqrt{B}$ $\sigma_{As} = 1\sigma$
MDA	$MDA = m \cdot MDC$ $MDC = \frac{2.71 + 4.65 \cdot \sqrt{B}}{\varepsilon \cdot T_s \cdot y \cdot m}$

GLOSSARY	
SUBJETC	**DESCRIPTION**
ε	peak efficiency
C	specific activity
A	activity
m	sample mass
M	out count rate
A_s	source activity
σ_A	activity uncertainty
G	gross number of counts in peak region
B	background counts in peak region (determined as average between left and right ROI's

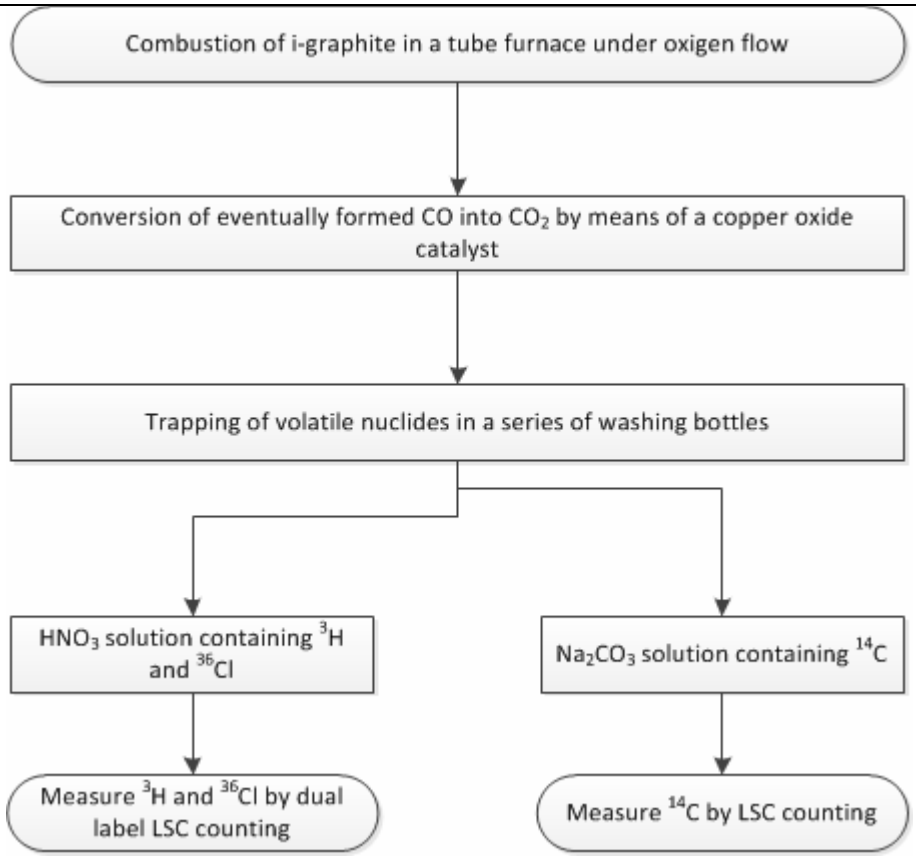
1σ	uncertainty of calibration source (from source certificate)
T_s	counting time
y	yield

References

3.7.2. TITLE: Determination of Tritium, Radiocarbon and Chlorine-36 in digested i-graphite samples

GENERAL INFORMATION	
SUBJECT	**DESCRIPTION**
CW Reference	CWAP-23-1
Scope & Range of Application	The procedure is used for the determination of ^{3}H, ^{14}C and ^{36}Cl in irradiated graphite samples.
Principle	About 200 mg of i-graphite is combusted in a tube furnace at min. 800°C and an oxygen flow rate of 100 $L.h^{-1}$. A copper oxide catalyst is used in order to convert CO in CO_2. The combustion gases are bubbled through a series of washing bottles in order to collect ^{3}H, ^{36}Cl and ^{14}C. Tritium and chlorine-36 are collected in the first washing bottle containing 0.1 $mol.l^{-1}$ HNO_3. Radiocarbon is collected in the next two washing bottles containing 4 $mol.l^{-1}$ Na_2CO_3. The obtained solutions are divided into three aliquots, which are measured by LSC. ^{3}H and ^{36}Cl are measured by dual label counting. .
Instrumentation	- Tube furnace (Behr CS 50 HT). - Liquid Scintillation Counter Quantulus 1220-002 with WinQ software - Liquid Scintillation Counter TriCarb 2900 TR with Quantasmart software

OPERATING PROCEDURE		
SUBJECT	**DESCRIPTION**	
Separation Method		No separation is performed.
Flow chart		

	
Chemical Yield	The chemical yield was determined by analysing spiked graphite samples.
Calibration	The LSC instrument is calibrated with reference standards.
Measurement geometry	From each Sr-fraction, 2 mL of sample is mixed with 18 mL of Optiphase Hisafe 3 LSC cocktail in a 20 mL counting vial.

EXPRESSION OF MEASUREMENT RESULTS	
SUBJECT	**DESCRIPTION**
Chemical Yield	$CY = \frac{m_f}{m_i}$
Activity	$A_e = \frac{N}{Eff \cdot CY \cdot M}$ $\quad M = \frac{m_{alq} \cdot DF_2}{DF_1}$
Efficiency	$Eff = \frac{N_{rs}}{A_{rs}}$
Uncertainty	

	$s_G = \sqrt{\frac{\sum_{i=1}^{n}(G_i - \overline{G})}{n-1}}$ $\quad$ $s_B = \sqrt{\frac{\sum_{i=1}^{n}(B_i - \overline{B})}{n-1}}$ $s_N = \sqrt{s_G^2 + s_B^2}$ $\frac{u_{CY}}{CY} = \sqrt{\left(\frac{u_{m_f}}{m_f}\right)^2 + \left(\frac{u_{m_i}}{m_i}\right)^2}$ $\frac{u_{Eff}}{Eff} = \sqrt{\left(\frac{s_{N_{Srs}}}{N_{rs}}\right)^2 + \left(\frac{u_{A_{rs}}}{A_{rs}}\right)^2}$ $\frac{u_A}{A} = \sqrt{\left(\frac{s_N}{N}\right)^2 + \left(\frac{u_{Eff}}{Eff}\right)^2 + \left(\frac{u_{CY}}{CY}\right)^2}$
MDA	$MDA = \frac{4.66 \cdot \sqrt{B \cdot t}}{Eff \cdot t \cdot CY \cdot M}$

GLOSSARY	
SUBJECT	**DESCRIPTION**
A_e	Specific activity
A_{rs}	Activity of reference standard
B	Blank count rate
CY	Chemical yield
DF	Dilution factor
Eff	Efficiency
G	Gross count rate
M	Mass of sample
m_{alq}	Mass of aliquot
MDA	Minimum detectable activity
m_f	Final mass of carrier
m_i	Initial mass of carrier
N	Net count rate
N_{rs}	Net count rate reference standard
t	Measurement time

3.7.3. TITLE: Determination of Tritium and Carbon-14 in i-graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
Reference	CWAP-16-2
Scope & Range of Application	The procedure is applied in the determination of ^{3}H and ^{14}C using the flame oxidation method as a sample preparation technique for liquid scintillation analysis.
Principle	The combustion system burns the sample in a continuous flow of oxygen. During the combustion process, the radionuclide components are separated as tritiated water (which is flushed down into the tritium counting vial with the tritium scintillator) and radioactive carbon dioxide (which is trapped in a column filled with a carbon dioxide absorbent and flushed into the ^{14}C counting vial using a proper scintillator). Tritium and ^{14}C are determined by liquid scintillation counting.
Instrumentation	• Sample Oxidizer, model 307 PerkinElmer™ • Liquid Scintillation Analyzer, model 2100 Tri-Carb® Packard

OPERATING PROCEDURE		
SUBJETC	**DESCRIPTION**	
Separation Method	Step 1.	$^{3}H/^{14}C$ chemical yield determination. To determine the ^{3}H chemical yield 10 combusto-cone were prepared by inserting a combusto-pad into each of the 10 combusto-cones; 0.02 g graphite and 2 g extra-pure, micro-crystalline cellulose were added into each of the ten combusto-cones; - the first cone was inserted into the ignition basket and the sample was burned. When the program cycle was complete, the tritium collection vial was removed and marked with B code; - the following three combusto-cones were burnes. Then, 0.1 mL of Spec-Chec tritium standard was pippeted into each of the three vials marked with S1, S2, S3 codes; - 0.1 mL of Spec-Chec tritium standard was pippeted into the fifth combusto-cone and immediately the sample was combusted. The tritium collection vial was marked with R4; - 0.1 mL of Spec-Chec inactive solution was pippeted into

		the sixth combusto-cone and immediately the sample was combusted. The tritium collection vial was marked with M5; - the last two operations were repeated two more times, sequentially marking the tritium collection vials with R6, M7, R8, and M9; - 0.1 mL of Spec-chec inactive solution was pippeted into the vials marked B, R4, M5, R6, M7, R8, M9. The same procedure is apply for ^{14}C chemical yield determination.
	Step 2.	Two times burning of a blank sample.
	Step 3.	One time burning of the radioactive sample (G1.1).
	Step 4.	The steps 2 and 3 repeated two more times (G1.2; G1.3).
Flow chart		
Chemical Yield	The chemical yield was determined by ^{3}H/ ^{14}C evaluation in *S1*, *S2*, *S3*, *R4*, *R6*, *R8* samples.	
Calibration	The LSC instrument is calibrated with reference standards. The efficiency is calculated with quenching curves established with ^{14}C and ^{3}H reference standards. The quench level was measured by the external standard method tSIE.	
Measurement geometry	The samples are directly ready from the Oxidizer to be measured by liquid scintillation counting.	

EXPRESION OF MEASUREMENT RESULTS	
SUBJETC	**DESCRIPTION**
Chemical Yield	$CY = \frac{DPM_{Rj}}{\overline{DPM_S}} \cdot 100$
Activity	The activity of $^{3}H/^{14}C$ is calculated in Bq per mass of the original sample. The formulae for the calculation are: $DPM_{G1.i}^{net} = \left(DPM_{G1.i} - \overline{DPM_B}\right) \cdot \frac{100}{\overline{CY}}$ $A = \frac{DPM_{G1.i}^{net}}{m \cdot 60}$

Efficiency	The counting efficiencies are calculated from the quenching curves performed with ^{14}C and ^{3}H reference standards and established as a function of a quench index parameter (tSIE).
Uncertainty	Identification of uncertainty sources: ♦ DF: • u from mass determination • u from volume of aliquots ♦ CY: • σ from counting of ^{3}H or ^{14}C standard direct measurement (dpm_{direct}) • σ from counting of ^{3}H or ^{14}C standard after combustion ($dpm_{combustion}$) ♦ N: u from net dpm (N) from the equation: **N**= dpm_{sample}-$dpm_{background}$ if single measurement if done absolute uncertainty is obtained by propagation of absolute uncertainties from sample and background measurements. $\sigma(N) = \sqrt{u^2_{dpm_{sample}} + u^2_{dpm_{background}}}$ Quasi-variance if n replicants are calculated: $\sigma(sample) = \sqrt{\frac{\sum(dpm_{sample} - \overline{dpm_{sample}})^2}{n-1}}; \sigma(B) = \sqrt{\frac{\sum(dpm_{background} - \overline{dpm_{background}})^2}{n-1}}$ $\sigma(N) = \sqrt{\sigma(sample)^2 + \sigma(B)^2}$ **Note:** Uncertainty regarding efficiency is taking into account directly into uncertainty of dpm given by the equipment. Expression of activity uncertainty in relative terms is given by: $\frac{U(A)}{A} = \sqrt{\left(\frac{\sigma(N)}{N}\right)^2 + \left(\frac{u(CY)}{CY}\right)^2 + \left(\frac{u(DF)}{DF}\right)^2}$ where: $\frac{u(DF)}{DF} = \sqrt{\left(\frac{u(m_{al})}{m_{al}}\right)^2}$ $\frac{u(CY)}{CY} = \sqrt{\left(\frac{\sigma(dpm_{combustion})}{dpm_{combustion}}\right)^2 + \left(\frac{\sigma(dpm_{direct})}{dpm_{direct}}\right)^2}$ The established coverage factor (**k**) is 2 for a confidence level of 95 % given the result expression: $A \pm 2 \cdot U(A)$
MDA	The minimum detectable activity is calculated in Bq per mass of the original sample:

	$MDA = \frac{4.66 \cdot \sqrt{B \cdot t}}{Eff \cdot t \cdot CY \cdot m}$

GLOSSARY	
SUBJETC	**DESCRIPTION**
CY	Chemical yield of the procedure
DPM_{Rj}	dpm in the vials marked with *Rj* code, where *j* = {4, 6, 8}
$\overline{DPM_S}$	Average dpm of the three standards (*S1*, *S2*, *S3*)
$DPM_{G1.i}^{net}$	net activity in the vial marked with G*1.i* code, where *i* = {1,2,3}
$DPM_{G1.i}$	gross activity in the vial marked with G*1.i* code, where *i* = {1,2,3}
$\overline{DPM_B}$	Average dpm of background (the six blank samples)
m	Mass of the radioactive sample
MDA	Minimum detectable activity
B	Blank count rate
t	Measurement time
Eff	Efficiency

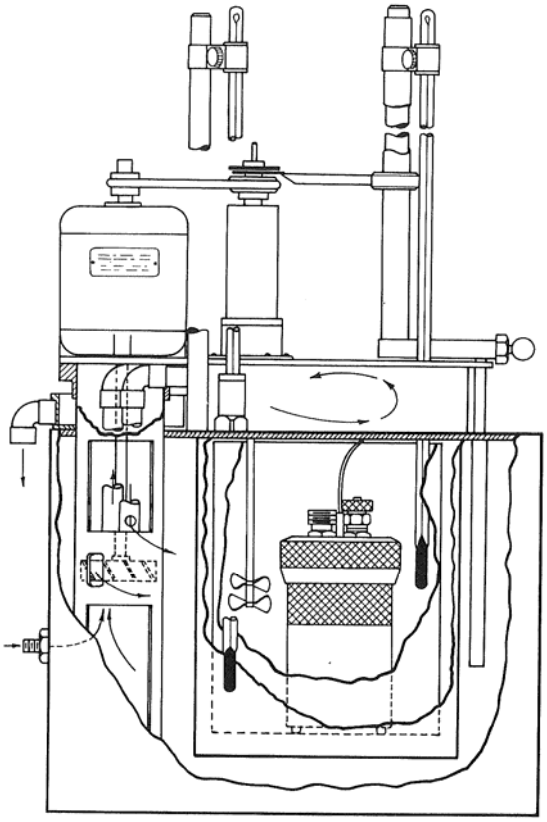
References

3.8. Procedures from Lab #22 NRG

3.8.1. TITLE: Determination of tritium and carbon-14 from i-graphite samples

GENERAL INFORMATION	
SUBJECT	**DESCRIPTION**
Reference	CWAP-22-1
Scope & Range of Application	The procedure is used in the determination of ^{3}H and ^{14}C in the samples of i-graphite.
Principle	Combustion of i-graphite with approximately 30 atm. oxygen in a pressure vessel using a Parr 1241 Calorimeter. Tritium is collected in acidic liquid after combustion. After its distillation, tritium is determined by Liquid scintillation counting (LSC). CO_2 is collected in gas bag after combustion, trapped by Carbosorb and measured by LSC.
Instrumentation	• Parr 1241 Calorimeter • TriCarb 2700 Low Level Liquid Scintillation Counter

OPERATING PROCEDURE		
SUBJECT	**DESCRIPTION**	
Separation Method	Step 1.	Sample preparation – graphite and benzoic acid are pressed into a pellet
	Step 2.	Samples are placed in the reaction vessel
	Step 3.	Combustion takes place
	Step 4.	Gas sampling – trap by Carbosorb – addition of scintillation cocktail
	Step 5.	Liquid sampling – distillation – addition of scintillation cocktail
	Step 6.	LCS measurements
	Step 7.	Activity determination and statistic evaluation

• Parr 1241 Calorimeter	 Calorimeter Cross-Section
Chemical Yield	During sample preparation a loss of activity of ^{3}H and ^{14}C are common. So it is necessary to determinate the chemical yield (CY) for correction of the measured activity. Thus 4 sub-aliquots of the non-active graphite were spiked with calibrated ^{3}H and ^{14}C spikes. Then the ^{3}H and ^{14}C spiked samples were prepared, and measured by LSC in the same way as the irradiated graphite samples. For the calculation of the ^{3}H CY it was possible to use the 4 spiked samples measurements, but no activity was measured in two of the spiked ^{14}C samples. So the CY for ^{14}C was calculated based on measurements of the other two spiked samples. It is not clear yet where the ^{14}C activity was lost during the sample preparation.
Calibration	The calibration of the LSC is carried out with a ^{14}C Insta Gel Quenched

	Standard Set and a ^{3}H Ultima Gold Quenched Standard Set from Perkin Elmer. The quality of measurements is guaranteed by participation of three intercomparison exercises per year. In addition, the performance of the instrument is checked periodically by a ^{14}C and ^{3}H standard.
Measurement geometry	^{14}C – After combustion the gaseous ^{14}C was trapped in Carbosorb E. 1 ml of Carbosorb was mixed with 10 ml Instagel scintillation cocktail and measured for 1 h. ^{3}H - After combustion the ^{3}H and some other nuclides which are formed during irradiation are caught in the aqueous phase. Tritium was separated by distillation. After distillation 10 ml of the distillate was mixed with 10 ml Ultima Gold LLT scintillation cocktail and measured for 1 h.

EXPRESION OF MEASUREMENT RESULTS	
SUBJECT	**DESCRIPTION**
Chemical Yield	$CY = \frac{A_{sample}}{A_{spike}}$
Specific activity	$A = \frac{A_{LSC} * m_{sample}}{Am_{graphite} * CY * m_{LSC}}$
Uncertainty	The overall uncertainty calculations by Kragten are performed.
MDA	The minimum detectable activity is calculated according to the Currie equation shown in the equation: $MDA = \frac{4.66 * \sqrt{B}}{\varepsilon * CY * m_{LSC}}$

GLOSSARY	
SUBJECT	**DESCRIPTION**
CY	Chemical yield of the procedure
A_{spike}	Added spike activity

A_{sample}	Activity measured in the combustion sample
A_{LCS}	Activity measured in the LSC sample
m_{sample}	Mass of the combustion sample
$m_{graphite}$	Mass of the graphite sample
m_{LSC}	Mass of the LSC sample
B	Blanco count rate
ε	Efficiency

References

[9]. H.L Cobussen "Combustion of irradiated graphite in project Carbowaste," reference K5041/10.105557 LCI/JC/PvS
[10]. Tanja Tomasberger, "Measurement of ^{3}H and ^{14}C in irradiated graphite samples," reference 22260/11.106352 RE/TT/ES.
[11]. *Certificate of Radioactivity*, ^{14}C Quenched Standard Quenched Set, NIST SRM 4947C, Perkin Elmer, 2010
[12]. *Certificate of Radioactivity*, ^{3}H Quenched Standard Quenched Set, NIST SRM 4222C, Perkin Elmer, 2010
[13]. Certificate of Calibration Carbon-14 low-level standard solution. NPL R1400, 2009
[14]. Kalibrierschein Tritiumhaltiges Wasser in Glasampulle. PTB 2005-1435, 2010
[15]. Nederlands Normalisatie-instituut, NEN 6420 Water - Bepaling van het gehalte aan getritieerd water door vloeistofscintillatietelling, 1986
[16]. T.W. Vetter "Quantifying measurement uncertainty in analytical chemistry – A simplified practical approach." NIST 301-975-4123, Gaithersburg

3.8.2. TITLE: Determination of Co-60 from i-graphite samples

GENERAL INFORMATION	
SUBJECT	**DESCRIPTION**
Reference	CWAP-22-2
Scope & Range of Application	The procedure is used in the determination of ^{60}Co in i-graphite samples.
Principle	Samples of i-graphite are measured by gamma spectrometry
Instrumentation	• Gamma spectrometer setup with HPGe-detector • NIAGADA neutron metrology software package

OPERATING PROCEDURE		
SUBJECT	**DESCRIPTION**	
	Step 1.	The graphite samples (six aliquots) were weighted on accurate balance and put in the measuring vials. This preparation took place in Ar –filled glove box.
	Step 2.	Calibration, background measurements
	Step 3.	Determination of the right measuring distance
	Step 4.	Samples measurements
	Step 5.	Quality measurements with a reference source background measurements
	Step 6.	Activity determination and statistic evaluation
Measurement geometry	Sample are measured directly in the Gamma spectrometer setup.	

EXPRESION OF MEASUREMENT RESULTS	
SUBJECT	**DESCRIPTION**
Activity	$$A = \frac{PA}{\varepsilon \mathrm{Y} t_m} \times \frac{\lambda t_m}{1 - e^{-\lambda t_m}} \times \frac{e^{\lambda (t_b - t_m)}}{\lambda (t_b - t_m)} \times e^{\lambda t_w} \times \frac{1}{1 - \frac{\tau N_{tot}}{t_m}}$$
Remarks I	[1] *Sample notation: "Aliquot-Subaliquot-Measurement set", Blank sample notation: "Blank-Measurement Set"* [2] *All activities correspond to a reference date of 01-10-2010* [3] *Calculated and reported by the evaluating software package*

Specific-Activity equation	$SA = \frac{A_{avg}}{M}$
MDA equation	$\frac{4.66 \times \sqrt{B}}{\varepsilon \times \mathrm{Y} \times M} = \frac{4.66 \times \sqrt{B} \times A}{PA \times M}$
Overall uncertainty equation	$\sqrt{\left(s^2 + \Delta^2\right)}$
Remarks II	[1] *Type A uncertainty is based on the standard deviation found in the three measurement sets carried out on each sub-aliquot (1σ). These uncertainties are not included in the overall uncertainties* [2] *Overall uncertainty in specific activity corresponds to a 68% confidence level (1σ)* [3] *MDA corresponds to a 99.7% confidence level (3σ) and is further the average of the three sets of measurements per each sub-aliquot. The standard deviations (not in %) are also indicated along with the MDA*

GLOSSARY	
SUBJECT	**DESCRIPTION**
PA	Net peak area
ε	Efficiency
Y	Emission probability
t_m	Preset counting time
λ	Decay constant
t_b	Real counting time
t_w	Waiting time
τ	Dead time constant
N_{tot}	Total number of counts in the γ-spectrum
A_{avg}	Average of the three sets of activity measurements
M	Mass of the sub-aliquot
A	Activity measurements
Δ	Systematic uncertainties
s	Random uncertainties

References

[1] R.K. Mutnuru: "Measurement of ^{60}Co activity in radioactive graphite samples," NRG note 22260/11.106404 I&D/RM/MB, NRG, Petten, 28 January 2011

[2] Mutnuru, R.K.: *"Measurement of ^{60}Co activity in radioactive graphite samples"*, NRG Note K5072/10.105562 LCI/RM/MK, NRG, Petten, December 2010.

[3] Wolters, J.I.: *"Werkinstructie voor activiteitsmetingen van radioactief materiaal"*, NRG report K5072/06.73422/I JIW/MMI/NO, NRG, Petten, April 2006.

[4] Burgers, A.R.: *"NIAGADA (1989): Automatische Analyse van Gamma Spectra"*, ENR rapport 231.

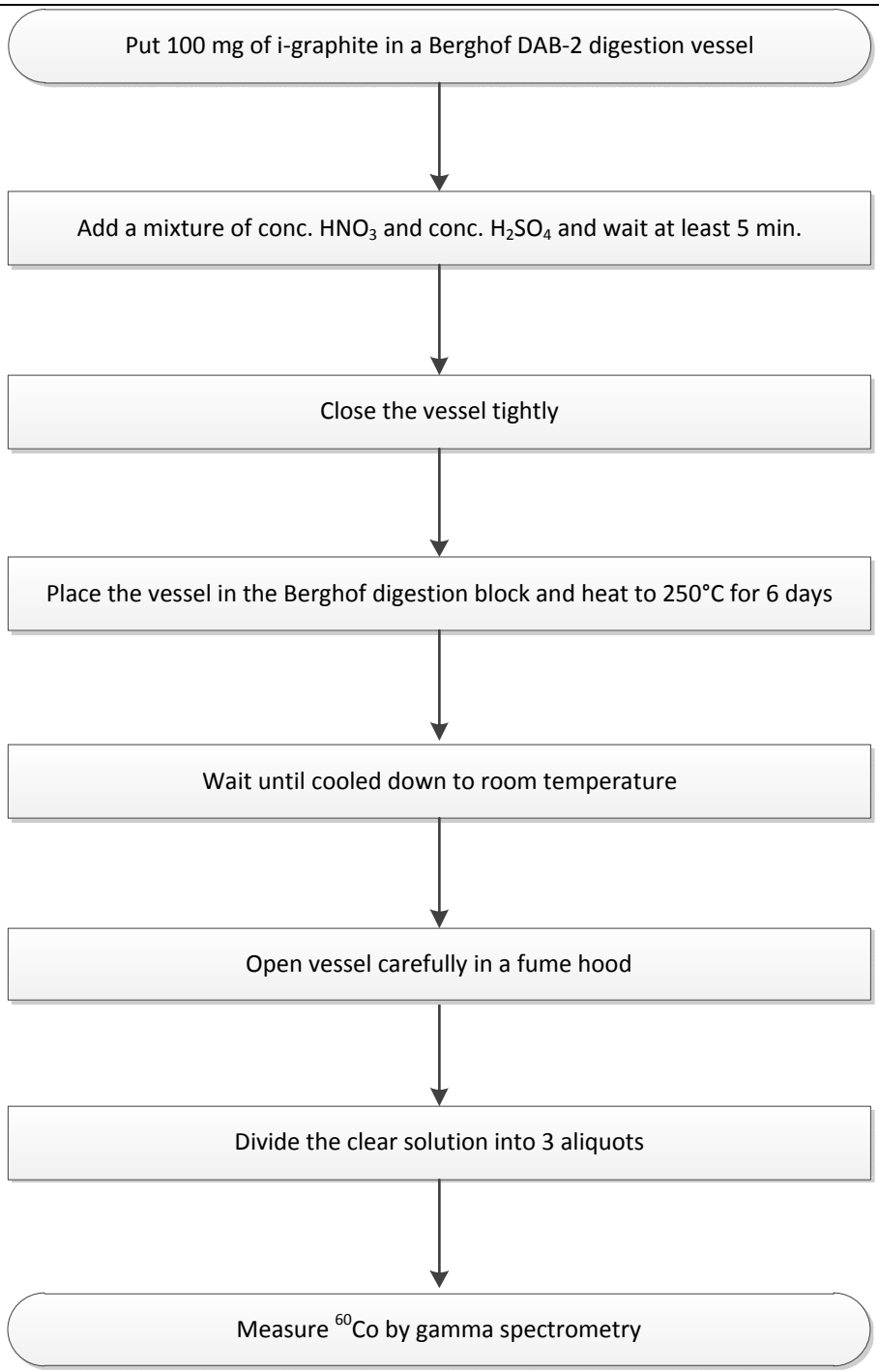
[5] Cobussen, H.L.: *"Sampling of irradiated graphite for Co-60 measurements"*, NRG Note, 2.2260.20/10.105566 LCI/JC/PvS, Petten, 13 December 2010.

3.9. Procedures from Lab #23 SCK·CEN

3.9.1. TITLE: Digestion of i-graphite samples and determination of Cobalt-60 in digested i-graphite samples

GENERAL INFORMATION	
SUBJECT	**DESCRIPTION**
CW Reference	CWAP-23-2
Scope & Range of Application	The procedure is used for the determination of ^{60}Co in irradiated graphite samples.
Principle	About 100 mg of i-graphite is placed in a digestion vessel type DAB-2. A mixture of concentrated nitric acid an concentrated sulphuric acid are carefully added. The mixture should be allowed to react at least 5 min. When the generation of gas bubbles has stopped, the vessel should be closed tightly. The digestion bombs are placed in the digestion block and heated to 250°C for 6 days. After cooling down to room temperature, the vessels can be opened in a fume hood and a clear solution is obtained. The solution is divided into three aliquots, which are measured by gamma spectrometry.
Instrumentation	- heating block with high pressure digestion bombs type DAB-2 manufactured by Berghof. The heating block is equipped with a BTC-3000 temperature controller (Berghof). - HPGe detectors and Genie 2000 software (Canberra)

OPERATING PROCEDURE		
SUBJECT	**DESCRIPTION**	
Separation Method		No separation has to be performed

Flow chart	
Chemical Yield	No chemical yield has to be determined since there is no separation
Calibration	The HPGe detector is calibrated with a multi-isotope reference standard.
Measurement geometry	The aliquots are transferred into three vials and diluted until a total volume of 20 mL is obtained.

EXPRESSION OF MEASUREMENT RESULTS	
SUBJECT	**DESCRIPTION**
Chemical Yield	\
Activity	$A_e = \frac{N}{Eff \cdot M}$ $\quad M = \frac{m_{alq} \cdot DF_2}{DF_1}$
Efficiency	$Eff = \frac{N_{rs}}{A_{rs}}$
Uncertainty	$s_n = \sqrt{s_I^2 + s_b^2 + s_c^2}$ $N = \frac{n}{t}$; $s_N = \frac{s_n}{t}$ $\frac{u_{Eff}}{Eff} = \sqrt{\left(\frac{s_{N_{Srs}}}{N_{rs}}\right)^2 + \left(\frac{u_{A_{rs}}}{A_{rs}}\right)^2}$ $\frac{u_A}{A} = \sqrt{\left(\frac{s_N}{N}\right)^2 + \left(\frac{u_{Eff}}{Eff}\right)^2}$
MDA	$MDA = \frac{2.71 + 4.653 \cdot \sqrt{2b + 2c}}{Eff \cdot t \cdot R \cdot M}$

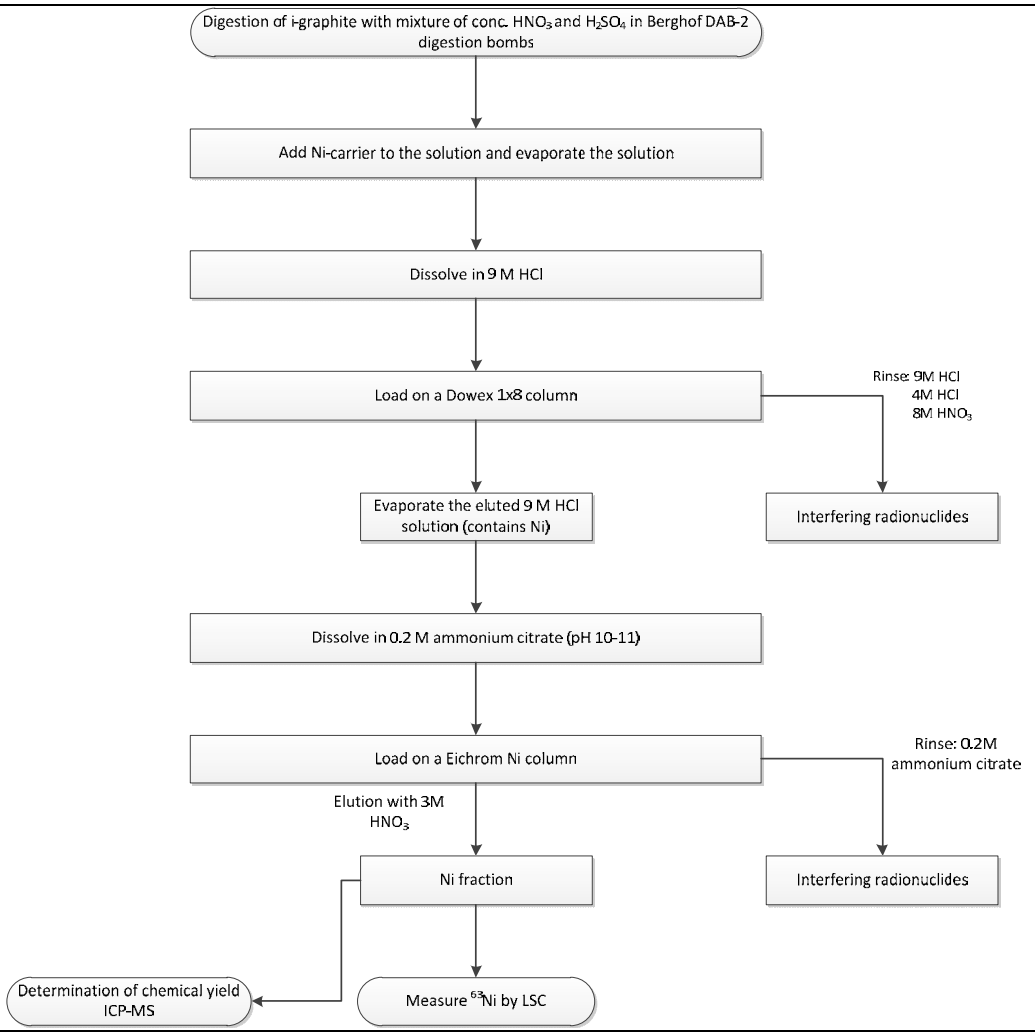
GLOSSARY	
SUBJECT	**DESCRIPTION**
A_e	Specific activity
A_{rs}	Activity of reference standard
b	Total blank counts
B	Blank count rate
c	Calculated continuum (counts)
DF	Dilution factor
Eff	Efficiency
G	Gross count rate
I	Total gross counts
M	Mass of sample
m_{alq}	Mass of aliquot

MDA	Minimum detectable activity
m_f	Final mass of carrier
m_i	Initial mass of carrier
n	Total net counts
N	Net count rate
N_{rs}	Net count rate reference standard
R	Branching ratio gamma line
t	Measurement time

3.9.2. TITLE: Determination of Nickel-63 in digested i-graphite samples

GENERAL INFORMATION	
SUBJECT	**DESCRIPTION**
CW Reference	CWAP-23-3
Scope & Range of Application	The procedure is used for the determination of ^{63}Ni in irradiated graphite samples.
Principle	The digestion of the i-graphite samples is performed as described in CWAP-8-2. The obtained solution is divided into three aliquots. Ni-63 will be measured by LSC. Therefore, chemical separations have to be carried out first. Interfering nuclides like Fe-55 and Co-60 are removed first by anion exchange chromatography. Nickel is then adsorbed on an Eichrom Ni-Resin column.
Instrumentation	- heating block with high pressure digestion bombs type DAB-2 manufactured by Berghof. The heating block is equipped with a BTC-3000 temperature controller (Berghof). - Liquid Scintillation Counter TriCarb 2900 TR with quantasmart software

OPERATING PROCEDURE		
SUBJECT	**DESCRIPTION**	
Separation Method	Step 1.	Addition of known amounts of stable Ni as carrier to each aliquot, then evaporation to dryness and dissolution in 9M HCl.
	Step 2.	The solution is loaded on a Dowex 1x8 column and Ni is eluted with 9M HCl.
	Step 3.	The HCl is evaporated to dryness and dissolved in 0.2M ammonium citrate with a pH between 10 and 11
	Step 4.	The ammonium citrate solution is loaded on an Eichrom Ni resin column and the column is rinsed with 0.2 M ammonium citrate
	Step 5.	The elution of Nickel is carried out with 0.05 M HNO_3

Flow chart	
Chemical Yield	A known amount of stable nickel carrier is added in the beginning of the separation procedure. The chemical yield is determined by measuring the stable nickel content of the final Ni-fraction by ICP-MS.
Calibration	The LSC instrument is calibrated with a Ni-63 reference standard.
Measurement geometry	From each Ni-fraction, 1 mL of sample is mixed with 18 mL of Optiphase Hisafe 3 LSC cocktail in a 20 mL counting vial and diluted to a total volume of 20 mL.

EXPRESSION OF MEASUREMENT RESULTS	
SUBJECT	**DESCRIPTION**
Chemical Yield	$CY = \frac{m_f}{m_i}$
Activity	$A_e = \frac{N}{Eff \cdot CY \cdot M}$ $\quad M = \frac{m_{alq} \cdot DF_2}{DF_1}$

Efficiency	$Eff = \frac{N_{rs}}{A_{rs}}$
Uncertainty	$s_G = \sqrt{\frac{\sum_{i=1}^{n}(G_i - \overline{G})}{n-1}}$ $\quad s_B = \sqrt{\frac{\sum_{i=1}^{n}(B_i - \overline{B})}{n-1}}$ $s_N = \sqrt{s_G^2 + s_B^2}$ $\frac{u_{CY}}{CY} = \sqrt{\left(\frac{u_{m_f}}{m_f}\right)^2 + \left(\frac{u_{m_i}}{m_i}\right)^2}$ $\frac{u_{Eff}}{Eff} = \sqrt{\left(\frac{s_{N_{Srs}}}{N_{rs}}\right)^2 + \left(\frac{u_{A_{rs}}}{A_{rs}}\right)^2}$ $\frac{u_A}{A} = \sqrt{\left(\frac{s_N}{N}\right)^2 + \left(\frac{u_{Eff}}{Eff}\right)^2 + \left(\frac{u_{CY}}{CY}\right)^2}$
MDA	$MDA = \frac{4.66 \cdot \sqrt{B \cdot t}}{Eff \cdot t \cdot CY \cdot M}$

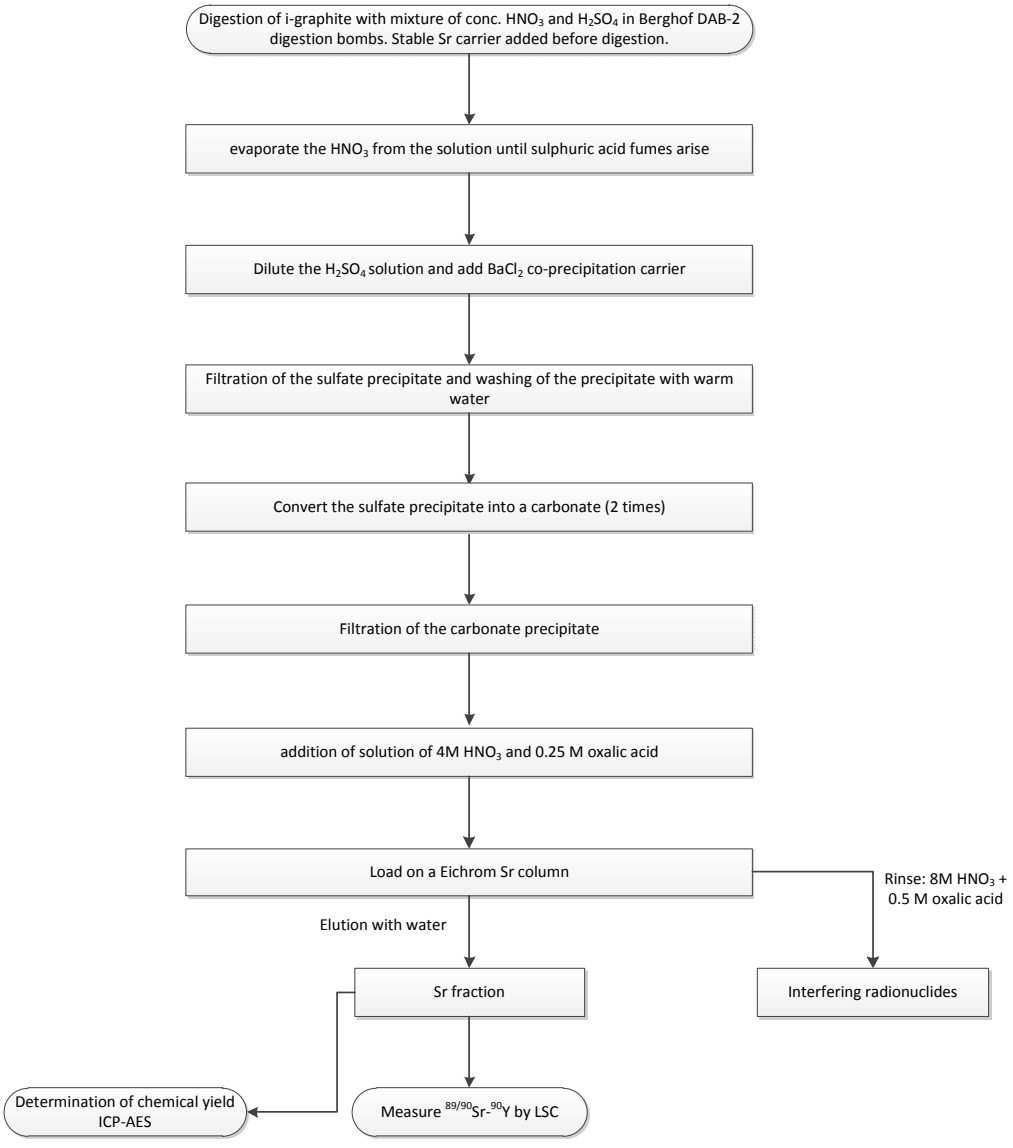
GLOSSARY	
SUBJECT	**DESCRIPTION**
A_e	Specific activity
A_{rs}	Activity of reference standard
B	Blank count rate
CY	Chemical yield
DF	Dilution factor
Eff	Efficiency
G	Gross count rate
M	Mass of sample
m_{alq}	Mass of aliquot
MDA	Minimum detectable activity
m_f	Final mass of carrier
m_i	Initial mass of carrier

N	Net count rate
N_{rs}	Net count rate reference standard
t	Measurement time

3.9.3. TITLE: Determination of Strontium-89 and Strontium-90 in digested i-graphite samples

GENERAL INFORMATION	
SUBJECT	**DESCRIPTION**
CW Reference	CWAP-23-4
Scope & Range of Application	The procedure is used for the determination of $^{89/90}$Sr in irradiated graphite samples.
Principle	The digestion of the i-graphite samples is performed as described in CWAP-8-2. The obtained solution is divided into three aliquots. Sr-89/90 will be measured by LSC. Chemical separations are performed in order to remove interfering nuclides. Most interfering nuclides can be removed by co-precipitation of Sr with $BaSO_4$. The sulphate precipitate is then converted into carbonate, which is soluble in nitric acid. Finally, the Sr-fraction is purified on a Eichrom Sr-resin column. LSC measurements are performed 2 weeks after the separation.
Instrumentation	- heating block with high pressure digestion bombs type DAB-2 manufactured by Berghof. The heating block is equipped with a BTC-3000 temperature controller (Berghof). - Liquid Scintillation Counter Quantulus 1220-003 with WinQ software

OPERATING PROCEDURE		
SUBJECT	**DESCRIPTION**	
Separation Method	Step 1.	Known amounts of stable Sr carrier were already added before the digestion procedure started. The clear solution obtained after digestion is divided into aliquots. The nitric acid should be removed by evaporation. The evaporation should be stopped as soon as white sulphuric acid fumes arise.
	Step 2.	The resulting H_2SO_4 solution is diluted 10 fold with water and $BaCl_2$ is added as co-precipitation carrier. This solution is stirred at 80°C for min. 30 min. Afterwards, the solution is filtered and the precipitate is washed with hot water until a neutral pH is obtained.
	Step 3.	The sulphate precipitate is now added into a beaker with Na_2CO_3 solution in order to convert the sulphate into carbonate. The solution is stirred on a hot plate during the night.

	Step 4.	After the filtration of the precipitate, step 3 is repeated.
	Step 5	The carbonate precipitate is dissolved in 4M HNO_3 and 0.25M oxalic acid.
	Step 6.	This solution is loaded on an Eichrom Sr-resin. The column is rinsed with 8M HNO_3 + 0.5M oxalic acid.
	Step 7.	The elution of Sr is carried out with water
Flow chart	
Chemical Yield	A known amount of stable strontium carrier is added in the beginning of the separation procedure. The chemical yield is determined by measuring the stable strontium content of the final Sr-fraction by ICP-AES.
Calibration	The LSC instrument is calibrated with Sr reference standards.
Measurement	From each Sr-fraction, 2 mL of sample is mixed with 18 mL of Optiphase Hisafe 3

geometry	LSC cocktail in a 20 mL counting vial.

EXPRESSION OF MEASUREMENT RESULTS	
SUBJECT	**DESCRIPTION**
Chemical Yield	$CY = \frac{m_f}{m_i}$
Activity	$A_e = \frac{N}{Eff \cdot CY \cdot M}$ $\quad M = \frac{m_{alq} \cdot DF_2}{DF_1}$
Efficiency	$Eff = \frac{N_{rs}}{A_{rs}}$
Uncertainty	$s_G = \sqrt{\frac{\sum_{i=1}^{n}(G_i - \overline{G})}{n-1}}$ $\quad s_B = \sqrt{\frac{\sum_{i=1}^{n}(B_i - \overline{B})}{n-1}}$ $s_N = \sqrt{s_G^2 + s_B^2}$ $\frac{u_{CY}}{CY} = \sqrt{\left(\frac{u_{m_f}}{m_f}\right)^2 + \left(\frac{u_{m_i}}{m_i}\right)^2}$ $\frac{u_{Eff}}{Eff} = \sqrt{\left(\frac{s_{N_{Srs}}}{N_{rs}}\right)^2 + \left(\frac{u_{A_{rs}}}{A_{rs}}\right)^2}$ $\frac{u_A}{A} = \sqrt{\left(\frac{s_N}{N}\right)^2 + \left(\frac{u_{Eff}}{Eff}\right)^2 + \left(\frac{u_{CY}}{CY}\right)^2}$
MDA	$MDA = \frac{4.66 \cdot \sqrt{B \cdot t}}{Eff \cdot t \cdot CY \cdot M}$

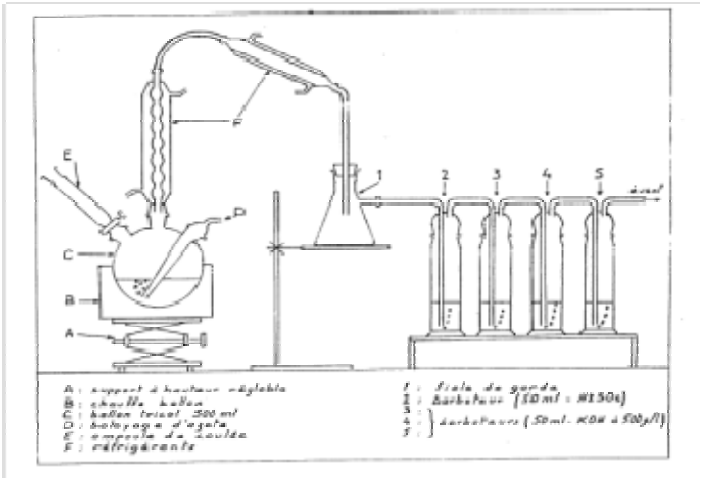
GLOSSARY	
SUBJECT	**DESCRIPTION**
A_e	Specific activity
A_{rs}	Activity of reference standard

B	Blank count rate
CY	Chemical yield
DF	Dilution factor
Eff	Efficiency
G	Gross count rate
M	Mass of sample
m_{alq}	Mass of aliquot
MDA	Minimum detectable activity
m_f	Final mass of carrier
m_i	Initial mass of carrier
N	Net count rate
N_{rs}	Net count rate reference standard
t	Measurement time

3.10. Procedures from Lab #26 SUBATEC

3.10.1. TITLE: Mineralization of i-graphite samples

GENERAL INFORMATION	
SUBJECT	**DESCRIPTION**
CW Reference	CWAP-26-1
Scope and range of application	This procedure described the mineralization of irradiated graphite samples by acid wet process and the recovery of all the radionuclides of interest (^{3}H, ^{14}C and ^{36}Cl).
Principle	A mass of graphite ranging from 0.3 to à.5g is dissolved in the mixture of concentrated acids (HNO_3+H_2SO_4+$HCLO_4$) in the distillation vessel (see below) which allows the recovery of ^{3}H, ^{14}C and ^{36}Cl. The distillation stage last about one hour for reaching the total dissolution of the graphite sample. ^{3}H (as HTO) and ^{36}Cl are recovered in the bubbling pots #1 and #2 containing an acid solution and ^{14}C is recovered in the bubbling pot # 3 containing an alkaline solution (NaOH). The chemical yields are determined by performing the same process with standard solutions of the RN of interest. At the end of the distillation stage, the other RN such as ^{60}Co, ^{63}Ni and ^{90}Sr which have not been distillated, are recovered in the acid concentrate.
Instrumentation	• A distillation system (see figure 1) • Usual glass (beakers) of laboratory • Scaling device
Reagents	• Deionized water (MilliQ®18 MilliQ® 18.2 MΩ.cm^{-1}) • Concentrated nitric acid (HNO_3) • Concentrated sulfuric acid (H_2SO_4) • Concentrated Perchloric acid ($HClO_4$) • NaOH (1M) for bubbling pots #3 and #4

Scheme	 Figure 1: Scheme of the distillation/dissolution system D: inert gas inlet; E: specific concentrated acids adding system

OPERATING PROCEDURE		
SUBJECT	**DESCRIPTION**	
Separation Method	Step 1.	Carry out the assembly following the scheme
	Step 2.	Check the cooling system (potential leaks)
	Step 3.	Introduced a volume of the concentrated acid mixture then the graphite powder.
	Step 4	Heat at temperature around 110°C during one hour
	Step 5	Recover the ^{3}H (as HTO) and ^{36}Cl fractions by combining the bubbling pots #1and #2 in a beaker (250 mL). Rinse bubbling pots #1 and #2 with acid and add the rinsing solutions. Volume precisely the final solution.
	Step 6	Recover the ^{14}C fraction by combining the bubbling pots #3 and #4 in a beaker (250 mL). Rinse bubbling pots #3 and #4 with soda solution and add the rinsing solutions to the beaker. Volume precisely the final solution
	Step 7	Recover the other RN by pouring the acid concentrate in a beaker (250 mL). Rinse the distillation vessel with nitric acid and combine this fraction with the concentrate. Volume precisely the final solution.

3.10.2. TITLE: Determination of High Energy γ emitters from i-graphite samples

GENERAL INFORMATION	
SUBJECT	**DESCRIPTION**
CW Reference	CWAP-26-2
Scope & Range of Application	This procedure is dedicated to the determination of the gamma emitters (^{60}Co) in irradiated graphite samples.
Principle	Aliquots from the acid concentrate obtained at the end of the distillation stage are sampled and transferred into specific pots for gamma spectrometry analysis.
Instrumentation	High purity Ge detectors with a very low background lead shielding and Genie 2000 software (Canberra)

OPERATING PROCEDURE	
SUBJECT	**DESCRIPTION**
Separation Method	No separation are needed
Calibration	The HPGe detector is calibrated with a multi-isotope reference standard solution.
Measurement geometry	HDPE 50 mL pot (SG 50 geometry).

EXPRESSION OF MEASUREMENT RESULTS	
SUBJECT	**DESCRIPTION**
Activity	Calculation of ^{60}Co activity: For a given aliquot *Vp* (50 mL) related to a given mass *mp* of dissolved graphite in the solution, the value mp is introduced in the Canberra software Genie 2000. The mass activity is then calculated from the calculation algorithm based on the ISO 10703 expressions which are integrated in the software.

3.10.3. TITLE: Determination of carbon-14 from i-graphite samples

GENERAL INFORMATION	
SUBJECT	**DESCRIPTION**
CW Reference	CWAP-26-3
Scope & Range of Application	This procedure is dedicated to the determination of ^{14}C in irradiated graphite samples.
Principle	^{14}C is present in the alkaline solution originated from the combining of the bubbling pots #3 and #4 plus rinsing after the mineralization stage. Part of this solution is mixed with a liquid scintillation cocktail in order to be analyzed by liquid scintillation counting.
Instrumentation	Packard Tricarb 3170 TR/SL Liquid Scintillation Counter
Reagents	- 20 mL liquid scintillation pots - Hionic Fluor (Perkin) scintillation cocktail dedicated to the measurement in alkaline solution

OPERATING PROCEDURE	
SUBJECT	**DESCRIPTION**
Separation Method	Mix 7 mL of the alkaline solution to 13 mL of Hionic Fluor cocktail. Shake vigorously, then put into the scintillation counter.

EXPRESSION OF MEASUREMENT RESULTS	
SUBJECT	**DESCRIPTION**
Activity	$c_{A(14C)} = \frac{(N - N_0)}{t_N . Vp \cdot m} x \frac{1}{\eta_{(T)}} x \frac{1}{Rdt} xV$
Efficiency	The counting efficiency is calculated from the quenching curve performed with ^{14}C reference standard. Quenching curve is established as a function of the quenching index parameter (tSIE for Tricarb counter). Increase of tSIE is obtained by mixing volume of reference standard solution with increasing volume of dichloromethane. The optimized window range is 0-152 keV.
Uncertainty	$\frac{u_c(c_{A(14C)})}{c_{A(14C)}} = 2.\sqrt{\left[\frac{\sqrt{N + N_o}}{N - N_o}\right]^2 + \left[\frac{u(\eta)}{\eta}\right]^2 + \left[\frac{u(V)}{V}\right]^2 + \left[\frac{u(Vp)}{Vp}\right]^2 + \left[\frac{u(m)}{m}\right]^2 + \left[\frac{u(Rdt)}{Rdt}\right]^2}$

GLOSSARY	
SUBJECT	**DESCRIPTION**
$C_{A(14C)}$	^{14}C mass expressed in Bq/kg
N	Gross impulse number (counts) related to ^{14}C window

N_0	Background impulse number (counts) related to ^{14}C window
t_N	Sample counting time in second (s)
t_{N0}	Background counting time in second (s)
V	Distillat volume in liter (L)
Vp	Aliquot volume in liter (L)
m	Sample graphite mass in kg
η	Detection yield in the ^{14}C window
Rdt	Chemical yield of the distillation stage

3.10.4. TITLE: Determination of tritium from i-graphite samples

GENERAL INFORMATION	
SUBJECT	**DESCRIPTION**
CW Reference	CWAP-26-4
Scope & Range of Application	This procedure is dedicated to the determination of ^{3}H as tritiated water (HTO) in irradiated graphite samples.
Principle	HTO is present in the acid solution originated from the combining of the bubbling pots #1 and #2 plus rinsing after the mineralization stage. Part of this solution is mixed, after neutralization, with a liquid scintillation cocktail in order to be analyzed by liquid scintillation counting.
Instrumentation	Packard Tricarb 3170 TR/SL Liquid Scintillation Counter
Reagents	- 20 mL liquid scintillation pots - Ultima Gold Low Level Tritium LLT (Perkin) scintillation cocktail

OPERATING PROCEDURE		
SUBJECT	**DESCRIPTION**	
Separation Method	Step 1.	Take an aliquot of the acid solution which contains HTO (and ^{36}Cl) and neutralize this aliquot with a NaOH solution.
	Step 2.	Distillate this neutralized solution (T = 100°C) Recover the HTO fraction in the condensate
	Step 3	Mix 10 mL of the HTO fraction to 10 mL of LLT cocktail. Shake vigorously, then put into the scintillation counter

EXPRESSION OF MEASUREMENT RESULTS	
SUBJECT	**DESCRIPTION**
Activity	$c_{A(T)} = \frac{(N - N_0)}{t_N . Vp \cdot m} x \frac{1}{\eta} x \frac{1}{Rdt} xV$
Efficiency	The counting efficiency is calculated from the quenching curve performed with ^{3}H reference standard. Quenching curve is established as a function of the quenching index parameter (tSIE for Tricarb counter). Increase of tSIE is obtained by mixing volume of reference standard solution with increasing volume of dichloromethane. The efficiency is around 25% on the optimized window (0-12 keV).
Uncertainty	$\frac{u_c(c_{A(T)})}{c_{A(T)}} = 2.\sqrt{\left[\frac{\sqrt{N + N_o}}{N - N_o}\right]^2 + \left[\frac{u(\eta)}{\eta}\right]^2 + \left[\frac{u(V)}{V}\right]^2 + \left[\frac{u(Vp)}{Vp}\right]^2 + \left[\frac{u(m)}{m}\right]^2 + \left[\frac{u(Rdt)}{Rdt}\right]^2}$

GLOSSARY	
SUBJECT	**DESCRIPTION**
$C_{A(T)}$	^{3}H mass expressed in Bq/kg

N	Gross impulse number (counts) related to ^{3}H window
N_0	Background impulse number (counts) related to ^{3}H window
t_N	Sample counting time in second (s)
t_{N0}	Background counting time in second (s)
V	Distillat volume in liter (L)
Vp	Aliquot volume in liter (L)
m	Sample graphite mass in kg
η	Detection yield in the ^{3}H window
Rdt	Chemical yield of the distillation stage

3.10.5. TITLE: Determination of Cl-36 from i-graphite samples

GENERAL INFORMATION	
SUBJECT	**DESCRIPTION**
CW Reference	CWAP-26-5
Scope & Range of Application	This procedure is dedicated to the determination of ^{36}Cl in irradiated graphite samples.
Principle	^{36}Cl is present in the acid solution originated from the combining of the bubbling pots #1 and #2 plus rinsing after the mineralization stage. Part of this solution is mixed with a liquid scintillation cocktail in order to be analyzed by liquid scintillation counting.
Instrumentation	- Filtration system - Usual glass of laboratory - Packard Tricarb 3170 TR/SL Liquid Scintillation Counter
Reagents	- NaOH solution (1M) - Sulfuric acid (1M) - Stannous sulfate solution (0;1 M) - Silver nitrate solution (0.1 M) -Deionized water (MilliQ® 18.2 MΩ.cm^{-1}) - 20 mL liquid scintillation pots - Ultima Gold Low Level Tritium LLT (Perkin) scintillation cocktail

OPERATING PROCEDURE		
SUBJECT	**DESCRIPTION**	
Separation Method	Step 1.	Take an aliquot of the acid solution which contains ^{36}Cl (and HTO) and neutralize this aliquot with a NaOH solution.
	Step 2.	Add H_2SO_4 in order to change from a Cl^- solution to a sulfate solution
	Step 3	Add the reducing specie ($SnSO_4$) in order to reduce all the oxydized species of chlorine which would have been formed during the distillation stage, into Cl^- species
	Step 4	Precipitate the Cl^- ions (including $^{36}Cl^-$) into $AgCl_{solid}$ by adding the solution of $AgNO_3$.
	Step 5	Filter the precipitate. Rinse it with deionized water
	Step 6	Dissolve the precipitate in water
	Step 7	Mix 10 mL of the solution with 10 mL of Ultima Gold LLT liquid scintillation cocktail.

		Shake vigorously, then put into the scintillation cou

EXPRESSION OF MEASUREMENT RESULTS	
SUBJECT	**DESCRIPTION**
Activity	$c_{A(36Cl)} = \frac{(N - N_0)}{t_N . Vp \cdot m} x \frac{1}{\eta_{(T)}} x \frac{1}{Rdt} xV$
Efficiency	The counting efficiency is calculated from the quenching curve performed with ^{36}Cl reference standard. Quenching curve is established as a function of the quenching index parameter (tSIE for Tricarb counter). Increase of tSIE is obtained by mixing volume of reference standard solution with increasing volume of dichloromethane. The efficiency is around 100% on the optimized window (0-2000 keV).
Uncertainty	$\frac{u_c(c_{A(36Cl)})}{c_{A(36Cl)}} = 2.\sqrt{\left[\frac{\sqrt{N + N_o}}{N - N_o}\right]^2 + \left[\frac{u(\eta)}{\eta}\right]^2 + \left[\frac{u(V)}{V}\right]^2 + \left[\frac{u(Vp)}{Vp}\right]^2 + \left[\frac{u(m)}{m}\right]^2 + \left[\frac{u(Rdt)}{Rdt}\right]^2}$

GLOSSARY	
SUBJECT	**DESCRIPTION**
$C_{A(36Cl)}$	^{36}Cl mass expressed in Bq/kg
N	Gross impulse number (counts) related to ^{36}Cl window
N_0	Background impulse number (counts) related to ^{36}Cl window
t_N	Sample counting time in second (s)
t_{N0}	Background counting time in second (s)
V	Distillat volume in liter (L)
Vp	Aliquot volume in liter (L)
m	Sample graphite mass in kg
η	Detection yield in the ^{36}Cl window
Rdt	Chemical yield of the distillation stage

3.10.6. TITLE: Determination of nickel-63 from dissolved i-graphite samples

GENERAL INFORMATION	
SUBJECT	**DESCRIPTION**
CW Reference	CWAP-26-6
Scope & Range of Application	This procedure is dedicated to the determination of ^{63}Ni in irradiated graphite samples.
Principle	^{63}Ni is present in the acid concentrate, resulting of the distillation stage. This concentrate contains also ^{90}Sr and ^{60}Co. After radiochemical separation stage based on the formation of the complex Ni-DiméthylGlyoxime on a resin, the activity of ^{63}Ni sample is then analyzed by liquid scintillation counting.
Instrumentation	- Usual glass of laboratory - Packard Tricarb 3170 TR/SL Liquid Scintillation Counter - ICP-MS quadrupolar Thermo Xseries 2
Reagents	- Certified Nickel chloride solution - Concentrated ammonia solution - Ammonium citrate solution - Dimethylglyoxime adsorbed onto a polymeric resin - Low pressure chromatography glass column - Nitric acid -Deionized water (MilliQ® 18.2 MΩ.cm^{-1}) - 20 mL liquid scintillation pots - Ultima Gold Low Level Tritium LLT (Perkin) scintillation cocktail

OPERATING PROCEDURE		
SUBJECT	**DESCRIPTION**	
Separation Method	Step 1.	Add a known amount of stable nickel (as a carrier) for the determination of the chemical yield
	Step 2	Take an aliquot of the acid solution which contains ^{36}Cl (and HTO) and neutralize this aliquot with a NaOH solution.
	Step 3.	Add volume of concentrated NH_3 solution for neutralizing the sample in the 8-9 pH values.
	Step 4	Add the ammonium citrate solution (5 10^{-4} mol/L)
	Step 5	Chromatography separation on the dimethylglyoxime resin put into a plastic column.
	Step 6	Elution with nitric acid (3M)
	Step 7	Mix 10 mL of the eluted solution with 10 mL of Ultima Gold LLT liquid scintillation cocktail
Chemical yield	At the end of the separation, an aliquot of the sample is analyzed by ICP-	

	MS in order to determine the chemical yield.

EXPRESSION OF MEASUREMENT RESULTS	
SUBJECT	**DESCRIPTION**
Activity	$c_{A(63Ni)} = \frac{(N - N_0)}{t_N . Vp \cdot m} x \frac{1}{\eta_{(T)}} x \frac{1}{Rdt} xV$
Efficiency	The counting efficiency is calculated from the quenching curve performed with ^{63}Ni reference standard. Quenching curve is established as a function of the quenching index parameter (tSIE for Tricarb counter). Increase of tSIE is obtained by mixing volume of reference standard solution with increasing volume of dichloromethane. The efficiency is around 100% on the optimized window (0-63 keV).
Uncertainty	$\frac{u_c(c_{A(63Ni)})}{c_{A(63Ni)}} = 2.\sqrt{\left[\frac{\sqrt{N + N_o}}{N - N_o}\right]^2 + \left[\frac{u(\eta)}{\eta}\right]^2 + \left[\frac{u(V)}{V}\right]^2 + \left[\frac{u(Vp)}{Vp}\right]^2 + \left[\frac{u(m)}{m}\right]^2 + \left[\frac{u(Rdt)}{Rdt}\right]^2}$

GLOSSARY	
SUBJECT	**DESCRIPTION**
$C_{A(63Ni)}$	^{63}Ni mass expressed in Bq/kg
N	Gross impulse number (counts) related to ^{63}Ni window
N_0	Background impulse number (counts) related to ^{63}Ni window
t_N	Sample counting time in second (s)
t_{N0}	Background counting time in second (s)
V	Distillat volume in liter (L)
V_p	Aliquot volume in liter (L)
m	Sample graphite mass in kg
η	Detection yield in the ^{63}Ni window
Rdt	Chemical yield of the distillation stage

3.10.7. TITLE: Determination of strontium-90 from dissolved i-graphite samples

GENERAL INFORMATION	
SUBJECT	**DESCRIPTION**
CW Reference	CWAP-26-7
Scope & Range of Application	This procedure is dedicated to the determination of ^{90}Sr in irradiated graphite samples.
Principle	^{90}Sr is present in the acid concentrate, resulting of the distillation stage. This concentrate contains also ^{63}Ni and ^{60}Co. The radiochemical separation stage is based on a chromatography separation by formation of the complex Sr-18-crown-6 ether. The 18-crown-6 ether is grafted on the resin. After the separation, the ^{90}Sr activity is analyzed by liquid scintillation counting.
Instrumentation	- Usual glass of laboratory - Packard Tricarb 3170 TR/SL Liquid Scintillation Counter - ICP-MS quadrupolar Thermo Xseries 2
Reagents	- Certified Strontium solution - Nitric acid - Chromatography resin containing 18-crown-6 ether - Low pressure chromatography glass column -Deionized water (MilliQ® 18.2 MΩ.cm^{-1}) - 20 mL liquid scintillation pots - Ultima Gold AB (Perkin) scintillation cocktail

OPERATING PROCEDURE		
SUBJECT	**DESCRIPTION**	
Separation Method	Step 1.	Add a known amount of stable strontium (as a carrier) for the determination of the chemical yield
	Step 2	Evaporation of the sample to dryness. The residue is then dissolved in nitric acid 8 M.
	Step 3.	Separation on the specific Sr-resin put into a glass column
	Step 4	Elution with nitric acid (0.05 M)
	Step 6	Mix 10 mL of the eluted solution with 10 mL of Ultima Gold AB liquid scintillation cocktail
Chemical yield	At the end of the separation, an aliquot of the sample is analyzed by ICP-MS in order to determine the chemical yield.	

EXPRESSION OF MEASUREMENT RESULTS	
SUBJECT	**DESCRIPTION**
Activity	$c_{A(90Sr)} = \frac{(N - N_0)}{t_N . Vp \cdot m} x \frac{1}{\eta_{(T)}} x \frac{1}{Rdt} xV$

Efficiency	The counting efficiency is calculated from the quenching curve performed with ^{90}Sr reference standard. Quenching curve is established as a function of the quenching index parameter (tSIE for Tricarb counter). Increase of tSIE is obtained by mixing volume of reference standard solution with increasing volume of dichloromethane. The efficiency is around 100% on the optimized window (0-2000 keV).
Uncertainty	$\frac{u_c(c_{A(90Sr)})}{c_{A(90Sr)}} = 2.\sqrt{\left[\frac{\sqrt{N+N_o}}{N-N_o}\right]^2 + \left[\frac{u(\eta)}{\eta}\right]^2 + \left[\frac{u(V)}{V}\right]^2 + \left[\frac{u(Vp)}{Vp}\right]^2 + \left[\frac{u(m)}{m}\right]^2 + \left[\frac{u(Rdt)}{Rdt}\right]^2}$

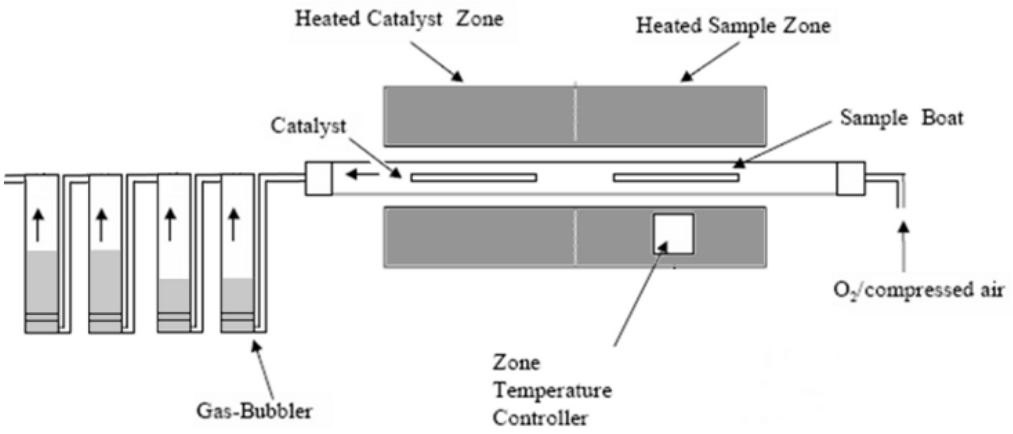
GLOSSARY	
SUBJECT	**DESCRIPTION**
$C_{A(90Sr)}$	^{90}Sr mass expressed in Bq/kg
N	Gross impulse number (counts) related to ^{90}Sr window
N_0	Background impulse number (counts) related to ^{90}Sr window
t_N	Sample counting time in second (s)
t_{N0}	Background counting time in second (s)
V	Concentrate total volume (after dissolution) in liter (L)
Vp	Aliquot volume in liter (L)
m	Sample graphite mass in kg
η	Detection yield in the ^{90}Sr window
Rdt	Chemical yield of the distillation stage

3.11. Procedures from Lab #27 UOM

3.11.1. TITLE: Determination of Tritium and carbon-14 from i-graphite samples

GENERAL INFORMATION	
SUBJECT	**DESCRIPTION**
Reference	CWAP-27-1
Scope & Range of Application	The procedure is used in the determination of ^{3}H and ^{14}C in irradiated graphite
Principle	0.5g of graphite powder is combusted in a tube furnace at 1000°C for 2 hours with oxygen flow rate of 100 $mL.min^{-1}$. A copper oxide catalyst is used in order to convert CO in CO_2 and HT to HTO. The off gases are passed through a series of gas bubbler in order to trap ^{3}H and ^{14}C. The first two bubblers contain 20mls of 0.1 $mol.l^{-1}$ HNO_3 to trap ^{3}H. The second two bubblers contain 40ml CarbonTrap® to trap CO_2. Two aliquots of trapping agent are taken form each bubbler. The ^{3}H and ^{14}C is measured via LSC.
Instrumentation	• Carbolite Carbon-14 and Tritium Analyser (MTT) Tube furnace • Liquid Scintillation Analyzer Tri-Carb 3100TR

OPERATING PROCEDURE		
SUBJECT	**DESCRIPTION**	
Separation Method	Step 1.	Combustion of sample and trapping of off-gases
	Step 2.	Measurement using LSC
	Step 3.	Recovery check carried out every 5 runs to monitor efficiency
	Step 4.	Blank runs carried out after each irradiated graphite run to ensure no cross contamination between runs

Flow chart	
Chemical Yield	The chemical yield is determined by comparison of direct measurement of a standard using LSC to measurement of a standard which has been combusted in the furnace. The quantity of this recovered standard is applied as a correction factor when calculating the isotopic content of graphite samples.
Calibration	The efficiency of the furnace is measured every five runs using ^{3}H and ^{14}C standards (provided by Perkin Elmer). The standards are prepared by dissolution in 10mls deionised water. A 1ml aliquot of each standard is combusted in the furnace and the amount recovered in the gas bubblers is measured by LSC. A second aliquot of standard is counted directly in the LSC. The LSC efficiency is calculated from a tSIE value with quenching curves established with ^{3}H and ^{14}C reference standards. Blank runs carried out after irradiated graphite runs. 0.5g of unirradiated graphite is combusted in the furnace with off gas collection. This shows the there is no retention and/or carry over of radioisotopes from one run to the next.
Measurement geometry	For tritium bubblers: 4ml of 0.1M HNO_3 into 16ml Scintisafe LSC cocktail For ^{14}C bubblers: 8ml CarbonTrap into 14ml Carboncount For background counting: same quantities of trapping agent/cocktail as above. For Standards: 1ml standard into 10ml Goldstar

EXPRESION OF MEASUREMENT RESULTS	
SUBJECT	**DESCRIPTION**
Chemical Yield	$CY = \frac{dpm_{Combustion}}{dpm_{direct}} = \text{recovery}$

Activity	The activity is calculated in $Bq.g^{-1}$ The formula for the calculation is: $A = \frac{[(dpm]_{sample} - dpm_{background}) \times DF}{60 \times CY} \times \frac{1}{Mass_{sample}}$ $DF = \frac{Mass_{TA}}{Mass_{Al}}$ $sf \frac{\square}{\square}$
Efficiency	Same as chemical yield
Uncertainty	Identification of uncertainty sources: ♦ DF: • u from mass determination • u from volume of aliquots ♦ CY: • σ from counting of ^{3}H or ^{14}C standard direct measurement (dpm_{direct}) • σ from counting of ^{3}H or ^{14}C standard after combustion ($dpm_{combustion}$) ♦ N: u from net dpm (N) from the equation: **N**= dpm_{sample}-$dpm_{background}$ if single measurement if done absolute uncertainty is obtained by propagation of absolute uncertainties from sample and background measurements. $\sigma(N) = \sqrt{u^2_{dpm_{sample}} + u^2_{dpm_{background}}}$ Quasi-variance if n replicates are calculated: $\sigma(sample) = \sqrt{\frac{\sum(dpm_{sample} - \overline{dpm_{sample}})^2}{n-1}}; \sigma(B) = \sqrt{\frac{\sum(dpm_{background} - \overline{dpm_{background}})^2}{n-1}}$ $\sigma(N) = \sqrt{\sigma(sample)^2 + \sigma(B)^2}$ **Note:** Uncertainty regarding efficiency is taking into account directly into uncertainty of dpm given by the equipment. Expression of activity uncertainty in relative terms is given by: $\frac{U(A)}{A} = \sqrt{\left(\frac{\sigma(N)}{N}\right)^2 + \left(\frac{u(CY)}{CY}\right)^2 + \left(\frac{u(DF)}{DF}\right)^2}$ where:

	$\frac{u(DF)}{DF}=\sqrt{\left(\frac{u(m_{al})}{m_{al}}\right)^2}$ $\frac{u(CY)}{CY}=\sqrt{\left(\frac{\sigma(dpm_{combustion})}{dpm_{combustion}}\right)^2+\left(\frac{\sigma(dpm_{direct})}{dpm_{direct}}\right)^2}$ The established coverage factor (**k**) is 2 for a confidence level of 95 % given the result expression: $A \pm 2 \cdot U(A)$
MDA	The minimum detectable activity is calculated according to the Currie equation shown in the equation: $MDA=\frac{4.66\times\sqrt{cpm_{background}/t}}{60}\times DF\times\frac{cpm_{background}}{dpm_{background}}$

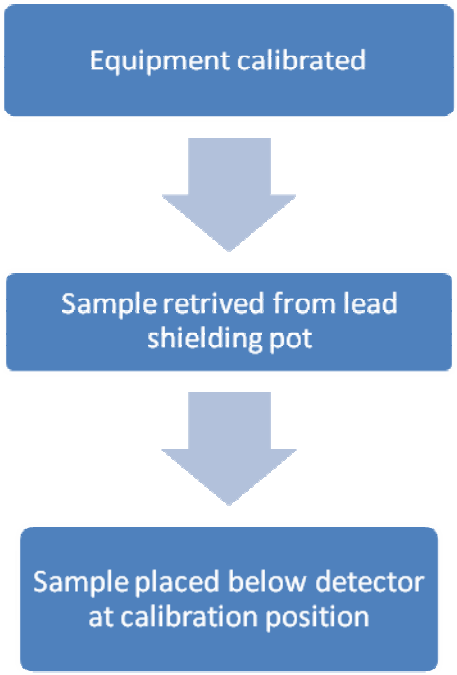
GLOSSARY	
SUBJECT	**DESCRIPTION**
CY	Chemical yield of the procedure
$dpm_{Combustion}$	dpm obtained in from combustion of the standard
dpm_{direct}	dpm obtained in from direct measurement of the standard
dpm_{sample}	Average activity of sample
$dpm_{background}$	Average activity of background (blank)
$cpm_{background}$	Average count rate of background (blank)
$Mass_{Al}$	Mass of the aliquot taken
$Mass_{TA}$	Mass of the trapping agent from which the aliquot was taken
DF	Dilution Factor of aliquot taken

References

3.11.2. TITLE: Measurement of Cobalt-60 in irradiated graphite samples

GENERAL INFORMATION	
SUBJETC	**DESCRIPTION**
Reference	CWAP-27-2
Scope & Range of Application	The procedure is used in the determination of ^{60}Co directly in the samples of graphite, without pre-treatment. This is a non-destructive technique.
Principle	The sample was measured directly using the NaI detector, no pre-treatment or preparation was performed. Care was taken to match sample geometry to that of calibration set-up.
Instrumentation	• Canberra Model 802.2x2 NaI(Tl) gamma spectrometer

OPERATING PROCEDURE	
SUBJETC	**DESCRIPTION**
Separation Method	No separation has been performed.

Flow chart	
Chemical Yield	There is no separation performed, therefore no chemical yield associated with this technique.
Calibration	The detector is calibrated with standards of known activity of 40kBq of each of the following radionuclides: ^{241}Am, ^{22}Na, ^{60}Co, ^{137}Cs, ^{152}Eu.
Measurement geometry	Samples were measured directly with full mass.

EXPRESION OF MEASUREMENT RESULTS	
SUBJETC	**DESCRIPTION**
Chemical Yield	N/A
Activity	$A = \frac{N}{LT \cdot Eff \cdot R \cdot M}$
Efficiency	$Eff = \frac{N}{LT \cdot A_R \cdot R}$
Uncertainty	$s_n = \sqrt{s_I^2 + s_b^2 + s_c^2}$

	$N = \frac{n}{t} \quad ; \quad s_N = \frac{s_n}{t}$ $\frac{u_{Eff}}{Eff} = \sqrt{\left(\frac{s_{N_{Srs}}}{N_{rs}}\right)^2 + \left(\frac{u_{A_{rs}}}{A_{rs}}\right)^2}$ $\frac{u_A}{A} = \sqrt{\left(\frac{s_N}{N}\right)^2 + \left(\frac{u_{Eff}}{Eff}\right)^2}$
MDA	$MDA = \frac{4.66 \cdot \sqrt{B}}{Eff \cdot M \cdot R \cdot LT}$

GLOSSARY	
SUBJECT	**DESCRIPTION**
A	Specific activity
A_{rs}	Activity of reference standard
B	Background count rate
c	Calculated continuum (counts)
Eff	Efficiency
M	Mass of sample
MDA	Minimum detectable activity
n	Total net counts
N	Net count rate
N_{rs}	Net count rate reference standard
R	Branching ratio gamma line
LT	Measurement time (Live Time)
t	Measurement time

References

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[3]. Lab, I. N. (1995). Gamma- Ray Catalogue Ge(Si).