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Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste

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CWRRT: Final Report on Statistical Evaluation & Conclusions (D.3.1.5)

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Document title

CWRRT. Final report on statistical evaluation & conclusions

Executive summary

The objective of the document is to present the results obtained in the radio-analytical inter-comparison Test on i-graphite or the so call Carbowaste Round Robin Test (CWRRT).

The Final statistical evaluation aims to identify the stronger and the weaker points in order to establish the continuous improvement lines of every lab and to establish new analytical procedures for i-graphite characterisation.

Another additional objective is the harmonisation of inventory determination within EU in order to increase the confidence in the nuclides determination in the whole life cycle of i-graphite from retrieval to final disposal

The results are presented and discussed by Lab and by nuclide along the five nuclides studied: H-3, C-14, Cl-36, Co-60, Ni-63 and Sr-90 based on the analytical methodologies-described in the CW-T-3-3-4, and the quote in the statistical evaluation.

Summary of the exercise in terms of quotation is done

Revisions

Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
00	01/02/2013	Issue	G. Piña, CIEMAT	M. Rodriguez, CIEMAT	G. Piña, CIEMAT	G. Piña, CIEMAT
01	21/04/2013	First issue	G. Piña, CIEMAT	M. Rodriguez, CIEMAT	G. Piña, CIEMAT	G. Piña, CIEMAT

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1. Introduction

1.1. Objectives and Strategic Aspects

An accurate knowledge of the inventory of radionuclides present in radioactive graphite waste from Nuclear Reactors is a critical parameter for a reliable categorisation of the waste in compliance with the existing disposal site regulations or future used. Therefore it is very important to have access to reliable radiochemical and radio-analytical procedures which provide results with a high accuracy.

The destructive measurement of the different nuclides present in the radioactive graphite from Nuclear reactors implies a complex process starting with the sampling up to the obtaining of the final result. It includes several steps such as mineralization or dissolution of the sample; radiochemical separation of the radionuclide needed for measurement; in some cases the preparation of the appropriate geometry for the measurement of the radiation; calibration of the measurement equipment; and finally the measurement itself. For each one of these steps different analytical techniques are available.

Various classic and recent techniques for radiochemical separation are in routine operation in the different labs as well as the measurement techniques commonly applied for alpha, beta and gamma emitting-radionuclides

The reliability of the final result at the end of the process cannot be evaluated in a simple way. The uncertainty of these results is a function of its precision (repeatability, reproducibility) and accuracy (proximity to the real value, that is to say the difference between a result (or mean) and the true value).

The precision of the result can be determined by an internal control in the laboratory using certified standards. However, the determination of the accuracy requires specific tasks such as:

- Carrying out repeated analysis using different methodology, different analysts and different techniques,
- Carrying out control analysis with a reference matrix, or
- Participation in interlaboratory comparison exercises.

Interlaboratory comparison studies are considered the most reliable and valid method to determine the precision and accuracy of the result.

The intense collaboration of scientists and the exchange of information, on waste samples and radio-analytical methods among the different beneficiaries will identify the scope of application, the strengths and weaknesses of the methods and provide opportunities for improvement, harmonisation, validation and finally qualification of selected methods within the European Community. The international character of the research programme will also lead to a higher confidence and acceptance of the applied procedures and of analytical results of each laboratory in the view of the Institutions that have the responsibility of the disposal facilities, the Regulatory Body and the public opinion. Besides, in this way, measurement and tests made in one country will be better accepted in another.

Steps to be taken to protect the environment from the short-term and long-term destructive effects of nuclear activities can be based upon reliable and accurate measurements.

2. CWRRT Roadmap

2.1. Type of proficiency Test. Scheme

The CWRRT is a proficiency testing organised under a co-operative study (Round Robin Test), where will be establish the laboratory assessment on a one-off basis. The sub-class of exercise selected is a "Split-level" scheme, where samples of a product or a material are divided into several parts with each participating laboratory testing one part of each sample and we can obtain information about systematic errors from the results of the participants.

Eleven involving Lab's from ten beneficiaries within CW-WP3 of eight Member states of UE:

- Bf:1 Fz Jülich (D)
- Bf:7 CIEMAT (S)
- Bf:8-C CEA-CADARACHE (F)
- Bf:8-S CEA-SACLAY (F)
- Bf:12 ENEA (IT)
- Bf:15 FI (LI)
- Bf:16 INR (RO)
- Bf:22 NRG (NL)
- Bf:23 SCK·CEN (B)
- Bf:26 SUBATECH (F)
- Bf:27 UoM (UK)

By consensus the Nuclides to be determined in CWRRT are:

^{3}H, ^{14}C, ^{36}Cl, ^{63}Ni and ^{60}Co; as mandatory additionally ^{90}Sr analyses can be done over the samples and others will be checked in function of lab members interested (^{152}Eu,…)

2.2. Execution scheme

The roadmap for CWRRT includes: (see figure 1)

- Sampling
- Testing homogeneity
- Transport scheme
- Packaging
- Transport
- Reception & Start CWRRT
- Interactive consultancies with coordinator
- Sending data first approach
- Sending final data
- Final evaluation

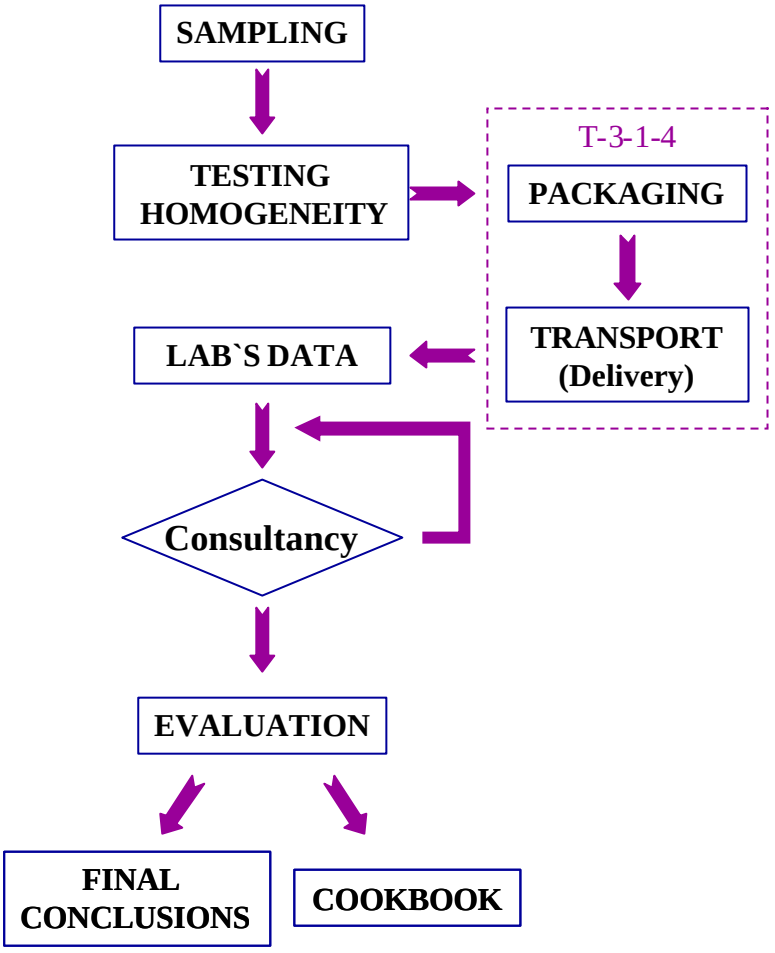

Figure 1- Roadmap of CWRRT

2.3. Sampling

Powder irradiated graphite from UNGG reactor sleeves was supplied for performing the CWRRT. About 55 g of this real waste were mechanically homogenize and sampling aliquots ~ 5 g per participant Lab. Each sample is subdivided into 2 blind sub-samples per partner (~ 2 g) and 1 g as reserve sample. Sampling homogeneity will be check by gamma spectrometry and performing an ANOVA for a F-test.

2.4. Packing and Transport

Samples Package must fill-in the ADR641 for exceptual materials, that means:

- Their individual contact package dose rate must be lower than 5 mSv·h-1
- Limited activity per Nuclide (specific and Total activity under values)
- Package must be labelled with UN2910.
- They need shielding, packages and over package
- Responsibility of coordinator (CIEMAT) till delivery (INCOTERM:DDP; ON SITE)

Transport details will be given in D-CW1003-WP3.3.1-2 "CWRRT TRANSPORT CONCEPT"

2.5. Split level and replications

A minimum number of aliquots and replications have been established in order to have an enough solid criterion for the statistical assessments of the proficiency test.

It was determined a minimum of three aliquots of sample, with similar amount of mass or volume. Two of those will be treated (mineralised, etc) for required analyses and the other one as a reserve aliquot to cover any accidental event that means loss of information.

It was recommended that each treated aliquot was divided in three equal aliquots for performing the separation procedure for each nuclide, which means six (6) sub-aliquots per nuclide and Lab.

Non-irradiated graphite was supplied to prepare the better blanks in order to subtract matrix effects in each determination and to perform a good estimation of minimum detectable activity in order to evaluate the determination capabilities of each procedure.

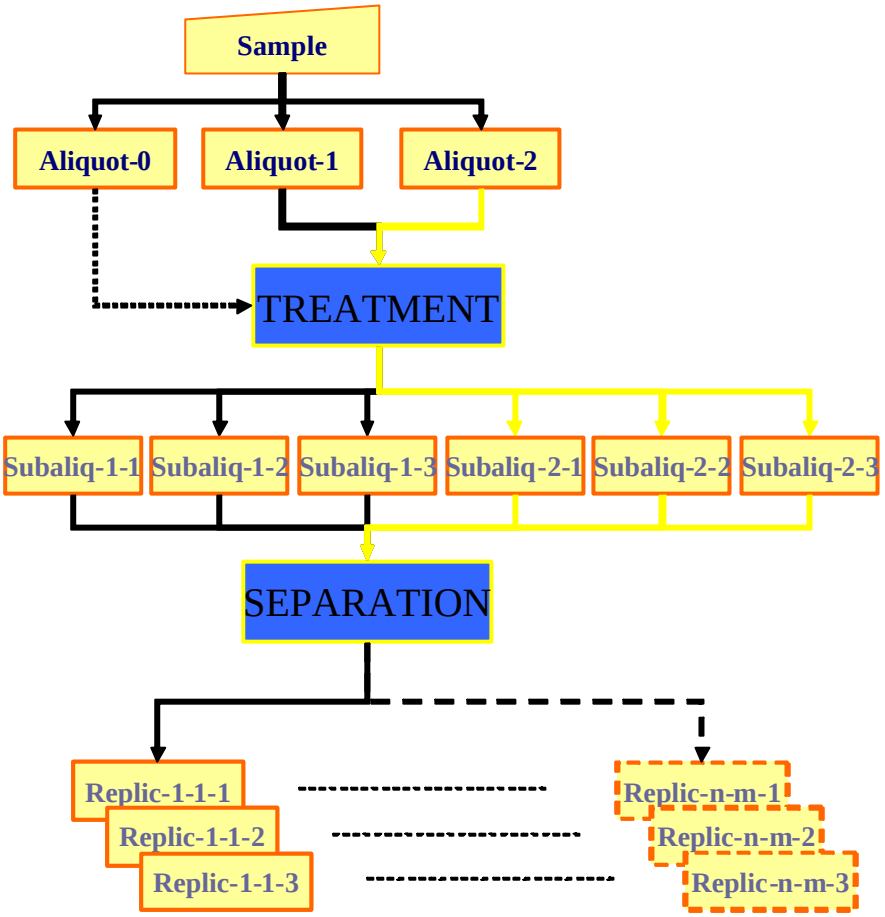

Figure 2. Samples, aliquot and determination flow-chart recommended

2.6. Data reporting

As is described in T-3.1.3 a data spread sheet was designed and distributed among partner Lab's in order to organise the reception of results and the communication between evaluator and responsible scientist of results given.

The data to be report are both identification data and data to be evaluated:

■

- Identification data
- ID -code of the LAB
- Responsible scientist
- Professional e-mail address
- Lab address

Determination data per sample/nuclide

- Separation method (3 characters code)
- Radiometric method (3 characters code)
- Activity calculation equation
- Minimum detectable activity (MDA) equation

Equations used for calculating specific activity and MDA is reporting also in T-3.3.4 using harmonised symbols and terms.

Result data per sample/nuclide

- Specific activity per sub-aliquot
- Specific MDA per sub-aliquot
- Type A uncertainty
- Type B uncertainty
- Determination date

To increase the reliability of counting statistics, it was recommended to perform not only one radiometric determination per sub-aliquot or blank but also at least three replications of each. In this way the counting value will be calculated through the arithmetic mean and the type A uncertainty will be calculated through the *quasi-variance* of the sample:

$$m_N = \mathbf{N} \quad \Rightarrow \quad m'_N = \bar{\mathbf{N}} = \frac{\mathbf{1}}{\mathbf{n}} \sum_{i=1}^{n} \mathbf{N}_i \qquad \textbf{(1)}$$

$$s_N = \sqrt{\frac{\mathbf{N}}{\mathbf{t}}} \quad \Rightarrow \quad s'_N = \sqrt{\frac{\sum_{i=1}^{n} \left(\mathbf{N}_i - \bar{\mathbf{N}}\right)^2}{\mathbf{n-1}}} \qquad \textbf{(2)}$$

Where:

N: Count rate of the sub-aliquot or blank

$\mathbf{N_i}$: Count rate of i replicant of any sub-aliquot or blank

$\bar{N}$: Arithmetic mean of n count rates of the same sub-aliquots or blank

m_N **or** m'_N: Estimation of population average of count rate of a sub-aliquot or a blank (*prima* means more than one observation)

s_N **or** s'_N: Estimation of standard uncertainty of count rate of a sub-aliquot or a blank (*prima* means of a population)

3. Statistical evaluation

3.1. Introduction

The unknown activity content and the matrix effects in the real sample used for proficiency test and inter-comparison exercise gives an additional difficulty to the knowing ones in this type of projects.

Reference values and target uncertainty must be evaluated by two alternative ways: consensus of expert and reliable laboratories or consensus of all participants in order to apply the statistical methods already existing.

First alternative is not in the scope of this project for two reasons:

- The most high qualify labs in E.U., for this kind of measurements, are part of the consortium and
- to devote a great budget for evaluation in labs outside the E.U. is not in the aim of the IP cost project of the Commission.

The second alternative is the one adopted with the restrictions and the limits that agreement values means for statistical evaluation.

3.2. Reference values

The evaluation of each individual Lab data (L) for each nuclide (j) will be done by weighted average of n replicates values given (μ), being the weighted factor the reported combined (type A and B) variance (u^2 (^{j}xi)).

$$ {}^{j}\mathbf{x}_{L} = \frac{\sum_{i=1}^{n} \left(\frac{{}^{j}\mathbf{x}_{i}}{\left(\mathbf{u}\left({}^{j}\mathbf{x}_{i}\right)\right)^{2}} \right)}{\sum_{i=1}^{n} \left(\frac{1}{\left(\mathbf{u}\left({}^{j}\mathbf{x}_{i}\right)\right)^{2}} \right)} \quad \textbf{(eq3)} $$

If the uncertainty estimation is done in the right way (taking into account all relevant contributions) the uncertainty associated with this value is:

$$ \mathbf{u}\left({}^{j}\mathbf{x}_{L}\right) = \sqrt{\frac{1}{\sum_{i=1}^{n} \left(\frac{1}{\left(\mathbf{u}\left({}^{j}\mathbf{x}_{i}\right)\right)^{2}} \right)}} \quad \textbf{(eq4)} $$

or if only type A uncertainty is evaluated the associated deviation will be given by:

$$s\left({}^{j}x_L\right) = \sqrt{\frac{\sum_{i=1}^{n}\left(\frac{\left({}^{j}x_i - {}^{j}x_L\right)^2}{\left(u\left({}^{j}x_i\right)\right)^2}\right)}{(i-1)\sum_{i=1}^{n}\left(\frac{1}{\left(u\left({}^{j}x_i\right)\right)^2}\right)}} \quad \textbf{(eq.5)}$$

It agreed that the estimation of population mean (μ) as reference value of specific activity (^{j}X) for each nuclide (j) is calculated by weighted average from data supplied ($^{j}x_L$) by each Lab (L) along the whole lab data (k) being the weighting factor the variance calculated for each Lab as above (u^2 ($^{j}x_L$)).

$${}^{j}X = \frac{\sum_{i=1}^{k}\left(\frac{{}^{j}x_L}{\left(u\left({}^{j}x_L\right)\right)^2}\right)}{\sum_{i=1}^{k}\left(\frac{1}{\left(u\left({}^{j}x_L\right)\right)^2}\right)} \quad \textbf{(eq.6)}$$

The uncertainty associated to this value is calculated by:

$$u\left({}^{j}X\right) = \sqrt{\frac{1}{\sum_{i=1}^{k}\left(\frac{1}{\left(u\left({}^{j}x_L\right)\right)^2}\right)}} \quad \textbf{(eq.7)}$$

3.3. Outliers

It is generally supposed that results that significantly deviate from the corresponding reference values can be recognised as outliers by means of tests as described in the IUPAC standard "Protocol for the design, conduct and interpretation of collaborative studies". The Outliers calculation procedure is indicates in figure 3.

The procedure essentially consists of sequential application of the Cochran and Grubbs tests (at 1% probability (P) level, 1-tail for Cochran, 2-tail for single Grubbs, overall for paired Grubbs) until no further outliers are flagged or until a drop of more than 22.2% (=2/9) in the original number of laboratories would occur:

The tests are applied over the mean values (non normalised), of each lab and nuclide, and their variance. -in this exercise two data per Lab due to that majority of participant Labs perform two analyses (six replicates per analysis) for samples G-1 and G-2.-

$$ {}^{j}m_{L} = \frac{\sum_{i=1}^{n} {}^{j}x_{i}}{n} \quad \text{(eq.8)} $$

$$ {}^{j}var_{L} = \frac{\sum_{i=1}^{n} \left({}^{j}x_{i} - {}^{j}m_{l} \right)}{n - 1} \quad \text{(eq.9)} $$

Where

$^{j}m_{L}$: Mean Value of n replicates of each Lab-sample (L)

$^{j}var_{L;}$ variance of n replicates of each Lab-sample (L)

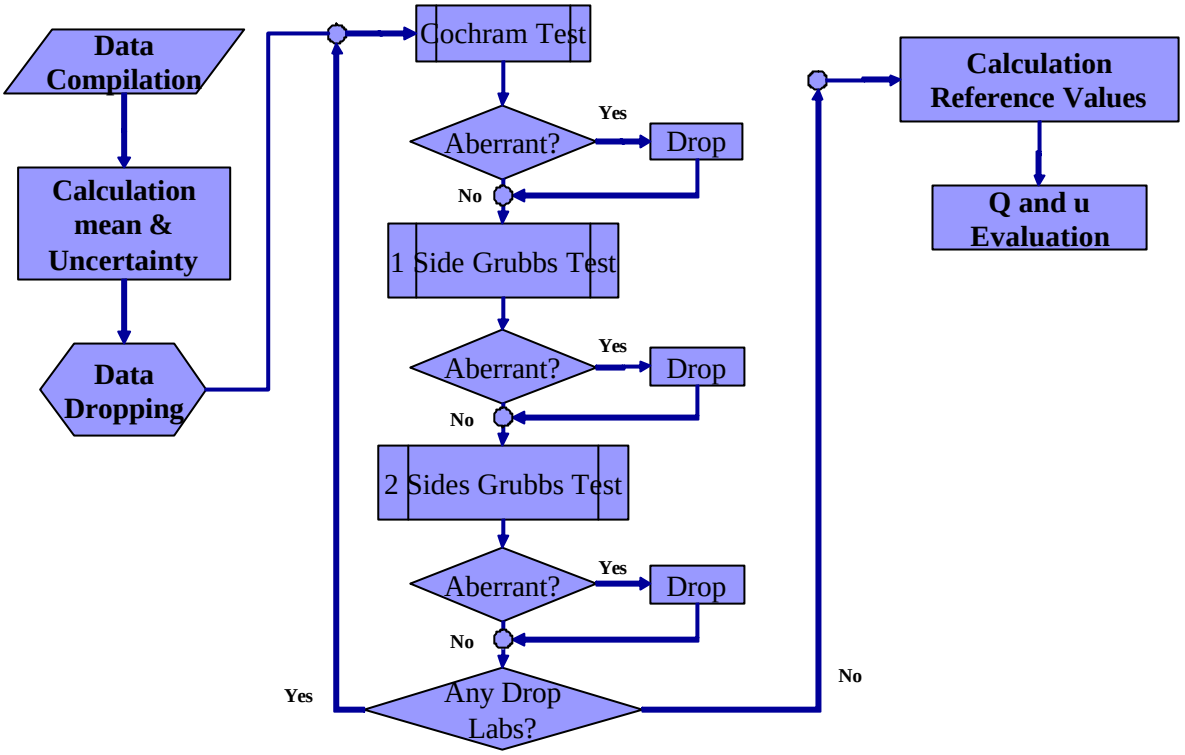

Figure 3. Outliers determination scheme

With the k values of means and variance is calculate the great mean value (^{j}M):

$$^{j}M = \frac{\sum_{L=1}^{k} {}^{j}m_{L}}{k} \quad \textbf{(eq.10)}$$

With k is calculated the maximum labs to be remove. The laboratories flagged by the following tests are removed till k is reduced in a ≥22.2% (2 of 9 laboratories) that means the lab limit k_{min} = k-[(2·k)/9)]

The outlier calculation is programmed in cycles that stops if the number of labs is reduced to k_{min} or in a complete cycle, one Cochran test and two Grubbs tests (single and pair) are completed, taking into account that both Grubbs tests have to be completed. Calculation finish if no outliers are found in a single cycle.

3.3.1. Cochran test

Firstly apply one-tail (at 1% of significance level) Cochran outlier test, this computes the intra-laboratory variance and removal of any laboratory whose critical value exceeds a tabular value given by number of labs tested and replicates per Lab. Six replicates are considered in this case for critical value comparison. If less data than six were given for Lab-sample the evaluator joint results in order to quote in the dropping test at similar significant than the others.

- First step of Cochran test is calculate the maximum variance ($Max({}^{j}var_L)$) and the limit number of Labs L', in order to know what is the maximum number of dropping cycles (C) to perform for finishing the outliers calculations
- The Cochran value is calculate using the following expression:

$$^{C}\mathbf{Cochran\_val}_{j} = \frac{\mathbf{Max}_{L=1}^{k}\left({}^{j}\mathbf{var}_{L}\right)}{\sum_{L=1}^{k} {}^{j}\mathbf{var}_{L}\,\mathbf{k}} \quad \textbf{(eq.11)}$$

- If the Cochran_val is higher than the Critical value (from the tables) for 1% of significance, L labs and 6 replicates, then the Lab with the $Max({}^{j}var_L)$ is flagged as outlier, eliminate from the Reference value calculation.
- Following the single-value Grubbs test (2-tail) as is explained below

3.3.2. Grubbs tests

Grubbs test is applied in order to eliminate aberrant values due to the mean value reporting, that is a inter-laboratory consistence test. To apply the single-value Grubbs test (2-tail) were proceeded as follow:

To calculate the maximum value of the means set excepted the maximum value and the minimum value of the means set excepted the minimum value:

$$\left[\underset{L=1}{\overset{k'}{Max}} - 1\right] = \underset{L=1}{\overset{k'-1}{Max}}\left({}^{j}m_L - \left[\underset{L=1}{\overset{k'}{Max}}\left({}^{j}m_L\right)\right]\right) \quad \text{(eq.12)}$$

$$\left[\underset{L=1}{\overset{k'}{Min}} - 1\right] = \underset{L=1}{\overset{k'-1}{Min}}\left({}^{j}m_L - \left[\underset{L=1}{\overset{k'}{Min}}\left({}^{j}m_L\right)\right]\right) \quad \text{(eq.13)}$$

Being k' the value of labs after the Cochran test performed.

Calculate de standard deviation of the k' mean values (S), the standard deviation of the k' mean values excepted the maximum mean value (SH) and the standard deviation of k' mean values excepted the minimum value of the means (SL).

$$S = \sqrt{\frac{\sum_{L=1}^{k'}\left({}^{j}m_L - {}^{j}M_{k'}\right)^2}{k' - 1}}; \quad \text{(eq.14)}$$

$$SH = \sqrt{\frac{\sum_{L=1}^{k'-1}\left({}^{j}m_L - \left[\underset{L=1}{\overset{k'-1}{Max}}\left({}^{j}m_L\right)\right] - {}^{j(H)}M_{k'-Max}\right)}{k' - 2}}; \quad \text{(eq.15)}$$

$$SL = \sqrt{\frac{\sum_{L=1}^{k'-1}\left({}^{j}m_L - \left[\underset{L=1}{\overset{k'-1}{Min}}\left({}^{j}m_L\right)\right] - {}^{j(L)}M_{k'-Min}\right)}{k' - 2}} \quad \text{(eq.16)}$$

The Grubbs Values: Grubbs_H and Grubs_L are calculated by:

$$Grubbs\_H = ABS\left(100 \times \left(1 - \frac{SH}{S}\right)\right) \quad \text{(eq.17)}$$

$$Grubbs\_L = ABS\left(100 \times \left(1 - \frac{SL}{S}\right)\right) \quad \text{(eq.18)}$$

The Higher value of Grubbs_H and Grubbs_L is compared with one side Grubbs critical value, taking from the tables of the single Grubs test for k' Labs and 1%(0.01) significant level, if the higher value is higher than Grubbs Critical value then the Lab is flagged as outlier and remove from reference value calculation. If Grubbs_H is the higher value found higher than critical value the Lab flagged is the one with the maximum mean, in the case that Grubbs_S is the higher the Lab with minimum mean is flagged as outlier.

Continuously is necessary to perform the pair value Grubbs Test over the k'' Labs remained not flagged as outliers. This test starts calculating the Maximum mean except the 2 high values and the Minimum mean except the 2 lower values.

$$\left[\underset{L=1}{\overset{k''}{Max}} - 2\right] = \underset{L=1}{\overset{k''-2}{Max}}\left({}^{j}m_{L}\right) - \left(\underset{L=1}{\overset{k''}{Max}}\left({}^{j}m_{L}\right) - \left(\underset{L=1}{\overset{k''-1}{Max}}\left({}^{j}m_{L}\right) - \left(\underset{L=1}{\overset{k''-1}{Max}}\left({}^{j}m_{L}\right)\right)\right)\right) \quad \text{(eq.19)}$$

$$\left[\underset{L=1}{\overset{k''}{Min}} - 2\right] = \underset{L=1}{\overset{k''-2}{Min}}\left({}^{j}m_{L}\right) - \left(\underset{L=1}{\overset{k''}{Min}}\left({}^{j}m_{L}\right) - \left(\underset{L=1}{\overset{k''-1}{Min}}\left({}^{j}m_{L}\right) - \left(\underset{L=1}{\overset{k''-1}{Min}}\left({}^{j}m_{L}\right)\right)\right)\right) \quad \text{(eq.20)}$$

Following is necessary to calculate the standard deviation of the mean values from the k''

$$SHL = \sqrt{\frac{\sum_{L=1}^{k'-2}\left[{}^{j}m_L - \left[Max\left({}^{j}m_L\right)\right] - \left[Min\left({}^{j}m_L - \underset{L=1}{\overset{k''-1}{Max}}\left({}^{j}m_L\right)\right)\right] - {}^{j(HL)}M_{k''-2}\right]^2}{k' - 3}};(eq.21)$$

$$SHH = \sqrt{\frac{\sum_{L=1}^{k'-2}\left[{}^{j}m_L - \left[Max\left({}^{j}m_L\right)\right] - \left[Max\left({}^{j}m_L - \underset{L=1}{\overset{k''-1}{Max}}\left({}^{j}m_L\right)\right)\right] - {}^{j(HH)}M_{k''-2}\right]^2}{k' - 3}};(eq.22)$$

$$SLL = \sqrt{\frac{\sum_{L=1}^{k'-2}\left[{}^{j}m_L - \left[Min\left({}^{j}m_L\right)\right] - \left[Min\left({}^{j}m_L - \underset{L=1}{\overset{k''-1}{Min}}\left({}^{j}m_L\right)\right)\right] - {}^{j(LL)}M_{k''-2}\right]^2}{k' - 3}};(eq.23)$$

Labs. except the higher and lower value (SHL), except the 2 higher values (SHH) and except the 2 lower values (SLL):

$$Grubbs\_pair = ABS\left(100 \times \left(1 - \frac{Min(SHL, SHH, SLL)}{S_{k'}}\right)\right);(eq.24)$$

Grubbs-pair statistics is calculate with the minimum value from SHL, SHH and SLL (S_{Min}) as: The critical value is taking from tables of pair Grubbs test for k'' Labs and 1%(0.01) significant level, and compared with Grubbs_pair value. If Grubbs pair is higher than Critical value the correspondence pair of means are flagged as outliers, i.e. if S_{Min} is SHL the Labs with the maximum and the minimum means are rejected for calculation of reference values, if S_{Min} is SHH the Labs with the two maximum means are dropped from this calculation and if S_{Min} is SLL the Labs with the two minimum means are flagged as outliers.

A new cycle is started at least the number of labs is k_{min} or not outlier is find in the complete cycle.

Finally the reference values are calculated removing laboratories flagged by the mentioned procedure.

3.4. Statistics for data evaluation

The first stage in the statistical evaluation of a proficiency test is to produce a score from a result x (a single measurement of analyte concentration in the material), obtaining an estimate of the bias (x-X), being X the real value or the assigned value as the best estimated of real value.

Proficiency test schemes proceed by comparing the bias estimate with a target value of standard uncertainty (σ).

Three procedures were pointed out, for discussion within the consortium, for statistical evaluation of data:

- Q-score
- z-score
- u-score

3.4.1. Q-score

Q-score is based not on standardised value but on the relative deviation:

$$ {}^{j}Q_{L} = \frac{{}^{j}x_{L} - {}^{j}X}{{}^{j}X} \quad \textbf{(eq.24)} $$

This type of score relates to analytical error without any reference to a target quality value of σ.

The distribution of Q-score can not be predicted but in practice the distribution is close to normal. It is expected that the overall distribution of Q would be centred on zero, in fact must be where the estimation of true value is all partners mean.

Q-score gives direct measure of the bias associated with determination, but the sensitivity to the outliners is rather low. It is necessary to examine the distribution of scores when laying down criteria.

With Q can be calculated:

- Q mean: ΣQ / (aliquots·samples)
- Q absolute: Σ| Q | / (aliquots·samples)
- Q maximum and Q minimum

3.4.2. u-score

Another way of evaluation is the use of u-score that is defined as the deviation of reference value regarding to the combined uncertainty between the one coming from the reference value calculation and the one coming from the individual determinations:

$$ {}^{j}u_{L} = \frac{{}^{j}x_{L} - {}^{j}X}{\sqrt{u^{2}\left({}^{j}X\right) + u^{2}\left({}^{j}x_{L}\right)}} \quad \textbf{(eq.25)} $$

The advantage of this evaluation method regarding to the others is that, on one hand it is not needed well-defined target values of the mean and standard deviation as in case of z–score. On the other hand this statistic parameter follows a well-known distribution and is sensitive to the outliners in order to detect inconsistencies in the declaration of activity and uncertainties opposite to Q-score parameter.

U-score follows a Student distribution and can be defined the criteria for evaluation just defining the degrees of freedom (ν). In this specific case performing 6 independent measurements the degrees of freedom are 5, searching in t student distribution the evaluation will be done:

Table 1. Evaluation parameters established for CWRRT Proficiency test

|u| Value	P (%)	Evaluation of x vs X	Qualification
|u| < 2.015	99.9	Values are **not significant** differences	Satisfactory (S)
2.015< |u| <2.571	99.0	Possibly Significant Doubts is cast on X, further evidences are needs for rejection	Acceptable (A1)
2.571< |u| <4.032	95.0	Significant X could have significant differences with x, is needed further data	Acceptable (A2)
4.032< |u| <6.869	90.0	Highly Significant. Probably the values have significant differences with X, needs further data to confirm	Acceptable(A3)
6.869< |u|	< 90	Very highly significant Values differ Significantly	Non Satisfactory (NS)

3.4.3. Z-score

The criterion of performance calling z-score, follows the equation:

$$ {}^{j}z_{L} = \frac{{}^{j}x_{L} - {}^{j}X}{s\left({}^{j}X\right)} \quad \textbf{(eq.26)} $$

Target value for σ can be achieved in several ways:

- By perception: σ is fixed arbitrarily
- By prescription: σ is an estimate of the precision required
- By reference to validate methodology: When a standard method is prescribed
- By reference to a generalised model: Derived to a general model of precision

If X and σ are good estimations of population mean and standard deviation and the underlying distribution were normal, the z would be normal distributed centred in zero [$z \rightarrow N(0,1)$]

The main characteristics of z for interpreting data are:

- z is standardised, so it is useful for compared between all analytes, test materials and analytical methods
- z can be combined (with due caution) to be a composite score for a laboratory in a proficiency test:
-
- Sum of z-scores (SZ = Σz) or normalised RSZ = $\Sigma z/\sqrt{m}$ that follows a normal distribution N (0,m), and allows the use of information about the sign of bias.
-
- Sum of squares scores, SSZ = Σz^2 or normalised RSSZ = $\Sigma z^2/m$; that follows a distribution χ^2 (m) and not allows the cancellation of different sign values with the same magnitude.
-
- Sum of absolute values of scores, SAZ = $\Sigma |z|$; It is useful if there are extreme outliners or many outline lab's

The meaning of z-score can be immediately appreciated:

- $|z| \leq 2$: Satisfactory
- $2 < |z| < 3$: Questionable
- $|z| \geq 3$: Unsatisfactory

4. RESULTS

4.1. Sampling and Homogeneity test

Samples were selected from irradiated graphite sleeves powder from an UNGG, selecting from different samples enough amounts to satisfying the analysis needs from the labs and to satisfy the transport concept.

The evaluator, in a conservative way, consider any aliquot deliver in each lab as different sample in order to assume a possible heterogeneity of the nuclide distribution, but according to the 'a priori' homogeneity study and 'a posteriori' homogeneity studies it is allow to consider

each aliquot of the same sample, therefore each aliquot result is considered in the evaluation as different Lab result, that means from Lab n the result from aliquot 1 is treated as Lab-n-1 and the one from aliquot 2 is treated as Lab-n-2. In this way the trueness of statistical evaluation increase (as the number of Labs increase) and the intra-lab evaluation can be checked in a more proper way.

The bulk material, prepared in this way, is thought to be homogeneous according to the method described.

Table 2. mass of samples delivery per Lab

LAB#	GO m(g)	G1 m(g)	G2 m(g)	TOTAL m(g)	GV m(g)
L1	1,3009	2,3698	2,2539	5,9246	1,3093
L2	1,2812	2,2327	2,2944	5,8083	1,0821
L3	1,2977	2,2505	2,2156	5,7638	1,0152
L4	1,0797	2,2594	2,1780	5,5171	1,0265
L5	1,1829	2,2114	2,0986	5,4929	1,0556
L6	0,9660	2,2706	2,1661	5,4027	1,0938
L7	1,0621	2,2685	2,0813	5,4119	1,0357
L8	1,1392	2,4432	2,2435	5,8259	1,0919
L9	1,1394	2,4946	2,1382	5,7722	1,0471
L10	1,0308	2,1974	2,1046	5,3328	1,1601
L11	0,9713	2,1978	2,1869	5,3560	1,1671
TOTAL (g)	12,4512	25,1959	23,9611	61,6082	12,0844

The material was divided into the containers that were used for dispatch to the participant Labs and in the stead of select a minimum of 10 containers by random, it was decided to check the homogeneity the whole population, 33 containers, 22 with approximately 2 g of i-graphite and 11 with approximately 1 g of i-graphite.

The 33 containers were measured by gamma spectrometry calibrated by LABSOCS software and validate by standards measurements spiked on virgin graphite. An estimation of sampling

variance and analytical variance by one way ANOVA without exclusion of outliers is done. An estimation of activity through the net peak counting rate by gram (CPS/g) of two lines of Co-60 (1173 and 1332 keV), one line of Eu-154 using (344 keV) and one line of Cs-137 (661 keV).

The F-Test were performed for a probability of 5% were the critical value for 33 samples (ν=32) is 3,9909237

Table 3. Data of the ANOVA test

ANOVA 1	**Summary**	**^{60}Co 1173 keV**				
Groups	**n**	**Sum**	**Average**	**Variance**		
m(g)	33	61,6082	1,8669152	0,2901356		
area Co-1	33	533,39851	16,163591	0,1025152		
Origin	**Sum X^2**	**Degree Fre.**	**SQ Aver.**	**F**	**Prob**	**Crit.Value**
Am. Group	3372,5167	1	3372,5167	**17178,201**	**1,678E-79**	**3,9909237**
In Group	12,564824	64	0,1963254			
Total	3385,0815	65				
ANOVA 2	**Summary**	**^{60}Co 1332 keV**				
Groups	**n**	**Sum**	**Average**	**Variance**		
m(g)	33	61,6082	1,8669152	0,2901356		
area Co-2	33	480,62681	14,564449	0,084741		
Origin	**Sum X^2**	**Degree Fre.**	**SQ Aver.**	**F**	**Prob**	**Crit.Value**
Am. Group	2660,2515	1	2660,2515	**14192,679**	**7,367E-77**	**3,9909237**
In Group	11,996051	64	0,1874383			
Total	2672,2476	65				
ANOVA 3	**Summary**	**^{152}Eu 334 keV**				
Groups	**n**	**Sum**	**Average**	**Variance**		
m(g)	33	61,6082	1,8669152	0,2901356		
area Eu	33	13,264833	0,4019646	0,0102967		
Origin	**Sum X^2**	**Degree Fre.**	**SQ Aver.**	**F**	**Prob**	**Crit.Value**
Am. Group	35,41032	1	35,41032	**235,72913**	**3,89E-23**	**3,9909237**
In Group	9,6138331	64	0,1502161			

Total	45,024153	65				
ANOVA 4	**Summary ^{137}Cs 662 keV**					
Groups	**n**	**Sum**	**Average**	**Variance**		
m(g)	33	61,6082	1,8669152	0,2901356		
area Cs	33	6,3882086	0,1935821	0,0061062		
Origin	**Sum X^2**	**Degree Fre.**	**SQ Aver.**	**F**	**Prob**	**Crit.Value**
Am. Group	46,200719	1	46,200719	**311,9123**	**2,7E-26**	**3,9909237**
In Group	9,4797353	64	0,1481209			
Total	55,680454	65				

In the results on the table we can see that in every case (even at micro-component level) the value of statistic F > Critical value, so that the sample can be distributed as homogeneous for the inter-comparison proposed and non correction of the values will be applied in function of the heterogeneity of activity content.

A second homogeneity test based on lab results were done over the values submitted in order to check qualitatively the homogeneity of pure beta emitters (C-14 and H-3) as more representative radionuclides (more data reported) and Co-60 as gamma emitters like in the case of ‘a priori’ homogeneity distribution.

The object of this homogeneity test is to ensure the homogeneity assumption based on ANOVA test in order to extend this result for non gamma emitters within the bulk material.

In figure 4 is plotted the frequency of the results for each activity range for H-3, C-14 and Co-60 representing the percentage of the results in each range, and in figure 5 the same representation but distinguishing the origin of the results. The activity values represented are in relative terms.

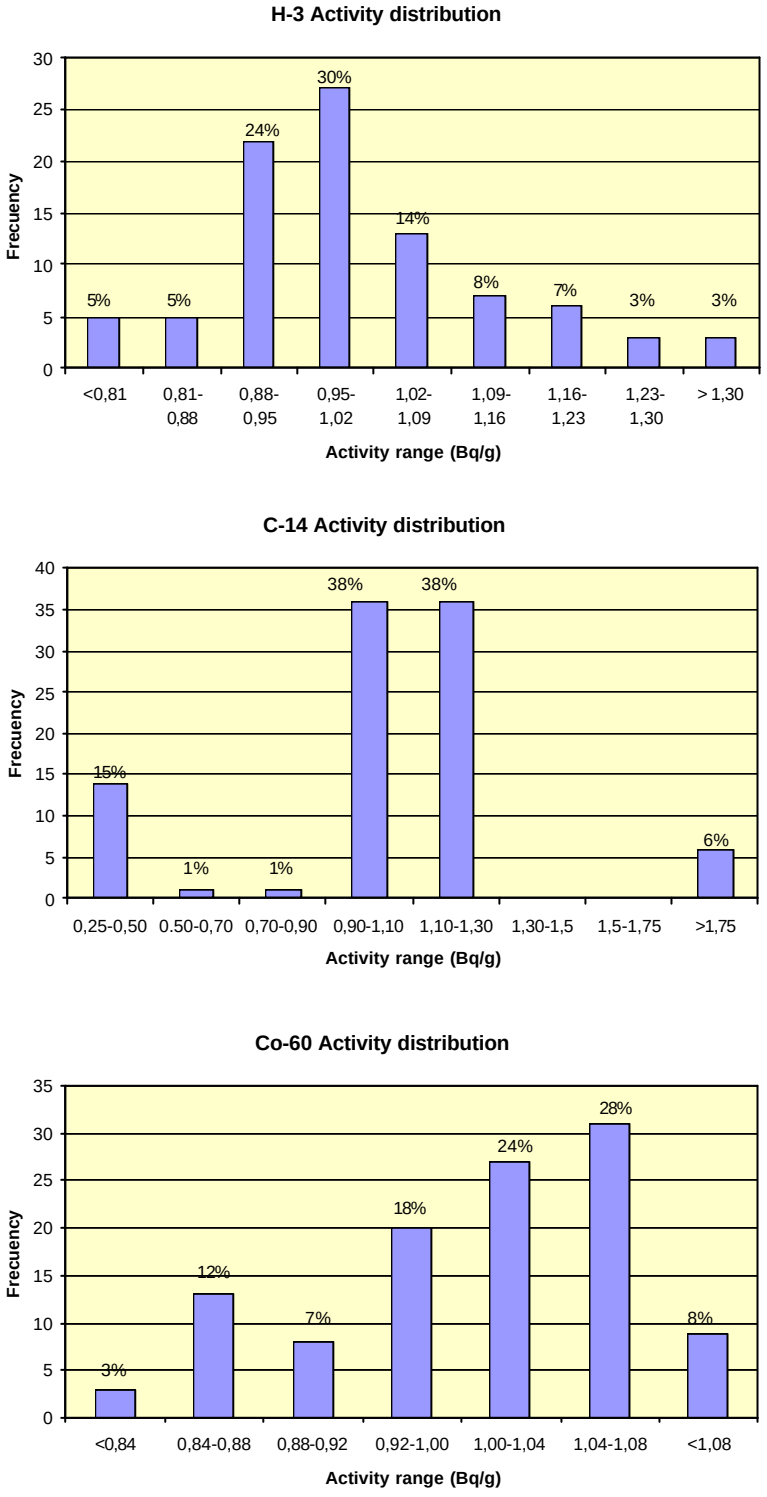

Figure 4. Frequency diagrams for " a posterior" homogeneity study by Nuclide

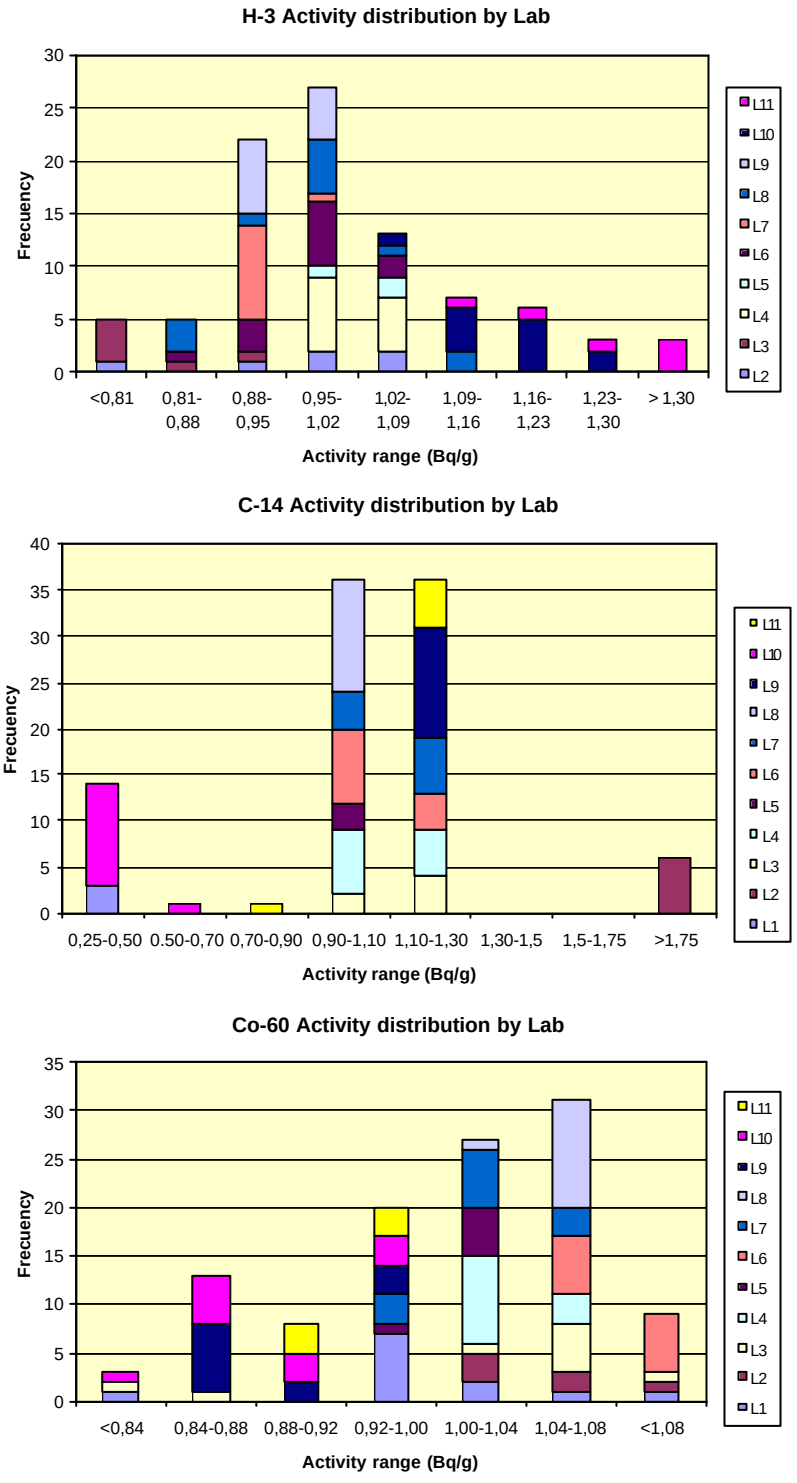

Figure 5. Frequency diagrams for " a posterior" homogeneity study by Nuclide/Lab

In figure 4 can see that in H-3 activity determination is found 68% of the results with a deviation of =10% around the reference value and a deviation =20% for the 88% of the results.

Analysis of C-14 determination results is found a 38% of the results with a deviation =10% around the reference value and a deviation of =30% in a 78% of the results.

Meanwhile the 77% of Co-60 results present deviation from reference value =10% and 97% of results has a deviation =15%. Since assuming this result as reference, due to that the F-test is performed with Co-60 line in the original samples and taking into account that the distribution of the results are found in the same range for H-3 and C-14 we can confirm the homogeneity of the samples distributed.

In figure 5 is seen that the outer values of ±10% and ±205 in H-3 plot and ±30% in C-14 frequency diagram are concentrate in a few set of labs that indicates more a systematic than a random effect in the deviation.

4.2. Reference Values Calculation

Calculation of weighted average of each Lab-aliquot and their uncertainty is made by equations 3 and 4 calculating the activities from decay from the data of calculation (submitted by each Lab) to the starting project date 1st April 2008.

Specific activity Reference Values and their Uncertainties are calculating by equations 5 and 6 and reporting normalised, so that in order to have a dimension the activity and uncertainty values are reported regarding to the lower activity value. (see table 4).

Table 4. Relative reference values data

Nuclide	Primary Data	Labs	OUTLIERS			X' (Bq/g)	U (Bq/g)
			Cochran	Grubbs_single	Grubbs_pair		
H-3	91	**16**	1	0	0	**3,65E+03**	1,38E+02
C-14	94	**17**	0	0	0	**8,50E+02**	1,03E+02
Cl-36	69	**12**	2	1	0	**1,00E+00**	5,02E-02
Co-60	111	**19**	2	0	0	**1,47E+03**	1,71E+01
Ni-63	72	**12**	1	0	2	**5,00E+03**	9,12E+01
Sr-90	27	**5**	1	0	0	**3,30E+00**	7,32E-01
Totals	**464**	**81**	**7**	**1**	**2**		

4.3. Statistical Evaluation by Nuclide and Discussion

The data treated are study for based on the intra-laboratory data and inter-laboratory in order to establish the best way of estimation of the procedures applied to i-graphite. It was extremely useful the procedure document in order to establish the explanation of the collected data.

The evaluation were performed using Q-score and u-score in order to have two quantitative and easy to understand parameter and statistical approach in a normal distribution that qualify the methods respectively. Z-score is also calculate as is indicate in 3.4.3 but results did not contribute for further information to the evaluation for this reason it is not studied in this document.

4.3.1. Evaluation of Tritium

The methods applied for H-3 determination are based on a complete combustion in a pure O_2 current with an inert gas (N_2) that is used as a carrier of the combustion gases. The chemical yield is calculated processing solid or liquid standards in both ways: always when a treatment is performed and prior to each separation process batch or regularly within a determined time period and independently of a determination process.

Trapping of H-3 is performed using a weak acidic media in trapping bottles and eventually associate a distillation process or using commercial trapping solutions. The methods used in the CWRRT are summarise in figure 6.
The methods by Lab are summarizing in Table 5.

Table 5. Methods applied for tritium determination

L2-1	L3-1	L4-1/2	L5-1	L6-1/2	L7-1/2	L8-1/2	L9-1/2	L10-1/2	L11-1
COM/DIT	REF	CAF	COM	CAF	CAF	CAF	CAF	CAF	CAF
LSC	LSC	LSC	LSC	LSC	LSC	LSC	LSC	LSC	LSC

Where:

- COM: is a combustion Chamber or a Calorimeter
- REF: Reflux dissolution
- DIT: Distillation
- CAF: Catalytic combustion furnace
- LSC: Liquid Scintillation Counting

Practically every Lab use the same method to separate H-3 and all Labs use LSC for determination, so that the differences found are not assignable to the method but to the operational or methodological reasons.

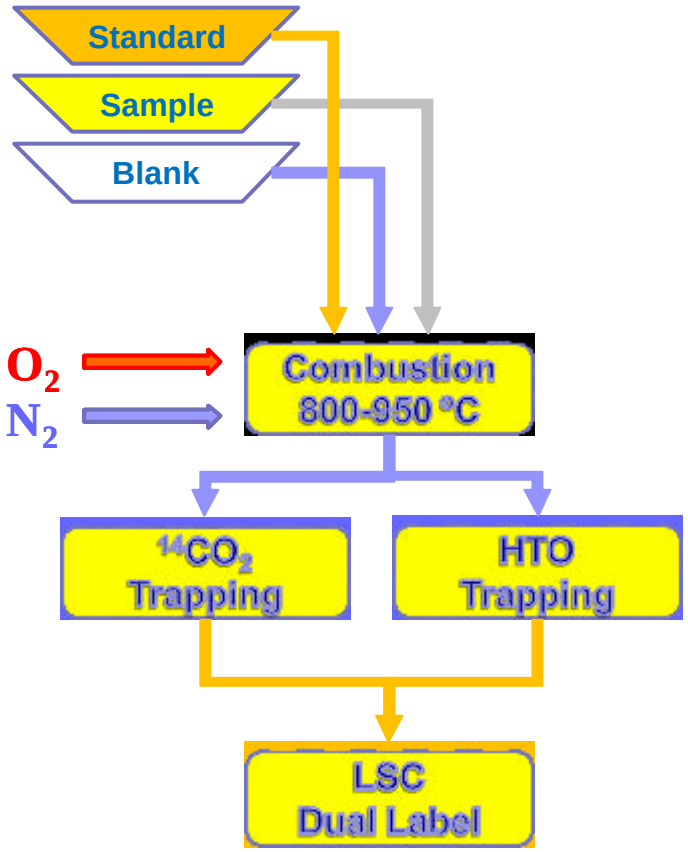

Figure 6. Flow chart for the H-3 determination methods

10 Labs supplied 91x4 primary data (Activity, uncertainty, MDA and determination date) to calculate 16 weighted average and their uncertainty, means and variance.

Normalize results is shown in figure 7. The outliers' calculation gives 1 outlier in the first Cochran Test (by internal variance) that is plotted as red dot in Figure 7.

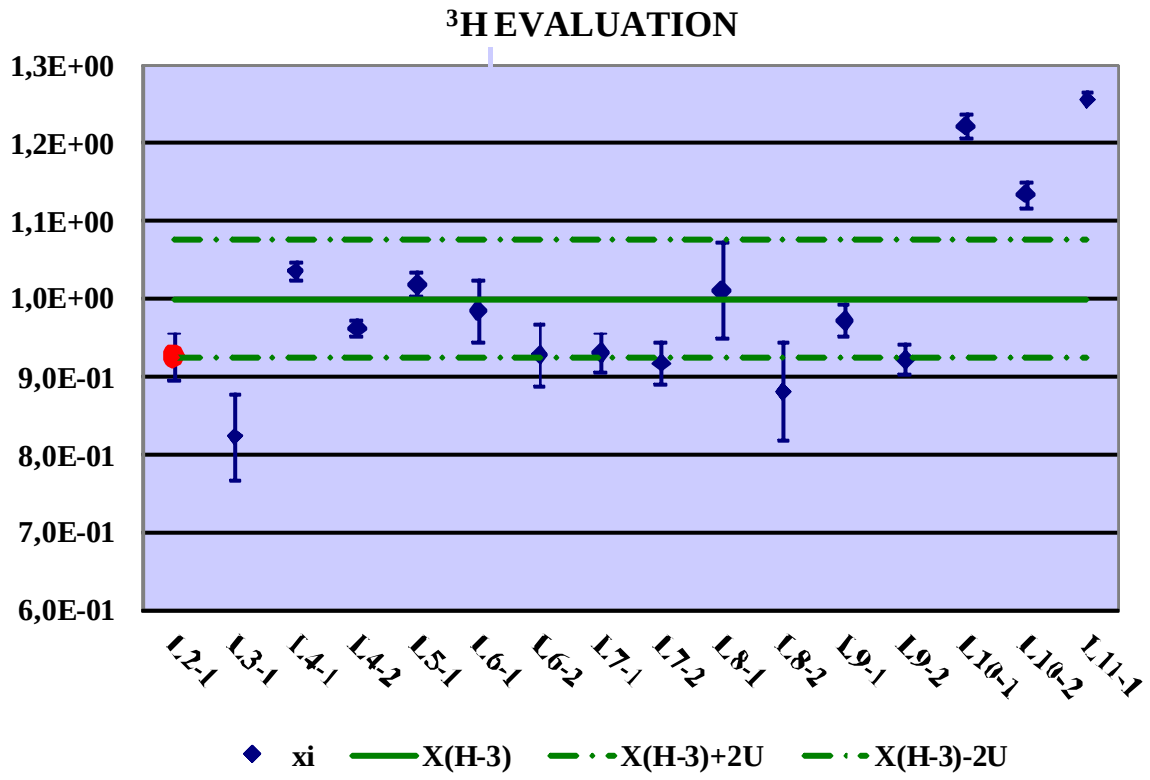

Figure 7. Reults for H-3 evaluation

It is observed that there are 4 values lower than $^{H-3}X-2\cdot(^{H-3}U)$ that use to be associated with the recovery of H-3 where several factors can have influence:

- The leaks of the systems specially in the conduction from combustion chamber to trapping bottles
- Trapping solution effectiveness, could be affected by storage condition or time degradation
- Not complete combustion of samples
- Chemical yield calculations use of standards to calibrate the recovery prior to separation process.

Also 3 values are higher than $^{H-3}X+2\cdot(^{H-3}U)$ that use to be associated with the LSC calibration when it is not use a double labelled counting method and the activity of radiocarbon interfere in the analysis window of H-3.

Relative difference calculation (Q-score) gives the following results:

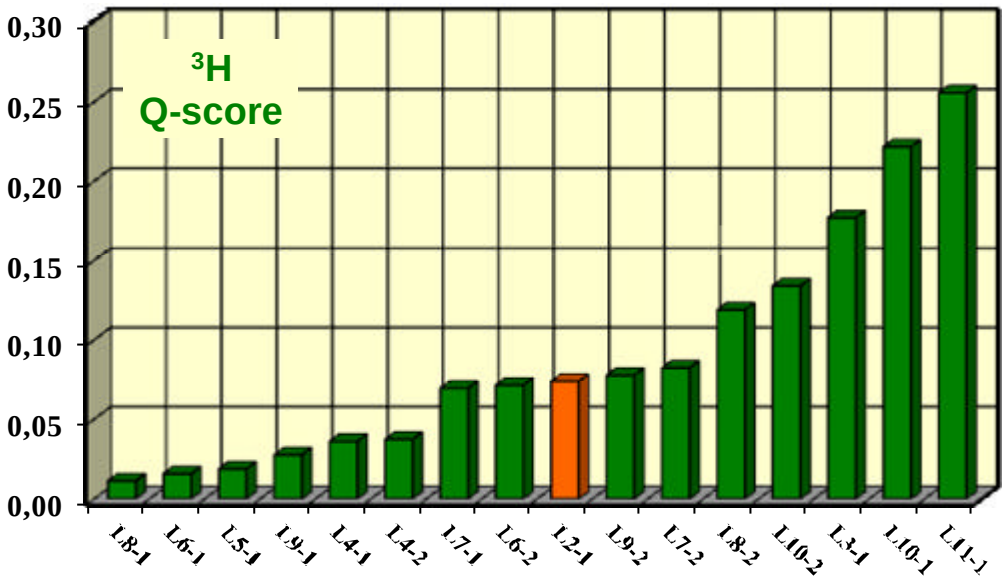

Figure 8. Q-score for H-3 evaluation

We can see that only 3 values quote up to 15% from reference value, even the one dropped from reference value calculation (L-2-1) quote less than 10% of relative deviation.

	n =	14
P		**u**
0.1	90	1.761
0.05	95	2.145
0.01	99	2.977
0.001	99.9	4.140

Levels for u–score evaluation for tritium were calculated from t-Student distribution for $\nu = k'-1 = 14$ degrees of freedom.

u-score calculation results are plotted in figure 9.

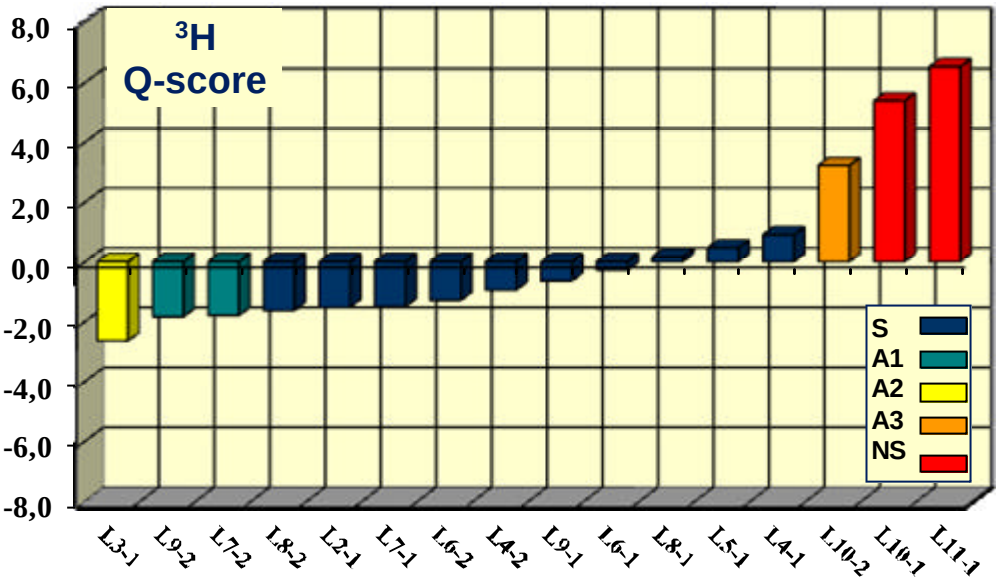

Figure 9. U-score triutium evaluation

Results are summarized in table 7

Table 7. Results of H-3 evaluation.

	xi	2·Ui	Q-score	u-score	
L2-1	9.26E-01	2.97E-02	0.07371	-1.53448	S
L3-1	8.23E-01	5.53E-02	0.17695	-2.64188	A2
L4-1	1.04E+00	1.29E-02	0.03596	0.90123	S
L4-2	9.63E-01	1.08E-02	0.03729	-0.94961	S
L5-1	1.02E+00	1.41E-02	0.01877	0.46546	S
L6-1	9.84E-01	4.02E-02	0.01579	-0.28612	S
L6-2	9.29E-01	4.02E-02	0.07131	-1.29213	S
L7-1	9.31E-01	2.62E-02	0.06927	-1.50656	S
L7-2	9.18E-01	2.59E-02	0.08226	-1.79746	A1
L8-1	1.01E+00	6.21E-02	0.01131	0.15565	S
L8-2	8.81E-01	6.21E-02	0.11869	-1.63337	S
L9-1	9.72E-01	1.99E-02	0.02761	-0.64669	S
L9-2	9.22E-01	1.87E-02	0.07762	-1.84242	A1
L10-1	1.22E+00	1.62E-02	0.22139	5.38816	NS
L10-2	1.13E+00	1.75E-02	0.13380	3.21634	A3
L11-1	1.26E+00	1.04E-02	0.25556	6.52595	NS

Over 16 data 37.5% present deviations lower than 5%, 31.25% in the range of 5-10%. 12.5% in the range of 10-15% and 18.75% a deviation higher than 15%.

In the case of u score there are 10/16 values quoted Satisfactory. 2/6 values quoted Aceptable at level 1. 1/16 quoted acceptable at level 2. 1/16 quoted acceptable at level 3 and 2/16 quoted non satisfactory, that means that ≈75% of the results has a probability higher than 99.9% of determine the right value of H-3 content of the sample. only 16% of the results has a probability lower than 90% to determine correctly H-3 in i-graphite.

4.3.2. Evaluation of Radiocarbon

The methods applied for C-14 determination are based on the same principle that H-3 described in the point 4.3.1. Normally the method is applied at the same time for both recovery HTO steam in a bottle and $^{14}CO_2$ in another with specific trap solutions respectively. Another alternative method was applied that consists in oxidizing dissolution of matrix and trapping $^{14}CO_2$ by alkaline media in carbonate form.

The methods are in the flow chart of figure 10 that keeps similarities to figure 6 also in Table 8 is summarized in codes the method used. L2-1 didn't use. obviously. in the case of C-14 separation distillation process being the same the rest of the procedure.

Table 8. Methods applied for radiocarbon determination

L1-1	L2-1	L3-1	L4-1/2	L5-1	L6-1/2	L7-1/2	L8-1/2	L9-1/2	L10-1/2	L11-1
OXD	COM	REF	CAF	COM	CAF	CAF	CAF	CAF	CAF	CAF
LSC	LSC	LSC	LSC	LSC	LSC	LSC	LSC	LSC	LSC	LSC

Where

OXD is oxidizing dissolution

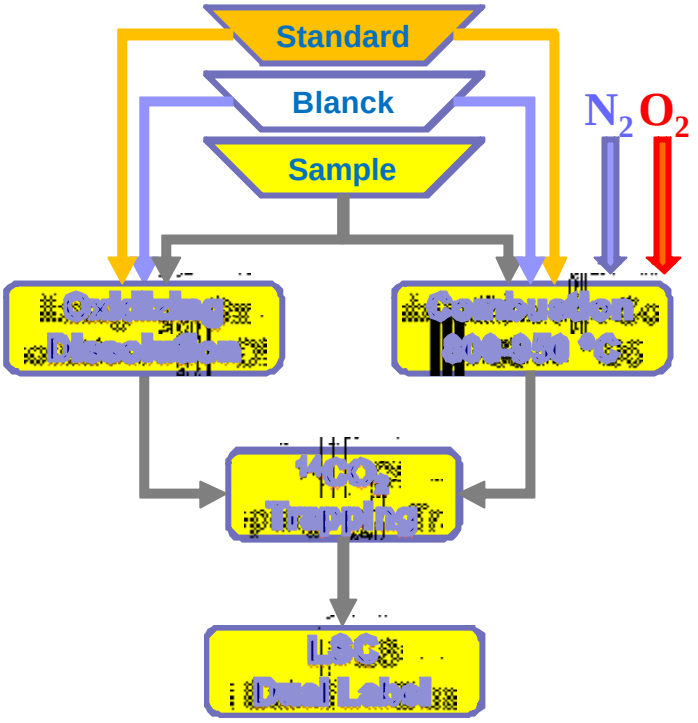

Figure 10. Flow chart for the C-14 determination methods

11 Labs supplied 94x4 primary data (Activity. uncertainty. MDA and determination date) to calculate 17 weighted average and their uncertainty. means and variance. Normalize results is shown in figure 11.

No outliers were found in the outliers' calculation that means all results contribute to reference value calculation.

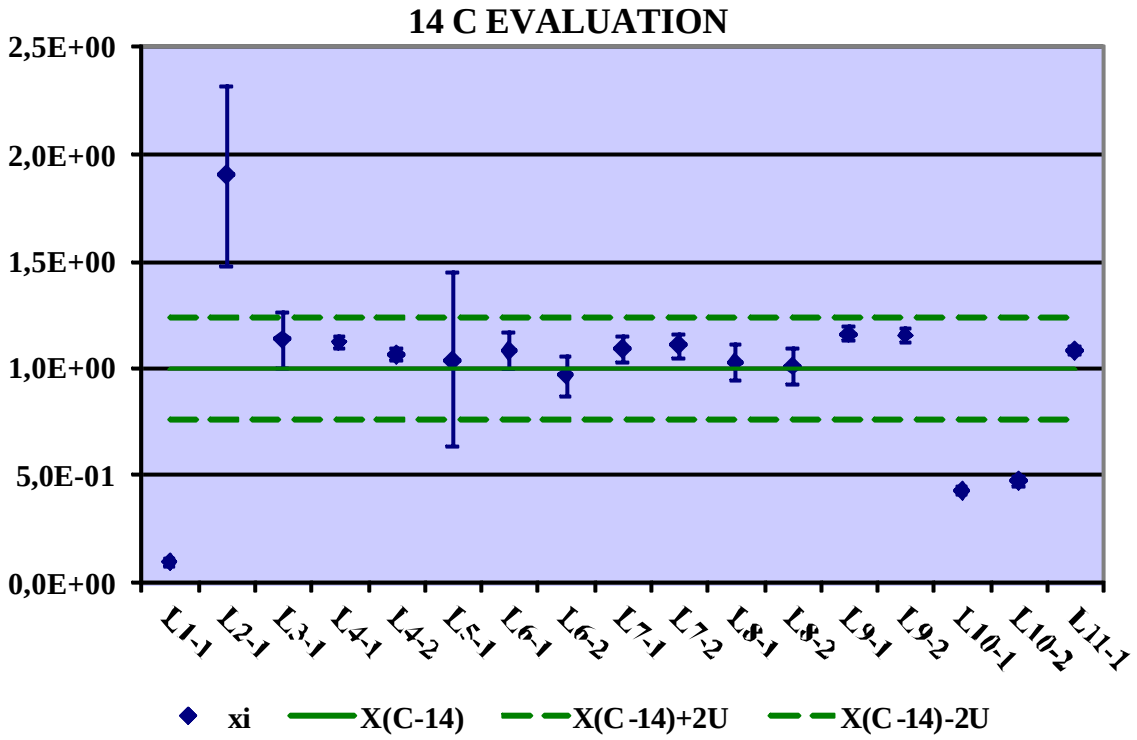

Figure 11. Reults for C-14 evaluation

It is observed that there are 3 values lower than $^{C\text{-}14}X\text{-}2\cdot(^{C\text{-}14}U)$ that use to be associated with the recovery of CO_2 where several factors can have influence:

- The leaks of the systems specially in the conduction from combustion chamber to trapping bottles
- Trapping solution effectiveness. could be affected by storage condition or time degradation
- Not complete combustion of samples
- Chemical yield calculations use of standards to calibrate the recovery prior to separation process.

One value is higher than $^{C\text{-}14}X+2\cdot(^{C\text{-}14}U))$ that use to be associated with the LSC calibration when it is not use a double labelled counting method and the activity of tritium interfere in the

analysis window of radiocarbon. Nevertheless it is notice that the uncertainty associated with this value (L-2-1) also is affected by a big uncertainty that may be leads to a contamination of some subsamples or calibration of calorimeter for recovery calculation.

Relative difference calculation (Q-score) gives the following results:

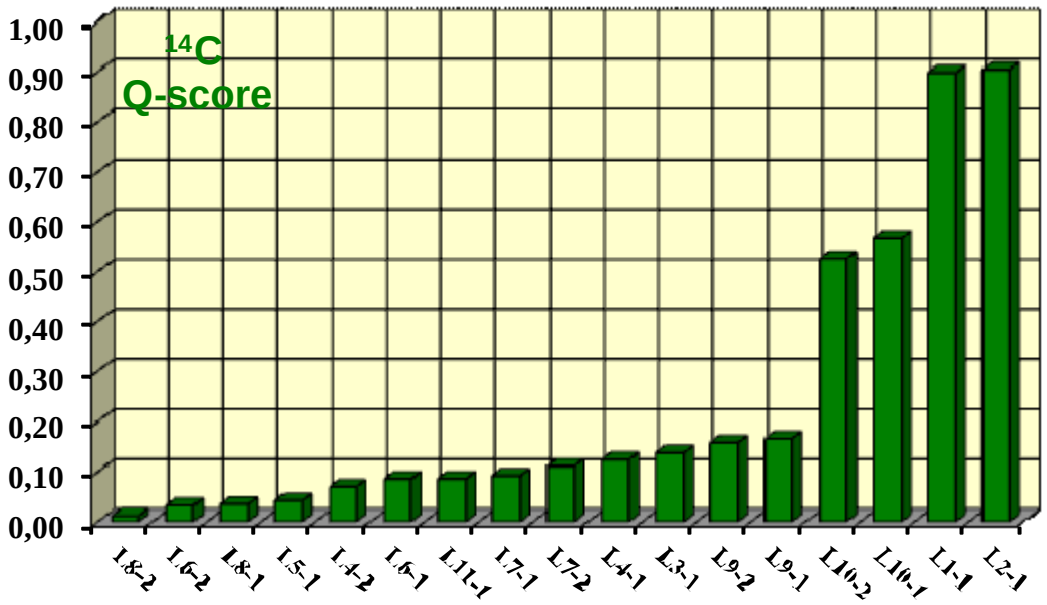

Figure 12. Q-score for C-14 evaluation

It can see in figure 12 that 4 values quote higher than 25% from reference value.

Levels for u-score evaluation for radiocarbon were calculated from t-Student distribution for $\nu = k'-1 = 16$ degrees of freedom.

u-score calculation results are plotted in figure 13.

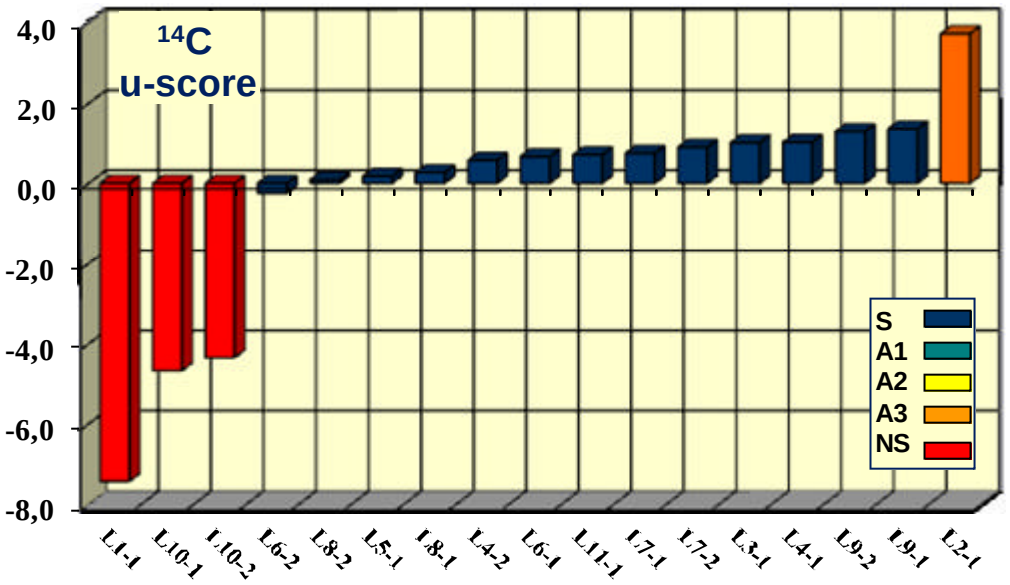

Figure 13. U-score radiocarbon evaluation

Results are summarized in table 9

	n =	16
P		**u**
0.1	90	1.746
0.05	95	2.120
0.01	99	2.921
0.001	99.9	4.015

Table 9. Results of C-14 evaluation.

	xi	2·Ui	Q-score	u-score	
L1-1	1.02E-01	1.80E-02	0.89752	-7.41962	NS
L2-1	1.90E+00	4.21E-01	0.90404	3.72879	A3
L3-1	1.14E+00	1.27E-01	0.13737	1.00719	S
L4-1	1.12E+00	2.80E-02	0.12373	1.01885	S
L4-2	1.07E+00	2.39E-02	0.06955	0.57375	S
L5-1	1.04E+00	4.07E-01	0.04127	0.17445	S
L6-1	1.09E+00	8.89E-02	0.08538	0.66412	S
L6-2	9.68E-01	8.89E-02	0.03151	-0.24505	S
L7-1	1.09E+00	5.39E-02	0.09199	0.74429	S
L7-2	1.11E+00	5.47E-02	0.11090	0.89654	S
L8-1	1.03E+00	8.45E-02	0.03422	0.26773	S
L8-2	1.01E+00	8.28E-02	0.01166	0.09143	S
L9-1	1.17E+00	3.81E-02	0.16600	1.35925	S
L9-2	1.16E+00	3.86E-02	0.15777	1.29148	S
L10-1	4.35E-01	1.81E-02	0.56472	-4.66830	NS
L10-2	4.74E-01	1.96E-02	0.52580	-4.34441	NS
L11-1	1.09E+00	1.58E-02	0.08566	0.70862	S

Over 17 data 23.5% present a deviation lower than 5%, 41.25% in the range of 5-15%,11.8% in the range of 15-25% and 23.5% a deviation higher than 25%.

In the u score evaluation there are 12/17 values quoted Satisfactory. 1/17 values quoted Acceptable at level 3 and 4/17 quoted non satisfactory. that means that ≈71% of the results has a probability higher than 99.9% of determine the right value of C-14 content of the sample, one lab (6%) have high significant difference with reference value and needs more data to evaluate the methodology and 18% of the results has a probability lower than 90% to determine correctly C-14 in i-graphite.

4.3.3. Evaluation of Chlorine-36

The methods applied for Cl-36 determination are based on the oxidation of chlorine from the sample using catalytic furnace, dissolution in reflux or dissolution in acidic/oxidizing media, and trapping in alkaline media. Afterwards some chemical processes could be applied in order to ensure the concentration of chlorine in the measured sample.

The scheme of methodologies is in the flow chart of figure 14. More detailed data of this methods are described in deliverable D- and in technical report CW1202-T-3.3.4.

Table 10 summarized in codes the methods used for Cl-36 characterisation.

Table 10. Methods applied for Chlorine-36 determination

L1-1	L3-1	L4-1/2	L7-1/2	L8-1/2	L9-1/2	L10-1/2
DIS/IEC	REF/TRP	CAF/RED	REF/TRP	CAF/TRP	DIS/EXT	CAF/TRP
LSC	LSC	LSC	LSC	LSC	LSC	LSC

Where

DIS: Dissolution

IEC: Ion Exchange Chromatography

RED: Red-ox process

TRP: Trapping

EXT: Extraction

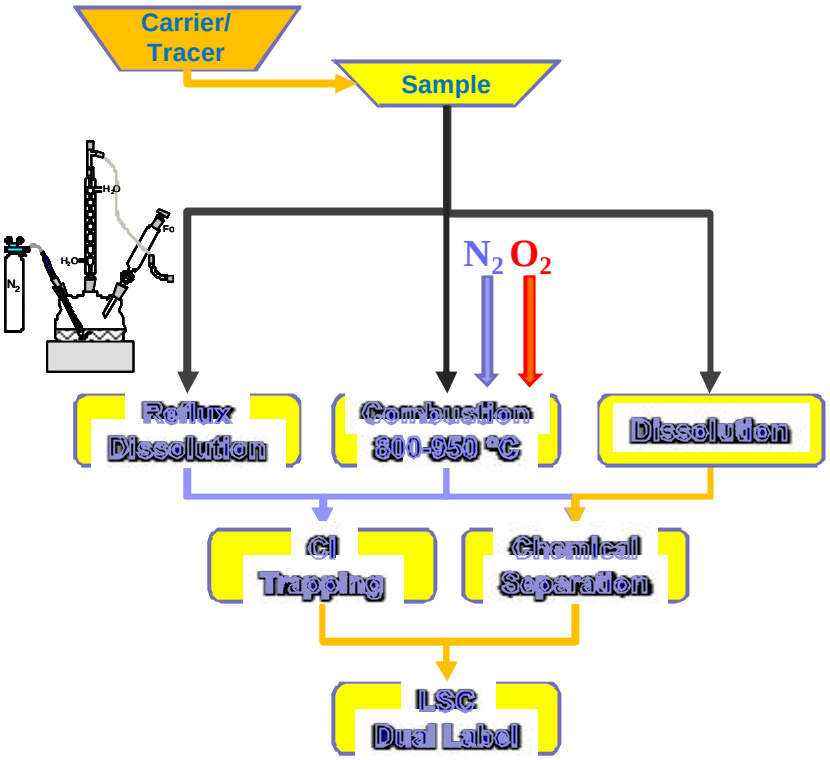

Figure 14. Flow chart for the Cl-36 determination methods

7 Labs supplied 69x4 primary data (Activity. uncertainty. MDA and determination date) to calculate 12 weighted average and their uncertainty, means and variance. Lab-8 submited 9 of 12 values as MDA, nevertheless the Lab-8 data are considered as activity value for calculations. Normalize results is shown in figure 15.

Three outliers were found, two of them by internal variance (by Cochran test) and one in the one-side Grubs Test by interlab means. This fact is due to that the rejected value is the one coming from MDA values. The outlier loop finishing by reaching the limits of labs.

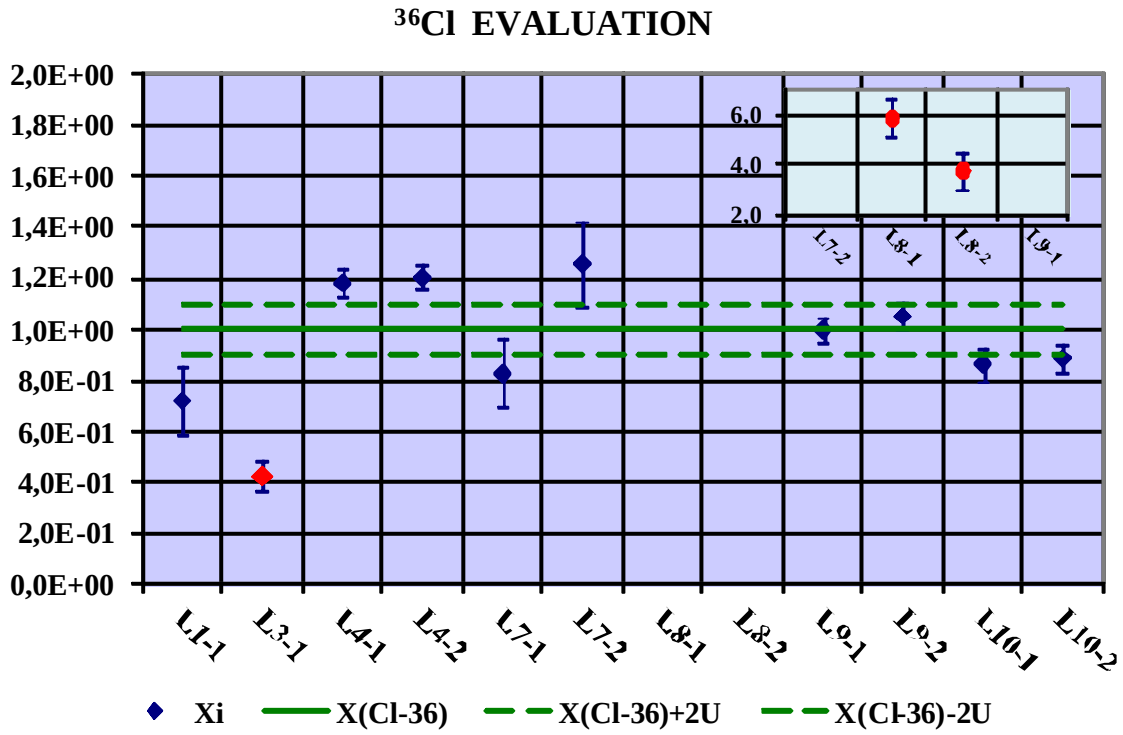

Figure 15. Reults for Cl-36 evaluation

Values obtained by Labs are more scattered than in the case of C-14 or H-3 due to several factors:

- The activity concentration range is smaller than other beta emitters (around factor 1000) as is shown in Table 4, and the results are close to detection limit depending on the mass of sample used to analyse Cl-36 concentration.
- As in other volatile material in graphite the use of mineralization, burning or evaporation methodologies leads to prevent leaks in the system and calculate in an appropriate, traceable and efficient way the recovery yield of the process, that is of special importance when the concentration is low.
- Complex and sophisticate sample preparation and radiochemical processes also contribute to underestimation as well as overestimation of activity and the well known heterogeneity distribution of chlorine-36 in the i-graphite as is demonstrate within the projects.

Excluding the Lab-8 data (reporting as MDA) there are only 2 data (from lab 9) within the range of $^{Cl\text{-}36}X \pm 2 \cdot (^{Cl\text{-}36}U)$). 3 of 10 higher than upper limit and 5 of 10 lower than lower limit.

Relative difference calculation (Q-score) gives the following results:

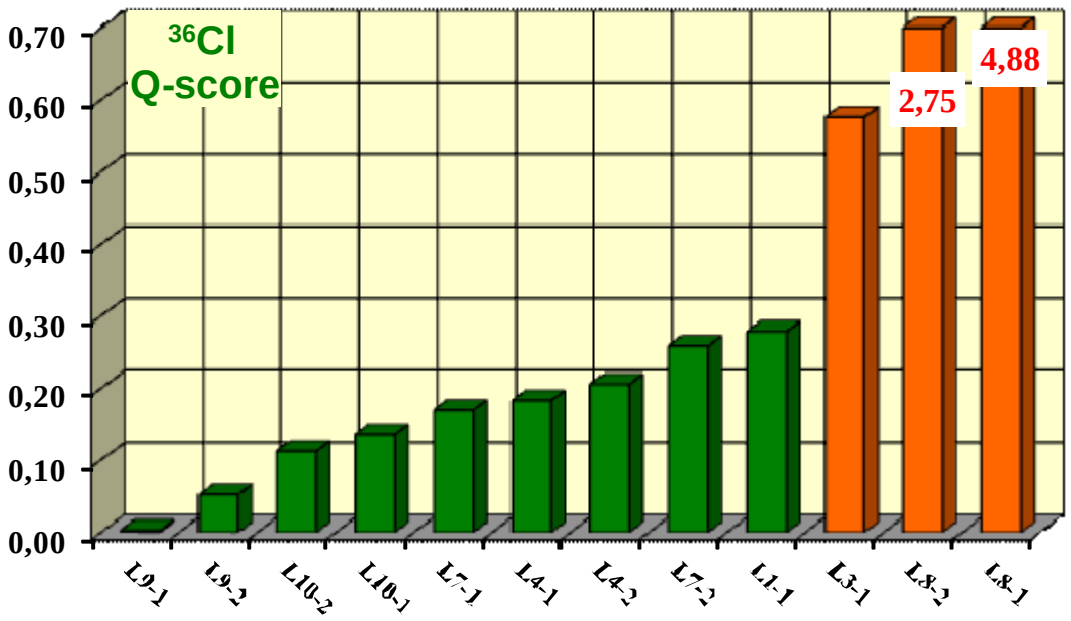

Figure 16. Q-score for Cl-36 evaluation

We can see in figure 16 that 3 values quote higher than 30% from reference value in coincidence with outliers.

Levels for u-score evaluation for chlorine-36 were calculated from t-Student distribution for $\nu = k'-1 = 16$ degrees of freedom.

	n =	8
P		**u**
0.1	90	1.860
0.05	95	2.306
0.01	99	3.355
0.001	99.9	5.041

u-score calculation results are plotted in figure 16.

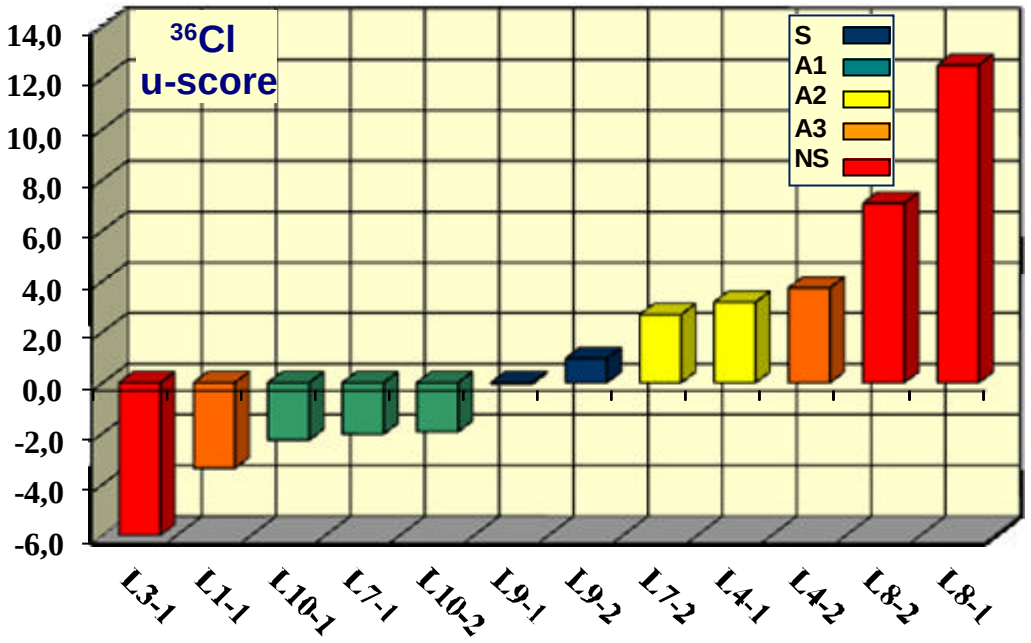

Figure 16. U-score chlorine-36 evaluation

Results are summarized in table 11

Table 11. Results of Cl-36 evaluation.

	Xi	2*Ui	Q	u	
L1-1	1.65E+01	3.01E+00	0.27863	-3.36846	A3
L3-1	9.72E+00	1.40E+00	0.57508	-9.77609	NS
L4-1	2.70E+01	1.30E+00	0.18250	3.16355	A2
L4-2	2.76E+01	1.05E+00	0.20546	3.72269	A3
L7-1	1.90E+01	3.02E+00	0.16909	-2.03664	A1
L7-2	2.88E+01	3.77E+00	0.25846	2.67473	A2
L8-1	1.34E+02	1.77E+01	4.87804	12.51189	NS
L8-2	8.59E+01	1.77E+01	2.75525	7.06706	NS
L9-1	2.28E+01	1.03E+00	0.00264	-0.04789	S
L9-2	2.41E+01	1.11E+00	0.05291	0.94787	S
L10-1	1.97E+01	1.51E+00	0.13649	-2.26969	A1
L10-2	2.03E+01	1.31E+00	0.11248	-1.94532	A1

Over 12 data 26.7% present a deviation lower than 10%, 33.3% in the range of 10-20%, 25% in the range of 20-30% and 25% a deviation higher than 30%.

In the u score evaluation there are 2/12 values quoted Satisfactory. 3/12 values quoted Acceptable at level 1, 1/12 Acceptable at level 2, 2/12 Acceptable at level 3 and 3/12 quoted non satisfactory. that means that ≈58% of the results has a probability higher than 95% of determine the right value of Cl-36 content of the sample, two lab results (16.7%) have high significant difference with reference value and needs more data to evaluate the methodology and 25% of the results has a probability lower than 90% to determine correctly Cl-36 in i-graphite due to basically to the sensitivity of the method applied.

4.3.4. Evaluation of Cobalt-60

The methods applied for Co-60 determination are basically the direct measurement of the bulk sample by gamma spectrometry. Nevertheless several approaches are applied that range from the measurement of the whole mass, in the order of magnitude of grams-,measurement of several sub-aliquots -in the order of magnitude of mg- in specific and dedicate geometries and the measurement of dissolved aliquots of irradiated graphite.

The methods are in the flow chart of figure 17 also in Table 12 is summarized in codes the method used. L6 is the only one that use low resolution gamma spectrometry.

Table 12. Methods applied for cobalt-60 determination

L1-1/2	L2-1	L3-1/2	L4-1/2	L5-1	L6-1/2	L7-1/2	L8-1/2	L9-1/2	L10-1/2	L11-1
DIM	DIM	DIS	DIS	DIM	DIM	DIM/SG	DIS	DIM	DIM	DIM
HRG	HRG	HRG	HRG	HRG	LRG	HRG	HRG	HRG	HRG	HRG

Where

DIM: Direct measurement

DIS: Dissolution of an aliquot

SG: Special Geometry

HRG: High Resolution gamma Spectrometry

LRG: High Resolution gamma Spectrometry

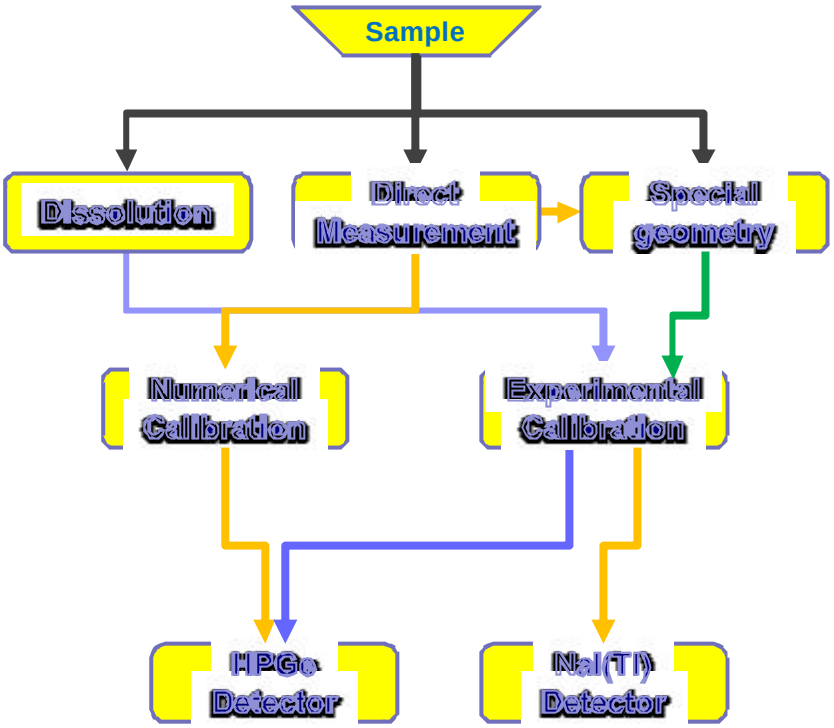

Figure 17. Flow chart for the Co-60 determination methods

11 Labs supplied 111x4 primary data (Activity. uncertainty. MDA and determination date) to calculate 19 weighted average and their uncertainty, means and variance. Normalize results is shown in figure 18.

Two outliers were found in 3 outliers' calculation loops performed. Both were rejected from reference data calculation by Cochran test (internal variance). In figure 18 we can see that these data are the ones that presents higher inner uncertainty and higher deviation from reference value.

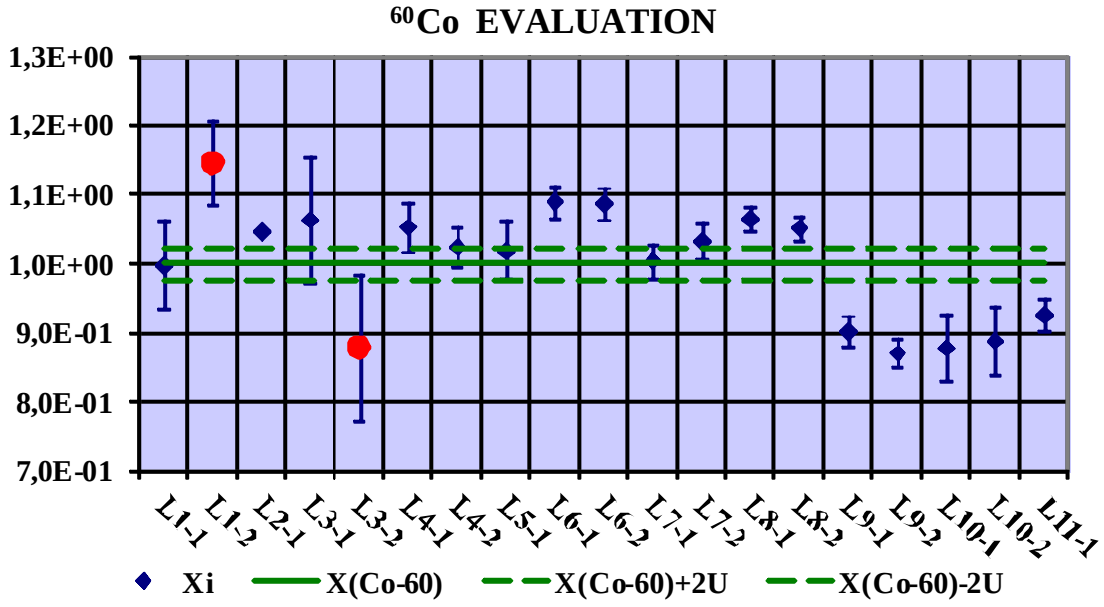

Figure 18. Results for Co-60 evaluation

Due to the concentration of data the uncertainty of the reference value is not higher than 1% so that the majority of values evaluated (13/17) are out of this range ($X_{Co\text{-}60}$ ±2 $U_{Co\text{-}60}$).

There are not tendencies in function of measurement systems, calibrations methods or sample preparation in the data treated. higher deviation can have explanation on random sources of uncertainty as dead time in the case of high amount of sample, appropriated calibration according to the geometry or self-attenuation and/or attenuation of the experimental geometry selected.

Relative difference calculation (Q-score) gives the following results:

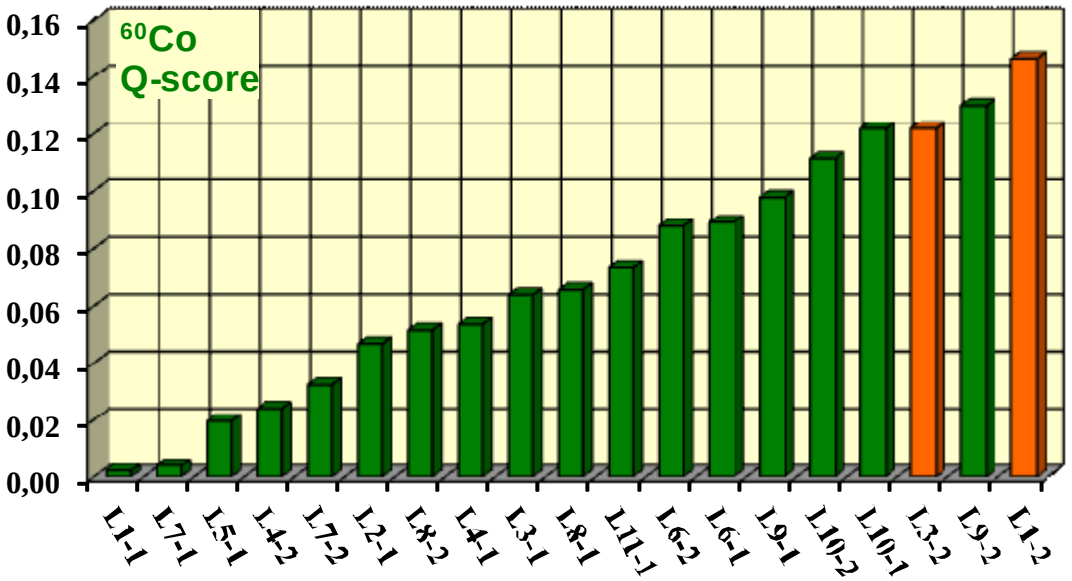

Figure 19. Q-score for Co-60 evaluation

We can see in figure 19 that 5 values quote higher than 10% from reference value.

Levels for u-score evaluation for radiocarbon were calculated from t-Student distribution for ν = k'-1= 16 degrees of freedom.

u-score calculation results are plotted in figure 20.

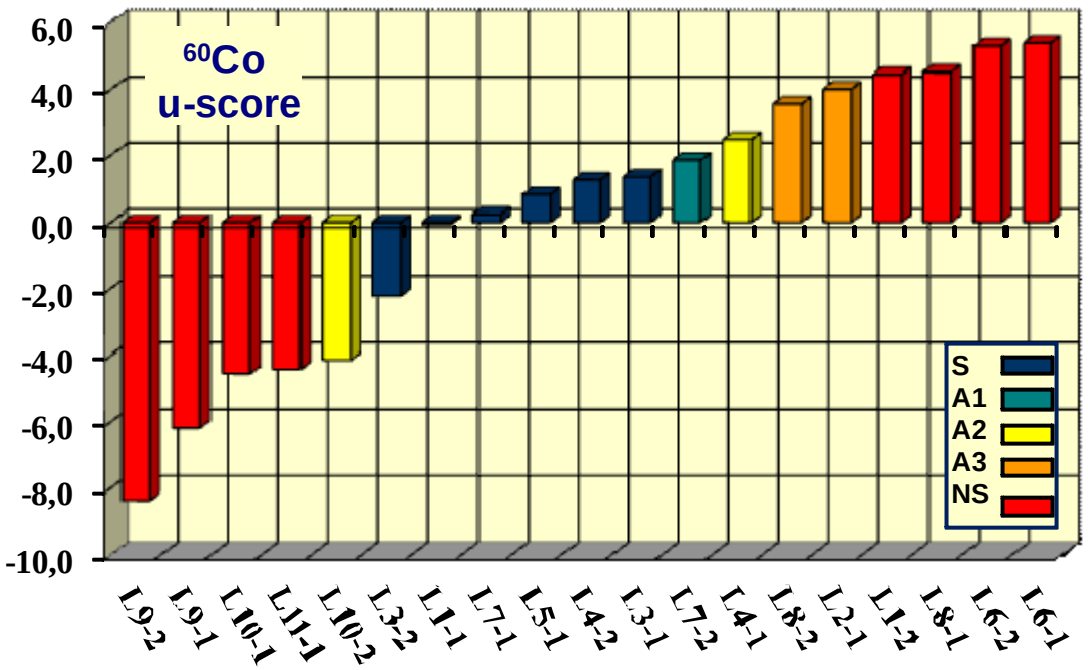

Figure 20. U-score cobalt-60 evaluation

Results are summarized in table 13

	n =	16
P		**u**
0.1	90	1.746
0.05	95	2.120
0.01	99	2.921
0.001	99.9	4.015

Table 13. Results of Co-60 evaluation.

	Xi	2*Ui	Q	u	
L1-1	9.98E-01	6.25E-02	0.00217	-0.06502	S
L1-2	1.15E+00	6.17E-02	0.14625	4.43524	NS
L2-1	1.05E+00	8.03E-05	0.04651	3.99930	A3
L3-1	1.06E+00	8.94E-02	0.06368	1.37912	S
L3-2	8.78E-01	1.06E-01	0.12176	-2.23657	A2
L4-1	1.05E+00	3.61E-02	0.05316	2.47791	A2
L4-2	1.02E+00	2.93E-02	0.02407	1.28786	S
L5-1	1.02E+00	4.08E-02	0.01957	0.83366	S
L6-1	1.09E+00	2.34E-02	0.08900	5.39478	NS
L6-2	1.09E+00	2.35E-02	0.08761	5.30397	NS
L7-1	1.00E+00	2.54E-02	0.00399	0.23156	S
L7-2	1.03E+00	2.61E-02	0.03217	1.83922	A1
L8-1	1.07E+00	1.74E-02	0.06545	4.50660	NS
L8-2	1.05E+00	1.72E-02	0.05118	3.54097	A3
L9-1	9.02E-01	2.13E-02	0.09772	-6.19465	NS
L9-2	8.70E-01	2.06E-02	0.12983	-8.36563	NS
L10-1	8.78E-01	4.81E-02	0.12171	-4.55762	NS
L10-2	8.89E-01	4.85E-02	0.11148	-4.14499	NS
L11-1	9.27E-01	2.37E-02	0.07348	-4.42560	NS

The data obtained have a lower deviation than 15%. Over 19 data 31.6% present a deviation lower than 5%, 42.1% in the range of 5-10%, 15.8% in the range of 10-12.5% and 10.5% a deviation higher than 12.5%.

In the u score evaluation there are 5/19 values quoted Satisfactory, 1/19 values quoted Acceptable at level 1, Aceptable at level 2 and level 3 there are 2/19 values respectively and 9/19 quoted non satisfactory. that means that ≈53% of the results has a probability higher than 90% of determine the right value of Co-60 content of the sample, 9 labs' (47%) have high significant difference with reference value.

These bad results in the Co-60 evaluation by u-score have a double origin, firstly the small uncertainty of reference value that oblige to quote in a very narrow window (6% around the

reference value) for a satisfactory evaluation of method. This reduce uncertainty of reference value is promoted by the small accuracy and high repetitively of the results obtained for every lab.

On the other hand the dispersion of the results obtained (according to a normal distribution around the reference value) gives a probability of quotation in non satis factory range.

In this specific case the penalty in the quotation comes from the accuracy of the methods but if we take into account the bias obtained by Q-score the results are excellent for every approaches even the ones with more scattered data.

4.3.5. Evaluation of Nickel-63

The methods applied for Ni-63 determination are based on the same principle the complexation of Ni with Dimethyl-Glyoxime (DMG). Nevertheless several approaches are used within CW-RRT as Complexation with DMG and Solvent Extraction, Precipitation and Extraction Chromatography and Ion Exchange Chromatography and Extraction Chromatography.

Chemical yield is calculate by addition of inactive carrier of nickel and determination by several analytical methods as spectrophotometry, ICP-MS, etc.

The methods are in the flow chart of figure 21 also in Table 14 is summarized in codes the methods used. by each Lab.

Table 14. Methods applied for nickel-63 determination

L1-1	L3-1	L4-1/2	L7-1/2	L8-1/2	L9-1/2	L10-1/2
IEC/AAS	EXC/ICP	EXS/ICP	EXS/SPH	EXC/ICP	EXS/ICP	EXC/ICP
LSC	LSC	LSC	LSC	LSC	LSC	LSC

Where

IEC is Ion Exchange Chromatography

EXC is Extraction Chromatography

EXS is Solvent Extraction

AAS is Atomic Absorption Spectrometry

ICP is ICP-MS or ICP-OS

SPH is spectrophotometry

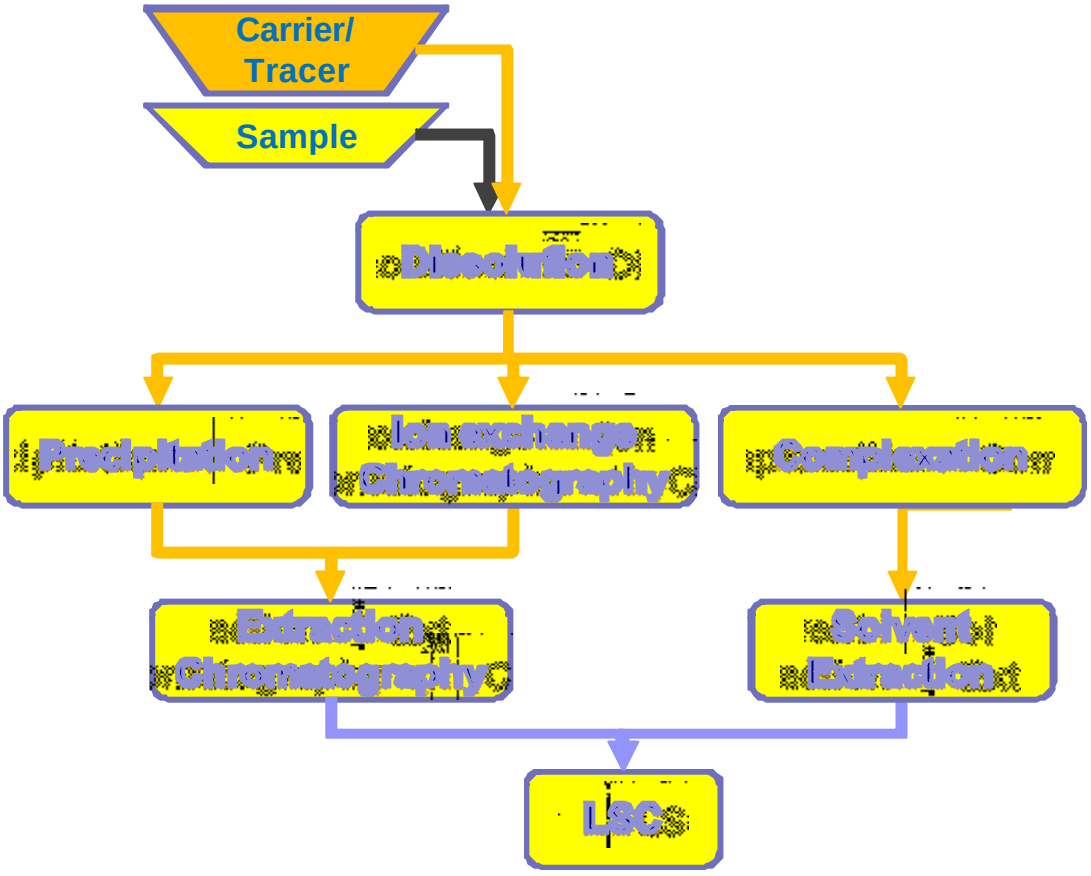

Figure 21. Flow chart for the Ni-63 determination methods

7 Labs supplied 72x4 primary data (Activity. uncertainty. MDA and determination date) to calculate 12 weighted average and their uncertainty, means and variance. Normalize results is shown in figure 22.

Three outliers were found in the loop performed until reaching labs limits number. One of them is intra-lab variance rejection and the other two by pair Grubbs test.

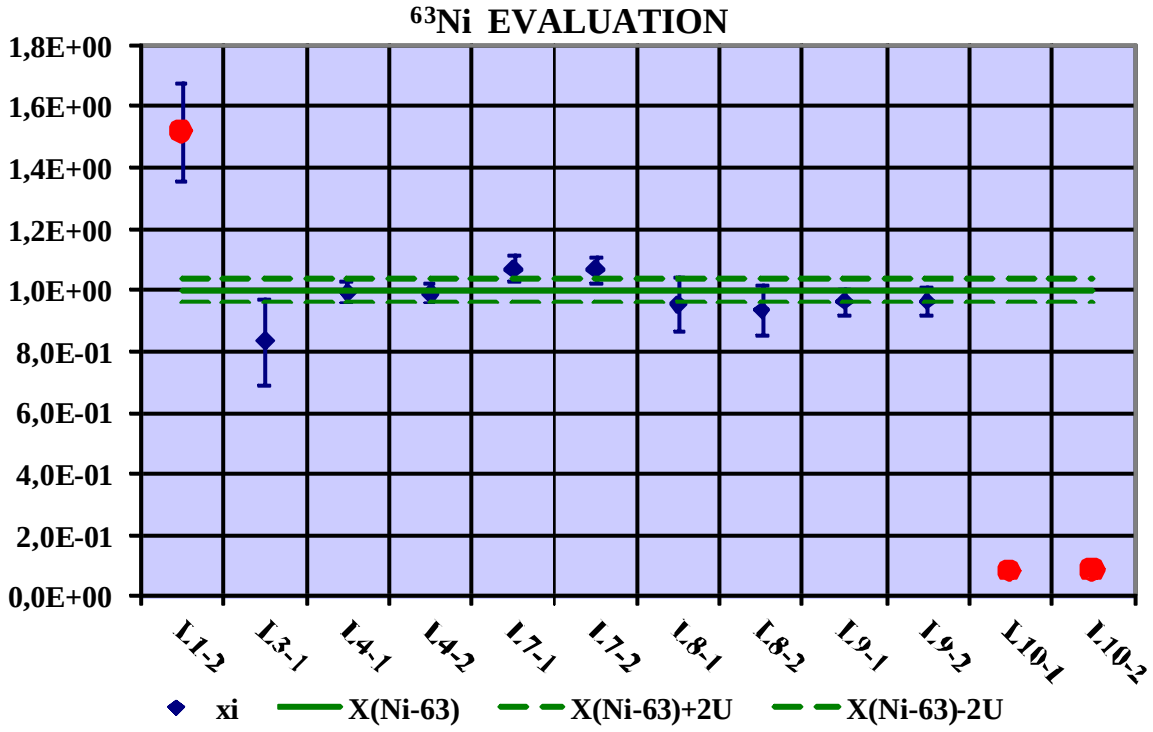

Figure 22. Reults for Ni-63 evaluation

It is observed that there are 3 values lower than $^{Ni-63}X-2\cdot(^{Ni-63}U)$ that use to be associated with the recovery factor of Ni in the chemical process.

One value is higher than $^{Ni-63}X+2\cdot(^{Ni-63}U)$ that use to be associated with the LSC calibration, so far the Ni-63 once separate from other interference is measured in a counting window

without interference, so that the possible contamination of other nuclides in the LSC measurement has a lower probability.

Any way except for the case of L-1 and L-10 the results obtained within the exercise are in a very good agreement with the reference value.

Relative difference calculation (Q-score) gives the following results:

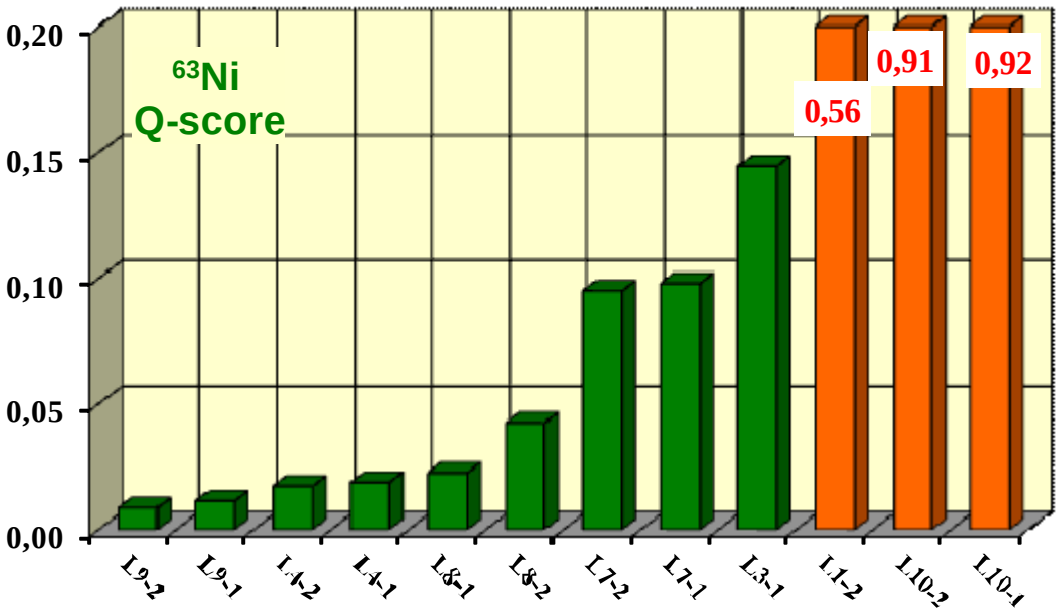

Figure 23. Q-score for Ni-63 evaluation

	n =	8
P		**u**
0.1	90	1.860
0.05	95	2.306
0.01	99	3.355
0.001	99.9	5.041

We can see in figure 23 that 3 values quote higher than 15% from reference value.

Levels for u-score evaluation for radiocarbon were calculated from t-Student distribution for $\nu = k'-1=$

8 degrees of freedom.

u-score calculation results are plotted in figure 24.

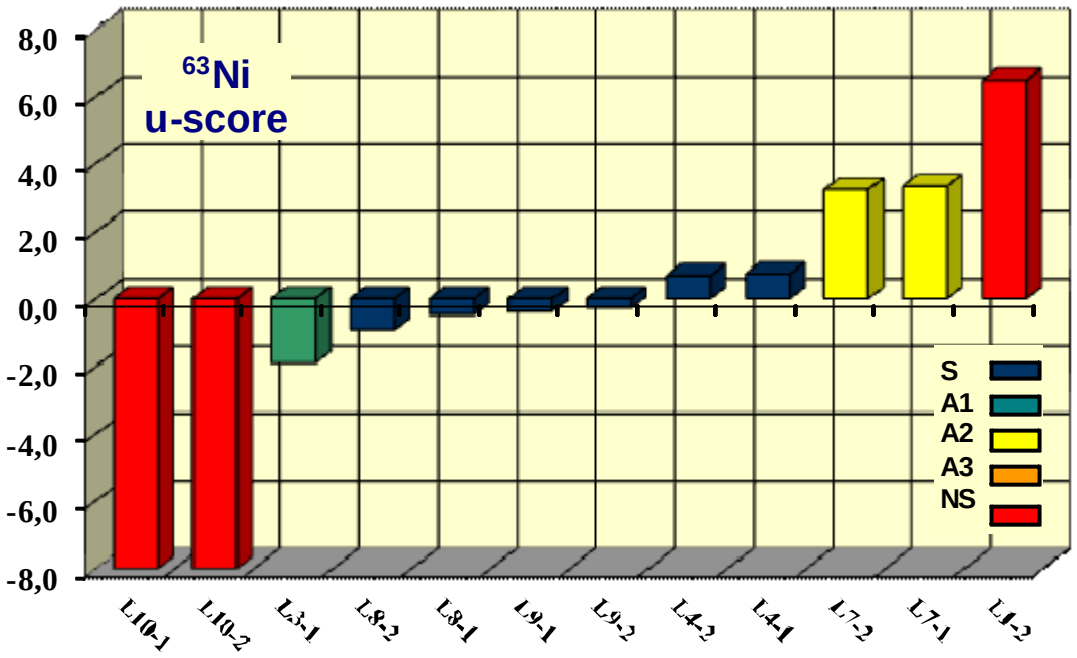

Figure 24. U-score nickel-63evaluation

Results are summarized in table 15

Table 15. Results of Ni-63 evaluation.

	Xi	2*Ui	Q	u	
L1-2	1.52E+00	1.63E-01	0.55478	6.48758	NS
L3-1	8.34E-01	1.42E-01	0.14418	-1.91130	A1
L4-1	9.93E-01	3.35E-02	0.01876	0.73799	S
L4-2	9.92E-01	3.26E-02	0.01725	0.68736	S
L7-1	1.07E+00	4.37E-02	0.09788	3.35185	A2
L7-2	1.07E+00	4.36E-02	0.09492	3.25546	A2
L8-1	9.53E-01	8.56E-02	0.02256	-0.47258	S
L8-2	9.34E-01	8.33E-02	0.04237	-0.90888	S
L9-1	9.64E-01	4.38E-02	0.01122	-0.38383	S
L9-2	9.67E-01	4.58E-02	0.00848	-0.28239	S
L10-1	8.32E-02	3.62E-03	0.91467	-48.62656	NS
L10-2	8.70E-02	4.06E-03	0.91081	-48.36035	NS

Over 12 data 41.7% present a deviation lower than 2.5%, 8.2% in the range of 2.5-5%, 16.4% in the range of 5-10% and 33.3% a deviation higher than 10%.

In the u score evaluation there are 6/12 values quoted Satisfactory. 1/12 values quoted Acceptable at level 1, 2/12 quote acceptable at level 2 and 3/12 quoted non satisfactory. that means that 50% of the results has a probability higher than 99.9% of determine the right value of Ni-63 content of the sample, 3 lab's (25%) have a moderate significant difference with reference value and needs more evidence to reject or to be considered satisfactory and 25% of the results has a probability lower than 90% to determine correctly Ni-63 in i-graphite.

4.3.6. Evaluation of Strontium-90

The methods applied for Sr-90 determination are based on the precipitation or use specific crown-ether chromatographic column, after dissolution of matrix in acidic media.

Chemical yield is calculate by addition of inactive carrier or standard of strontium and determination by several analytical methods as gravimetric determination, ICP-AES or ICP-MS.

The methods are in the flow chart of figure 21 also in Table 16 is summarized in codes the methods used. by each Lab.

Table 16. Methods applied for Strontium-90 determination

L3-1	L7-1/2	L8-1/2
EXC/ICP	EXC/GRV	PRE/ICP
LSC	LSC	LSC

Where
PRE is Specific Precipitation
GRV is Gravimetric Determination
ICP is ICP-MS or ICP-AES

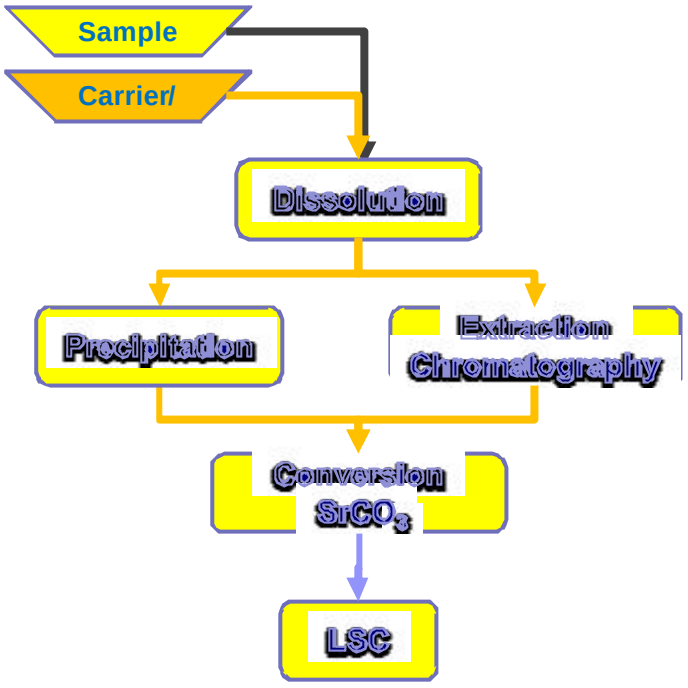

Figure 25. Flow chart for the Sr-90 determination methods

3 Labs supplied 27x4 primary data (Activity. uncertainty. MDA and determination date) to calculate 5 weighted average and their uncertainty, means and variance. Normalize results is shown in figure 26.

One outlier was found in the loop performed until reaching labs limits number. The lab was rejected for reference value calculation by intra-lab variance defined by Cochran test.

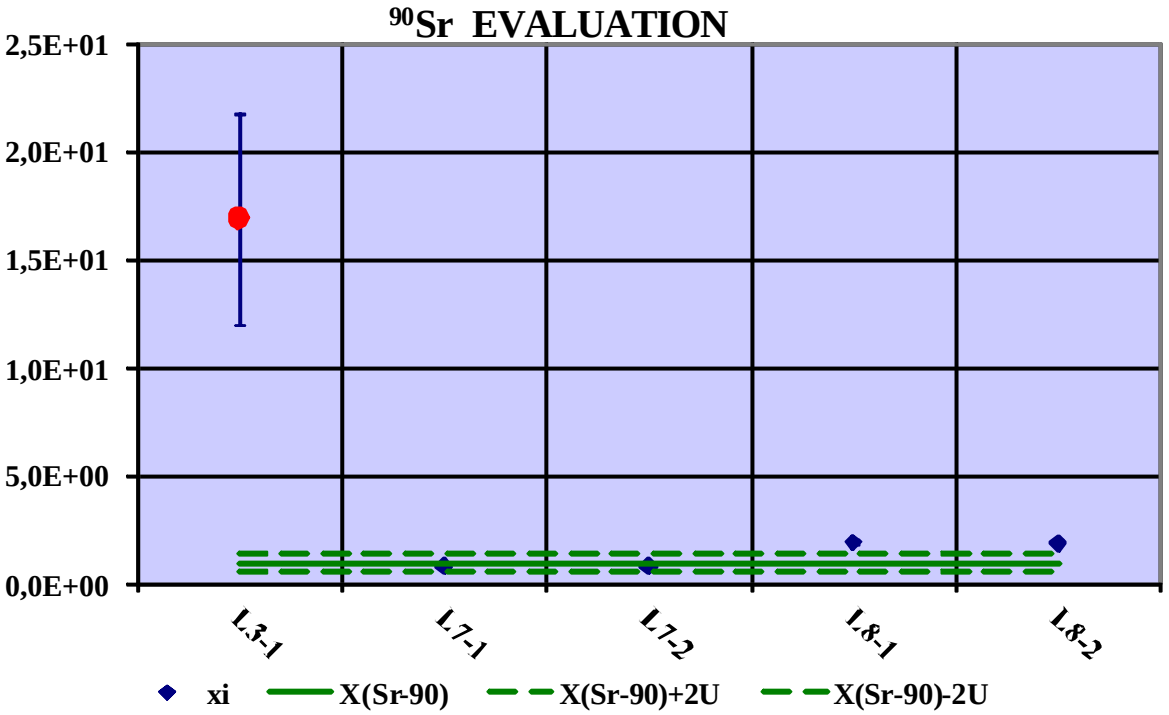

Figure 24. Results for Sr-90 evaluation

One values is higher than $^{Sr\text{-}90}X+2\cdot(^{Sr\text{-}90}U)$ that use to be associated with the LSC calibration, In this case due to that the few data managed and the relative low activity concentration in the samples the deviations can consider insignificant under qualitative point of view.

Relative difference calculation (Q-score) gives the following results:

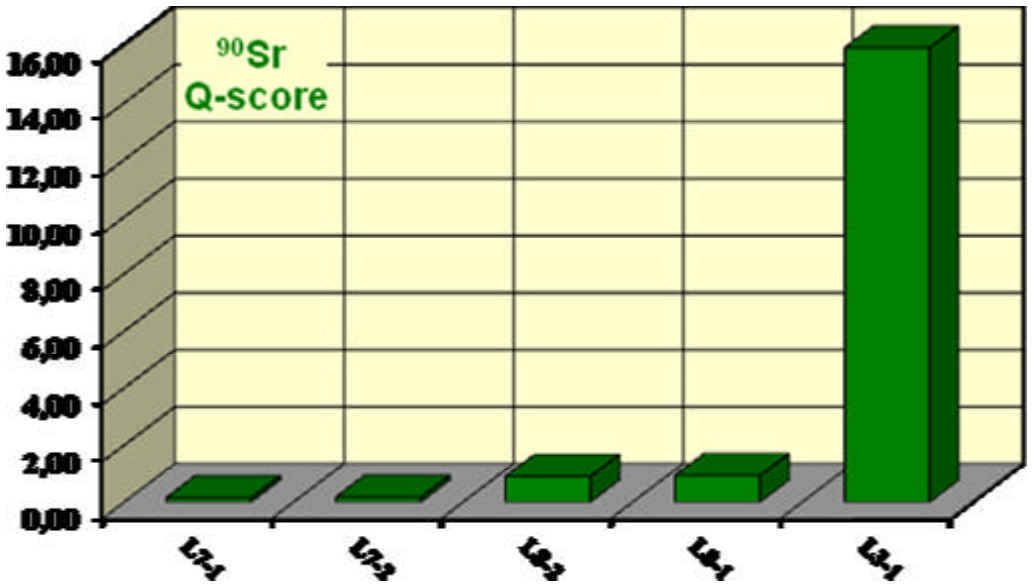

Figure 25. Q-score for Ni-63 evaluation

We can see in figure 25 that all values quoted lower than 15% from reference value.

Levels for u-score evaluation for radiocarbon were calculated from t-Student distribution for $\nu = k'-1 = 8$ degrees of freedom.

	n =	3
P		**u**
0.1	90	2.353
0.05	95	3.182
0.01	99	5.841
0.001	99.9	12.924

u-score calculation results are plotted in figure 26.

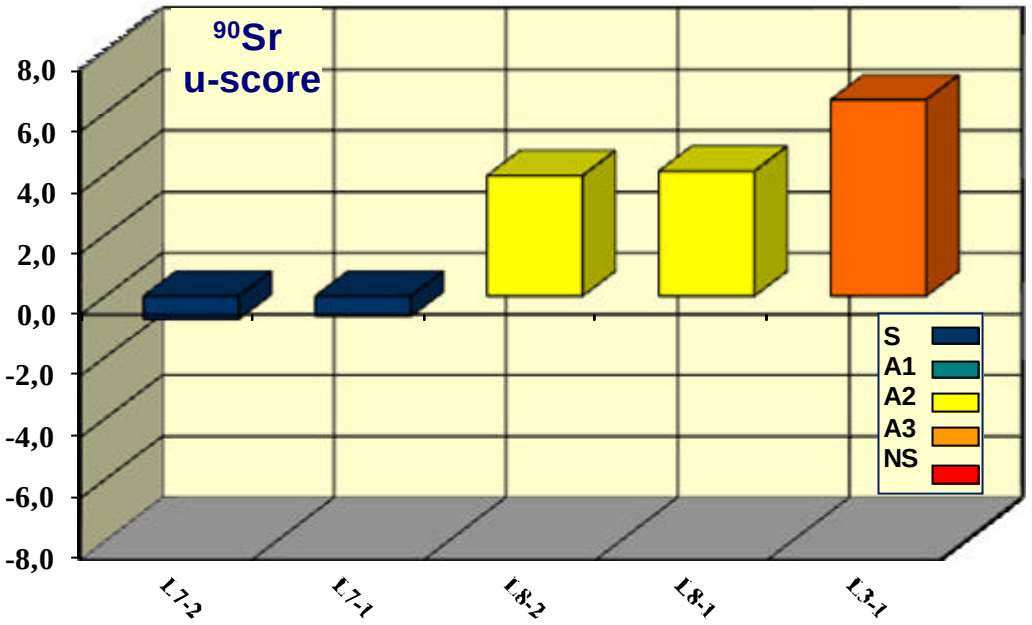

Figure 26. U-score strontium-90 evaluation

Results are summarized in table 17

Table 17. Results of Sr-90 evaluation.

	xi	2*Ui	Q	u	
L3-1	1.69E+01	4.93E+00	15.92377	6.42952	A3
L7-1	8.49E-01	3.48E-02	0.15079	-0.66606	S
L7-2	8.30E-01	3.54E-02	0.16984	-0.75012	S
L8-1	1.94E+00	8.50E-02	0.93862	4.08653	A2
L8-2	1.90E+00	8.36E-02	0.90432	3.93938	A2

Over 5 data 2 present a deviation lower than 20%, 2 in the range of factor 2, and one in a factor 15.

In the u score evaluation there are 2/2 values quoted Satisfactory. 2/5 values quoted Acceptable at level 2, and 1 value that quoted acceptable at level 3...that needs more data for evaluate the acceptability of the values.

4.4. Statistical Evaluation by Lab

In this section it is discussed the data by individual Lab contribution and their evaluation, in order to reach general conclusion on the analytical methodologies approaches. With these data each individual Lab can improve the methods applied and/0r use the results for QA of the graphite characterisation and accreditation.

4.4.1. Laboratory #1 Evaluation

Results of Lab#1 are summarize in table 18 and figure 27

Table 18. Data for Lab#1 evaluation

LAB# 1	x_i	x_{Ai}	2*Ui	X_A	$2*U_X$	SEP	DET	u score	qualify	Q score
H-3-1										
H-3-2										
C-14-1	3	1.02E-01	1.80E-02	1.00E+00	2.41E-01	OXD	LSC	-7.420	NS	0.898
C-14-2										
Cl-36-1	6	7.21E-01	1.31E-01	1.00E+00	5.02E-02	DIS/IEC	LSC	-3.368	A3	0.279
Cl-36-2										
Co-60-1	6	9.98E-01	6.25E-02	1.00E+00	2.33E-02	DIM	HRG	-0.065	S	0.002
Co-60-2	6	1.15E+00	6.17E-02	1.00E+00	2.33E-02			4.435	NS	0.146
Ni-63-1	6	1.52E+00	1.63E-01	1.00E+00	3.65E-02	IEC/AAS	LSC	6.488	NS	0.555
Ni-63-2										

Lab#1 reported 4 nuclides of 5 in mandatory, the data supplied are simple (only one set of six data) may be due to the amount of sample needs to carry out the procedures. Co-60 is reported double because of the analysis of gamma emitting nuclide is performed by non-destructive assay.

In the case of radiocarbon determination only 3 values are computed this fact implies a worse quotation in the outliers' calculation and statistical evaluation for these nuclides.

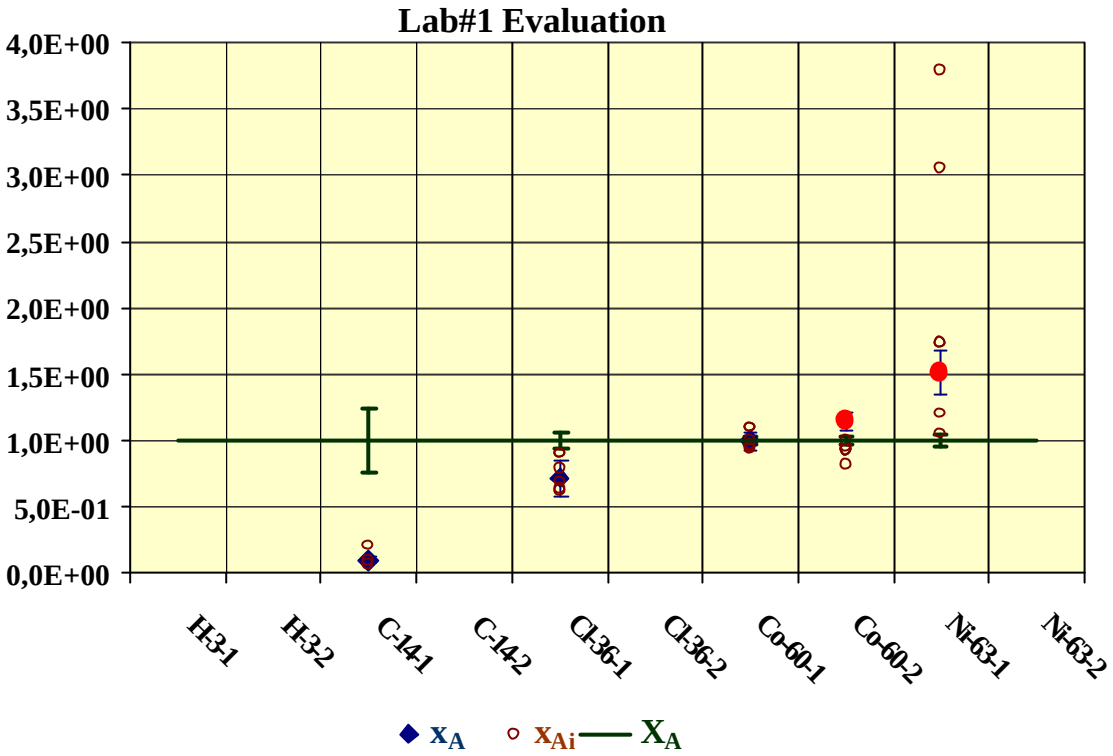

Figure 27. Results of Lab#1

Analysing the data of Figure 27 is observed that

- C-14 determination has 3 data without significant scattering but the weighted average has one order of magnitude lower than the reference value this difference (-90%) indicates an overestimation of recovery factor probably by no control leaks in the combustion system or estimation in CO2 conversion or gas trapping system. The uncertainty associate with the weighted average is ≈18%

- Chlorine-36 determination presents six values concentrates around the weighted average (STD =12%) that have an uncertainty associate of 9%. The difference with reference value is ≈30%. As in the case of radiocarbon the value underestimates the reference value that means again a defect in the recovery of chlorine separation or trapping.

- The nickel-63 determination presents a high scattering in the original values (54.3 %) that leads to an outlier by intra-lab variance. Another important factor for a non satisfactory quote is that the value recorded is 50% higher than reference value. The weighted average has an associate uncertainty around 5%. The overestimation can leads to calibration of LSC system or a chemical yield underestimate.

- The case of Co-60 estimation presents some remarkable characteristics, both values calculate comes from low scattered results (STD of Co-60-1 = 3.1% and STD of Co-60-2 = 2.7%) and really close to the reference value (≈2% and ≈15% respectively). Even with tis low scattered values the mean of Co-60-2 is rejected as outlier by intra-lab variance, this fact is due to a good repeatability of results within the exercise in this nuclide.

The values of Q-score (figure 28) reinforce the information observed in the paragraphs above:

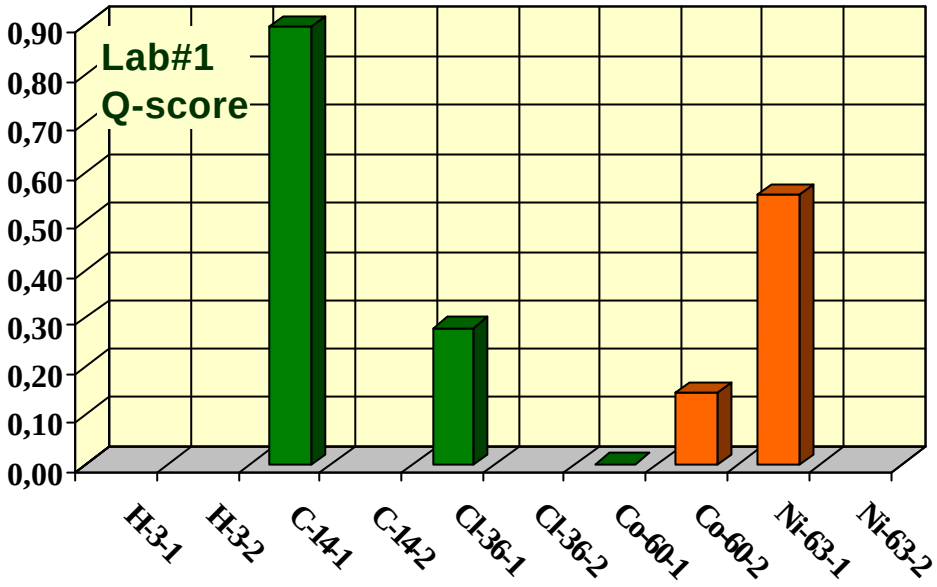

Figure 28. Q-score for Lab#1

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The u-score evaluation of lab#1 is plotted in figure 29, where we can see that is quoted Non satisfactory in C-14, with a relative difference with reference value of 90% and in Ni-63 with a 52% of relative difference.

Two values quoted Acceptable at level 3 for Cl-36 (with a bias in the order of 28%), and Co-60-2 (with a bias of 5%), these A3 values must be discussed in a different way, in the case of Cl-36 data could be significant difference with $^{Cl\text{-}36}$X but we need more data to reject the result, nevertheless the recovery of chlorine from the dissolution of matrix have to be recalibrate and/or revised. In the case of Co-60-2 the bias is very low and the poor quotation is more an effect of the uncertainty of reference value and the contribution of the other 18 lab-inputs than a problem in the determination method or calibration. This fact is supported by the quotation of Co-60-1 that is satisfactory with 0.2% of bias.

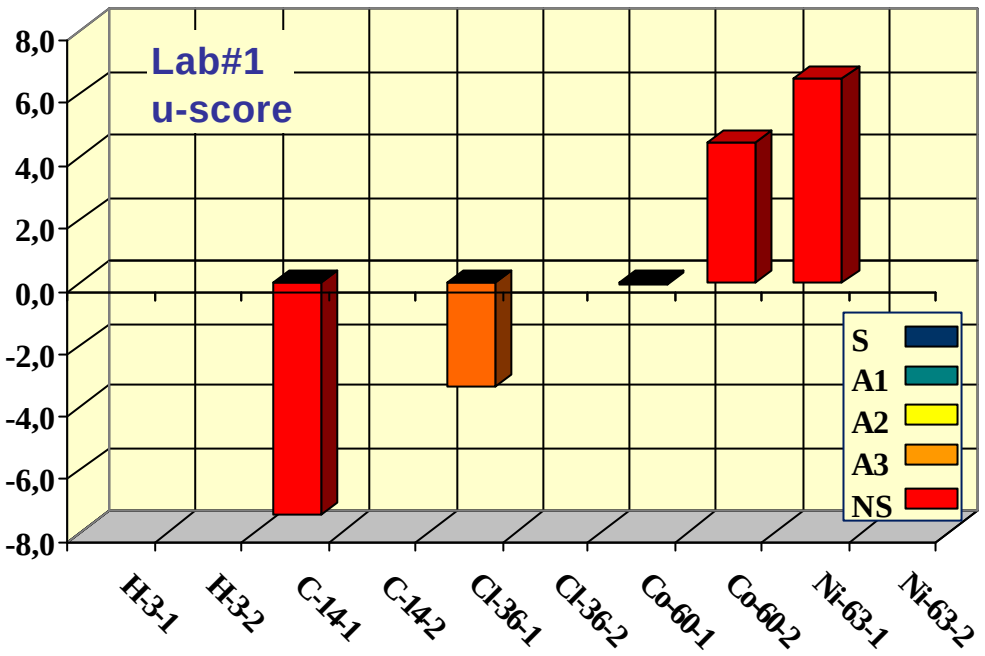

Figure 29. u-score of Lab#1

4.4.2. Laboratory #2 Evaluation

Results of Lab#2 are summarize in table 19 and figure 30

Table 19. Data for Lab#2 evaluation

LAB# 2	x_i	x_{Ai}	2*Ui	X_A	$2*U_X$	SEP	DET	u score	qualify	Q score
H-3-1	6	9,26E-01	2,97E-02	1,00E+00	7,55E-02	COM/DIS	LSC	-1,534	S	0,074
H-3-2										
C-14-1	6	1,90E+00	4,21E-01	1,00E+00	2,41E-01	COM	LSC	3,729	A3	0,904
C-14-2										
Cl-36-1										
Cl-36-2										
Co-60-1	6	1,05E+00	8,03E-05	1,00E+00	2,33E-02	DIM	HRG	3,999	A3	0,047
Co-60-2										
Ni-63-1										
Ni-63-2										

Lab#2 reported 3 nuclides of 5 in mandatory, the data supplied are simple (only one set of six data) the evaluator guess that this lack of information is due to the amount of sample needs to carry out the procedures.

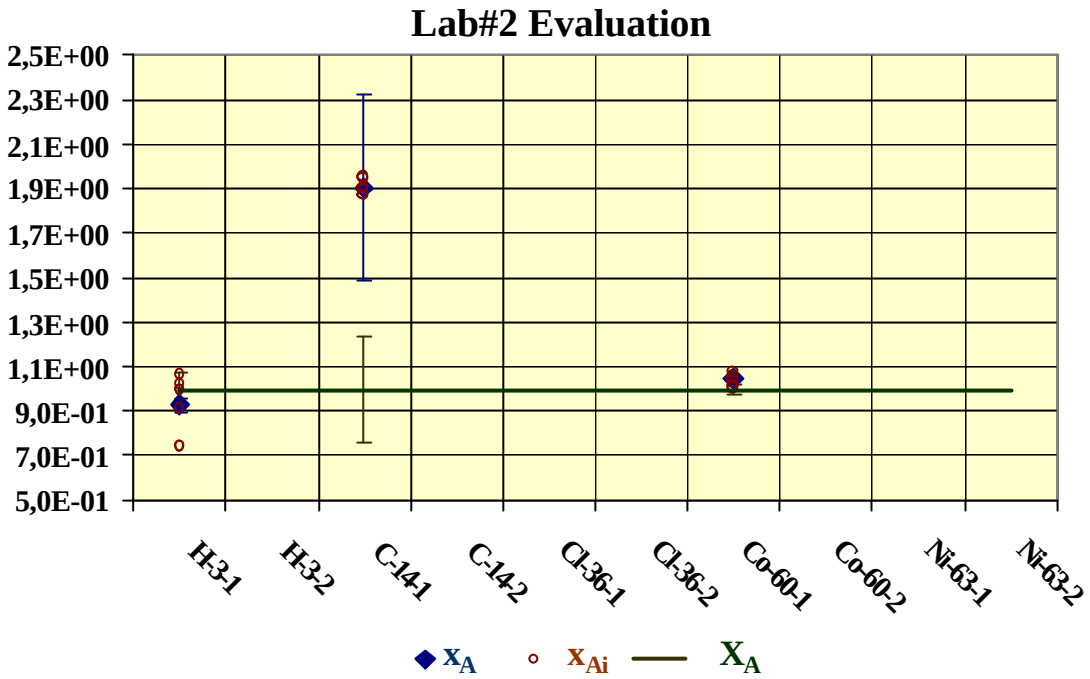

Figure 30. Results of Lab#2

The Analysis of the data in Figure 30 gives the following topics:

- Tritium determination presents a low scattered data (STD = 12.2%) and the weighted average is close to the reference value (underestimation in 7%), probably this data comes from the extra distillation process as the difference with other methods that not include this purification stage.

- C-14 determination has 6 data without significant scattering (STD=2%) but the uncertainty associate is close to 22% of the weighted average. Overestimation regarding to reference value is detected in practically factor 2 (90%) may be due to a cross contamination of the method or a defect in calibration.

- Cobalt-60 determination is also reported in single set of six data even the Lab use the non-destructive assay method that allows replicates without mass consume. The STD of data submitted is 3% that means a high reproducibility and a small uncertainty associate (3.8%). The weighted average differs overestimating 5% from reference value.

The values of Q-score (figure 31) and u-score (figure 32) gives a quantitative and qualitative idea of the bias regarding reference values and the statistical evaluation of the lab#2 approach:

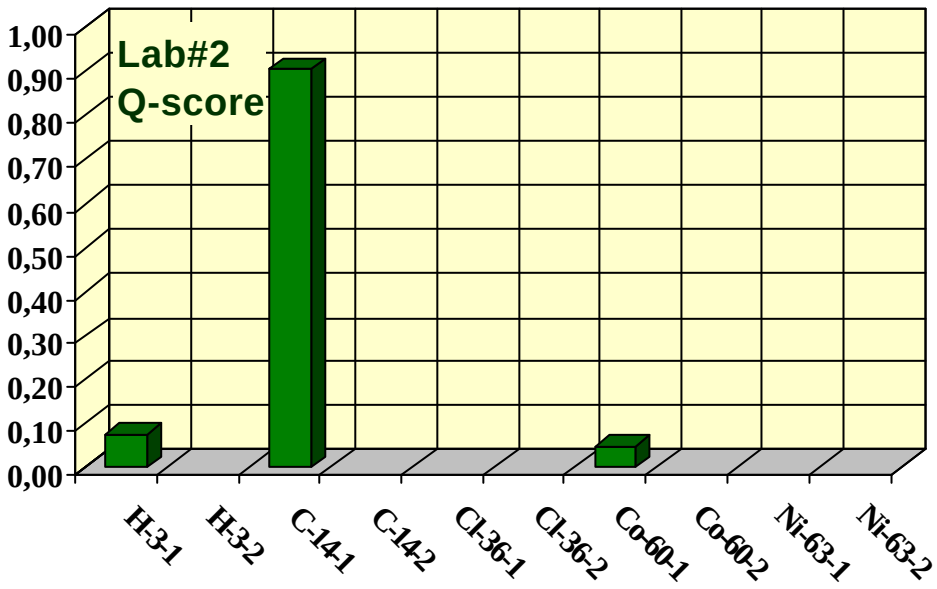

Figure 31. Q-score for Lab#2

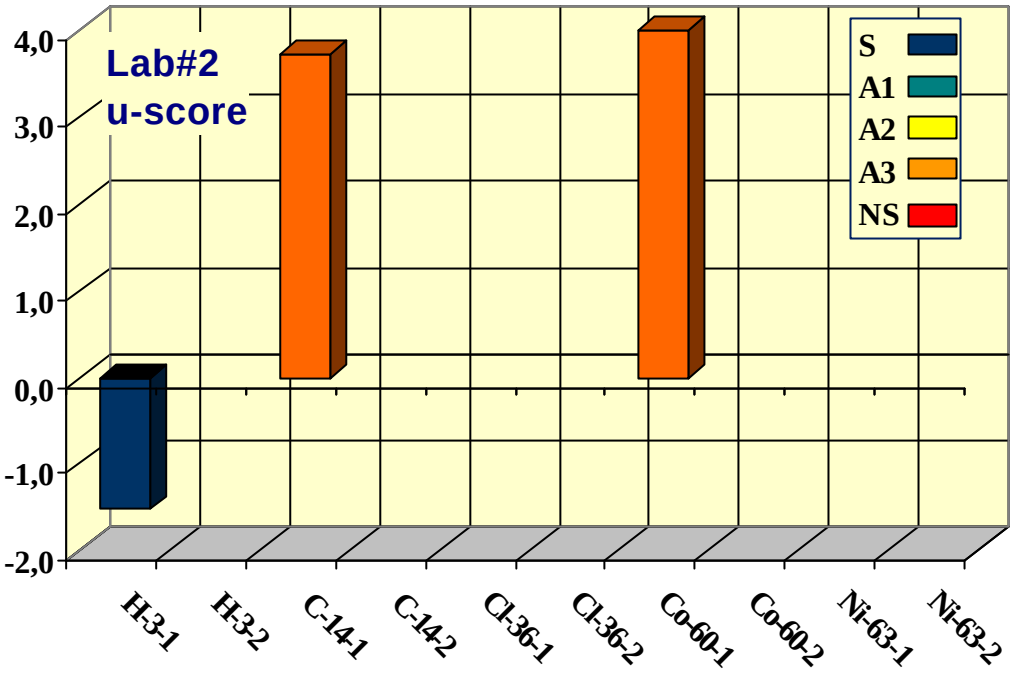

Figure 32. u-score for Lab#2

Lab#2 has no evaluation as non satisfactory. C-14 evaluation gives a overestimate value quoted as Acceptable at level 3, that means a 95% of probability to find reference value in the determination and the value given has a significant difference with the reference value but is not enough to qualify as non satisfactory: it is needed further data for make a decision about the procedure and result. The q-score indicates a 85% bias, so that it is necessary to review the methodology in order to find the factor that duplicates the reference value.

The u-score for Co-60 is also acceptable at level 3 but in this case we have to take into account that the bias is 4.7%, so that this u-score quote is promoted by the formation of reference value and above all the uncertainty of the reference value (1.2%). The procedure of Lab#2 is not different than the others applied in the exercise and the results can considered excellent.

Tritium is quoted as satisfactory in u-score and presents a bias of -5.4%. The methodology for H-3 determination can considered as appropriate and accurate for i-graphite determination.

The Lab#2 approach can be considered as enough good and only need to review the procedure of radiocarbon. The uncertainty sources that lead to these differences can be mostly due to operational or random origin than a systematic effect. It has to be considered as evidence, in order to evaluate the radiocarbon method, the approach for H-3 based on the same chemical principle than radiocarbon and in the same operational procedure that gives an excellent quotation in the exercise.

4.4.3. Laboratory #3 Evaluation

Results of Lab#3 are summarized in table 20 and figure 33

Table 20. Data for Lab#3 evaluation

LAB# 3	x_i	x_{Ai}	2*Ui	X_A	$2*U_X$	SEP	DET	u score	qualify	Q score
H-3-1	6	8,23E-01	5,53E-02	1,00E+00	7,55E-02	REF/TRP	LSC	-2,642	A2	0,177
H-3-2										
C-14-1	6	1,14E+00	1,27E-01	1,00E+00	2,41E-01	REF/TRP	LSC	1,007	S	0,137
C-14-2										
Cl-36-1	6	4,25E-01	6,12E-02	1,00E+00	5,02E-02	REF/TRP	LSC	-9,776	NS	0,575
Cl-36-2										
Co-60-1	6	1,06E+00	8,94E-02	1,00E+00	2,33E-02	DIS	HRG	1,379	S	0,064
Co-60-2	6	8,78E-01	1,06E-01	1,00E+00	2,33E-02	DIS	HRG	-2,237	A2	0,122
Ni-63-1	3	8,34E-01	1,42E-01	1,00E+00	3,65E-02	EXC/ICP	LSC	-1,911	A1	0,144
Ni-63-2										
Sr-90-1	3	1,69E+01	4,93E+00	1,00E+00	2,22E-01	EXC/ICP	LSC	6,430	A3	15,9
Sr-90-2										

Lab#3 reported 6 nuclides, 5 in mandatory, and additionally the determination of Sr-90 concentration. Data supplied were simple (only one set of six data) except for Cl-36 and Sr-90 that only submitted 3. The data with 3 replicates were dropped from reference values calculation as outliers by internal variance.(Cochran test).In this case is associated to the amount of original sample that a single procedure needs to perform a quality determination so that, the reduction (sometimes dramatically regarding the mass forecast for perfume a quality analysis) of mass determination obligates to work outside of the standards in the routine operation and consequently produce a non consistent results.

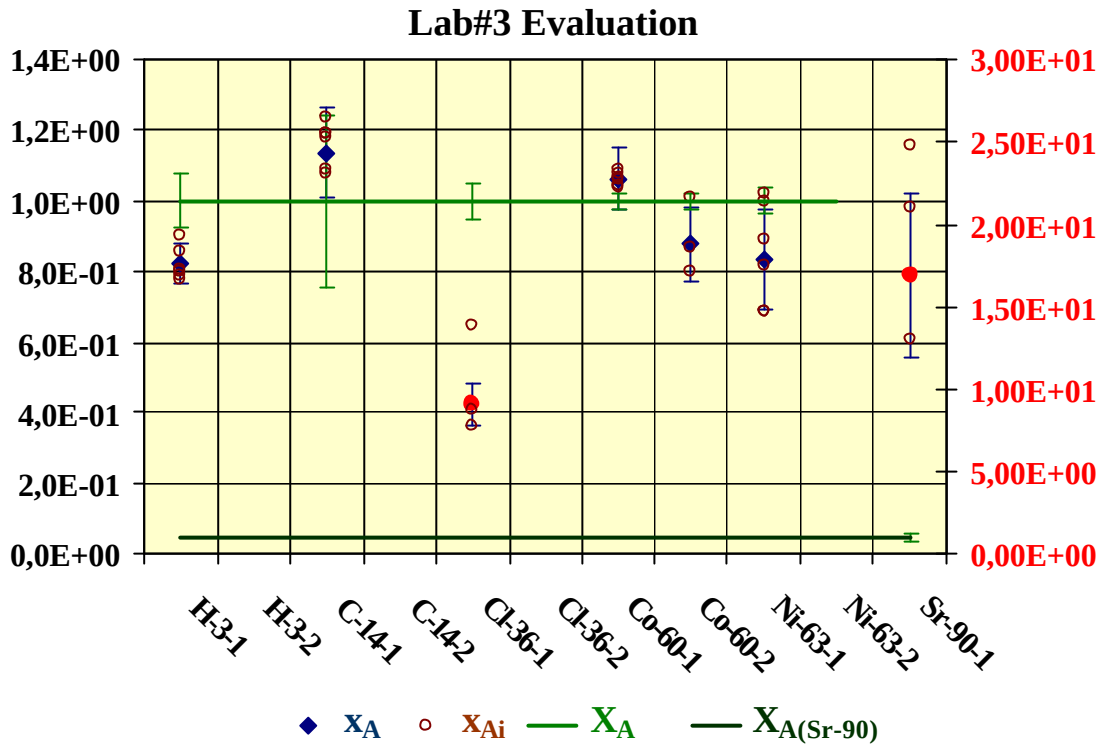

Figure 33. Results of Lab#3

Some remarks can extract from the analysis of the data in Figure 33:

- Tritium determination presents a low scattered of the six data (STD=5.6%) and the weighted average underestimating the reference value in 18%. The weighted average has an uncertainty associated of 3.4% and the reference value has an uncertainty of 12%, so that the difference between both can not be considered due to calculation of reference value and the data indicates possibly not controlled losses of material in the process of separation and concentration.

- C-14 determination has 6 data without significant scattering (STD =5.3% close to the one of tritium determination) the uncertainty associate to the weighted average is 5.6%. Weighted average is overestimate in 14% regarding to reference value which has a uncertainty of ~12%. The result can be considered excellent. and do not need changes in the methodology.

- Chlorine-36 determination presents 3 values with high scattered and the weighted average,— rejected for reference value calculation by internal variance — underestimating the reference value in more than 57%. We must take into account the relative concentration of the Cl-36 in the sample that is a micro-component (3 orders of magnitude lower than H-3 or C-14) and the small amount of i-graphite for performing complex analyses of six nuclides. Nevertheless the uncertainty associate to the weighted average is 7.2 % that is in the same range that the uncertainty of reference value (5%).

- Cobalt-60 determination is reported in double being the data from G-2 a set of 3, Lab#3 use the dissolution of sample for determination and the evaluator consider that the fraction needed to have a quality measure only gives amounts for 9 measurements. The result of Co-60-1 is very accurate with a low scattered and high reproducibility (STD = 1.8%) and a small uncertainty associate (4.2%).to weighted average. The weighted average overestimates the reference value in a 6% but the uncertainty of the reference value is ~1.2 % so that is difficult to quote in the ±2U area around reference value even for this excellent results. Co-60-2 has a STD of 17% in the three values submitted that build a weighted average12% lower than reference value with a uncertainty of 8.5%, due to the good data from every lab in this nuclide this value is considered very faraway from the standard of approaches.

- Nickel-63 evaluation presents highly scattering (STD12.1%) six values around a weighted average with 8% of uncertainty that underestimate the reference value in 17%. The data was valid to contribute in the calculation of reference value and the approach can consider good for this nuclide.

- It was submitted 3 values for Strontium-90 determination, as in the case of Cl-36 and Co-60-2. Applying the evaluation scheme the mean value obtained was considered an outlier by internal variance. In fact the three data are high scattered (STD=30%) and weighted average overestimates reference value in a factor 16). This numbers has to be considered with the limitations that reference value build-up with 4 of 5 values, but a deviation of factor 16 needs to find an explanatory conclusion in the methodology applied: calibration, masses, cross contamination or anything else. Probably a random effect of uncertainty is on the base of this explanation taking into account the results of other difficult to measure nuclides in the exercise of this lab

The values of Q-score (figure 34) where it is observed that the bias of the values with six replicates (4 of 6) are lower than 16%.

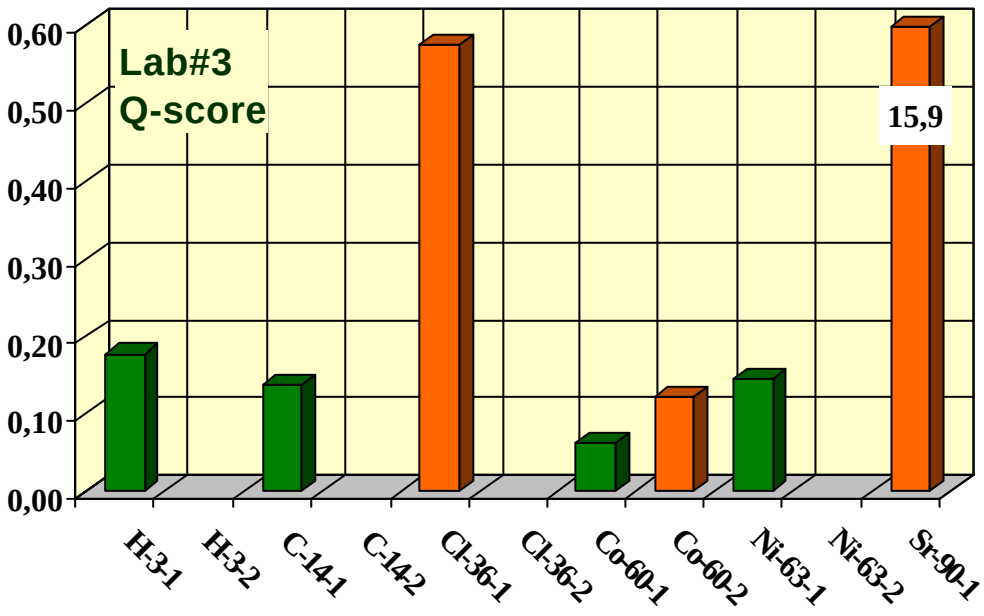

Figure 34. Q-score for Lab#3

The u-score (figure 35) gives a quantitative and qualitative idea of the the statistical evaluation of the lab#3 approach:

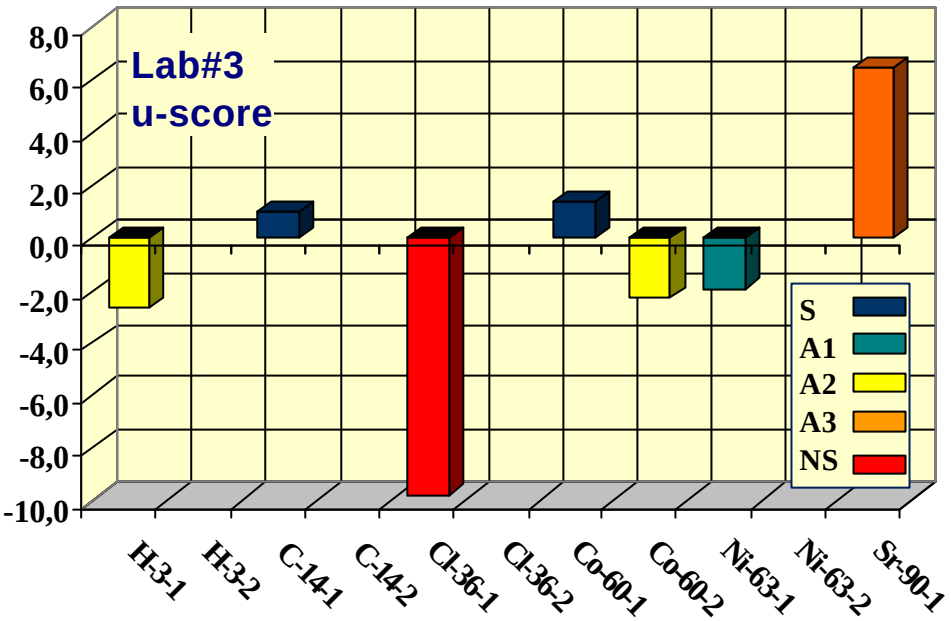

Figure 35. u-score for Lab#3

Cl-36 determination of Lab#3 quoted as non satisfactory and the bias obtained is 57.5%, it is recommended to check the method for small amounts of original samples and due to the underestimation check also the trapping efficiency and or the leaks of the system.

Strontium-90 evaluation gives a 95% of probabilities to find the real value in the result calculate by Lab#3. It is necessary more data to ensure this relative poor quotation due to that the reference value in not as statistically robust. On the other hand it must take into account that the standard deviation of the values from Lab#3 are high scattered (30% standard deviation) and the activity content reported is factor 17 higher than the reference value. As is mentioned a cross contamination could have happened or, with less probability, problem in the calibration of LSC system, also a small mass of graphite was treated in this exercise and

could be a important factor in the quality of the result when the concentration of the nuclide is close to the sensitivity of the detection system.

Statistical evaluation of H-3 is acceptable at level 2 that means H-3 determination could have significant differences with reference value. On the other hand the repeatability of data is high (less than 6% of STD of primary data) and the method for separation is contrasted by C-14 results. So that the conclusion is that the deviation regarding the reference value is more affected by the other lab approaches of tritium content than for the methodology of lab#3, but we must take into account the underestimation and review the trapping and the losses in the analytical system.

The u score of Ni-63 quoted as Acceptable at level 1 that means that the significance of the difference between de data reporting and the reference value is negligible (≥99 % probability to find the real value in the lab#3 weighted average) that means excellent results for this nuclide.

The u score of C-14 and Co-60-1 quoted as satisfactory, that means that the significance of the difference between de data reporting and the reference value is negligible (≥99.9 % probability to find the real value in the lab#3 determination) that means excellent results for this nuclides. Also Co-60-2, that quotes as Acceptable at level 2 can be considered excellent results looking to the bias and the uncertainty of the weighted average (even with three original data) the u-score registered is due to the accurate of the reference value more than a defect in the determination procedure as is demonstrate in Co-60-1 determination

In general terms the evaluation of Lab#3 indicates that their methods and expertise are prepared for i-graphite radiological characterisation quoted satisfactory and acceptable in important nuclides in the inventory. The relative overestimate bias (excluding Sr-90 determination) $\Sigma|Q|/\text{aliquot} = 0.101$) and the the underestimate one is $\Sigma|Q|/\text{aliquot} = 0.254$. Evaluator guest that minor deviations arise in the evaluation results are coming from the mass of i-graphite and the activity level of the samples.

4.4.4. Laboratory #4 Evaluation

Results of Lab#4 are summarized in table 21 and figure 36

Table 21. Data for Lab#4 evaluation

LAB#4	x_i	x_{Ai}	2*Ui	X_A	$2*U_X$	SEP	DET	u score	qualify	Q score
H-3-1	6	1.04E+00	1.29E-02	1.00E+00	7.55E-02	CAF	LSC	0.901	S	0.036
H-3-2	6	9.63E-01	1.08E-02	1.00E+00	7.55E-02			-0.950	S	0.037
C-14-1	6	1.12E+00	2.80E-02	1.00E+00	2.41E-01	CAF	LSC	1.019	S	0.124
C-14-2	6	1.07E+00	2.39E-02	1.00E+00	2.41E-01			0.574	S	0.070
Cl-36-1	6	1.18E+00	5.68E-02	1.00E+00	5.02E-02	CAF/RED	LSC	3.164	A2	0.182
Cl-36-2	6	1.21E+00	4.58E-02	1.00E+00	5.02E-02			3.723	A3	0.205
Co-60-1	6	1.05E+00	3.61E-02	1.00E+00	2.33E-02	DIS	HRG	2.478	A2	0.053
Co-60-2	6	1.02E+00	2.93E-02	1.00E+00	2.33E-02			1.288	S	0.024
Ni-63-1	6	9.93E-01	3.35E-02	1.00E+00	3.65E-02	EXS/ICP	LSC	0.738	S	0.019
Ni-63-2	6	9.92E-01	3.26E-02	1.00E+00	3.65E-02			0.687	S	0.017

Lab#4 reported 5 nuclides of 5 in mandatory, supplied two sets of six determinations per nuclide that were treated individually as different lab inputs. No outliers were found in the exercise for lab#4 so that all the 60 data were use for reference values calculations.

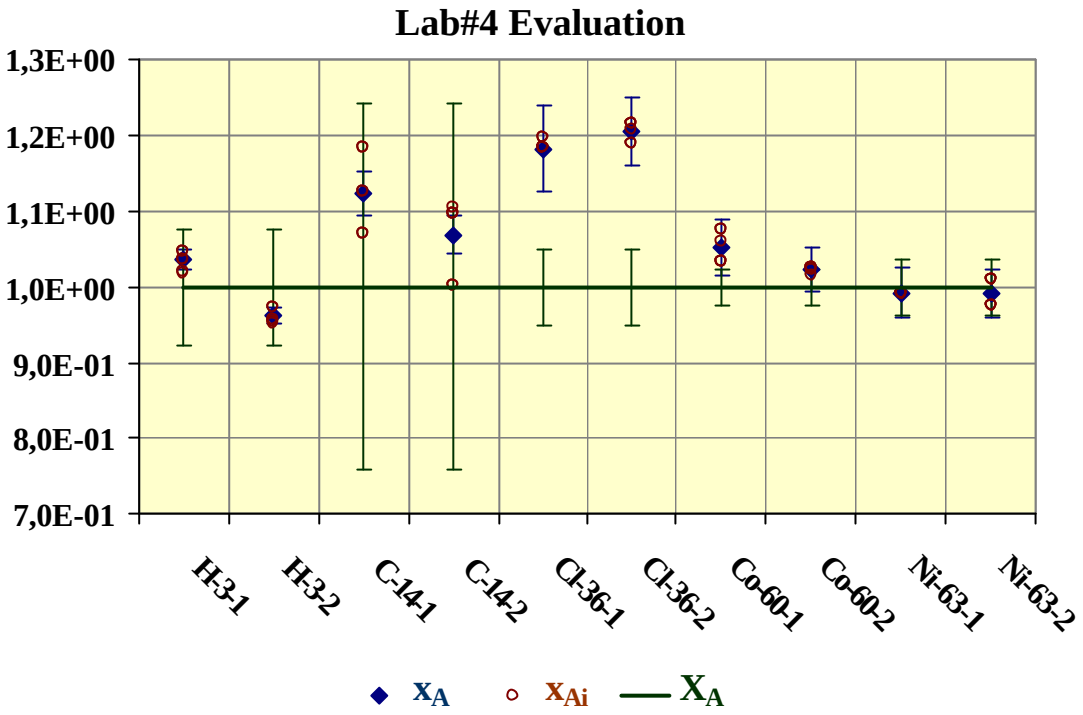

Figure 36. Results of Lab#4

The Analysis of the data in Figure 36 gives the following topics:

- Tritium determination in the sample G-1 (H-3-1) presents a low scattered of the six data (1% of STD) and the weighted average overestimates in a 6% the reference value that have an uncertainty of 3.1%. The uncertainty associate to weighted average is 1.2%. The second set of data coming from G-2 sample gives a underestimation of the reference value in less than 4%, data in the set H-3-2 is also highly accurate with STD of 1.2% over the mean. The uncertainty associate with the weighted average for H-3-2 determination is 1.12%.

- Lab#4 submitted also two sets of data for C-14 determination. C-14-1 has a weighted average that overestimates reference value in 12% with a standard deviation among primary data of 4.5% around the mean value and an uncertainty of 2.5%. Similar results were calculated for the second set of C-14 determination data (C-14-2). The weighted average differs from reference value in a 4% also overestimating it and the

uncertainty of weighted average is 2.2%. The data in the set are lighted scattered with a standard deviation of 4.6%. The uncertainty of reference data is always higher than the deviation observed in the results of Lab #4 for C-14 (12.1%).

- Lab#4 presented two sets of replicates for Chlorine-36 determination. Cl-36-1 data scattered 0.95% and the weighted average calculate with them has an uncertainty of 4.6%. This weighted average differs from reference value in 18% overestimating it and the calculate uncertainty associate with reference value is 5%. The second set of data from Cl-36 determination, labelled as Cl-36-2, has a deviation of 21% from reference value over six data (with a STD of 1.1% around mean value). The weighted average calculate from these low scattered data has an associate uncertainty of 3.4%,

- Cobalt-60 determination is also reported in a double set of six values. Co-60-1 determination comes from another set of low scattered data (STD 2%) with a weighted average that differs 5% from reference value overestimating it, being the associated uncertainty of the weighted average 3.4% and the one of reference value 1.25%. Co-60-2 is more precise than Co-60-1 set with a STD of 0.4% around mean value and a overestimated (2%) value of weighted average regarding reference value. The uncertainty of the reference value is 2.3%.

- The replicates of Ni-63-1 set of data are no scattered that could mean a replication only in the measurement and no in the separation method. This set of data gives a weighted average that underestimates the reference value in a 7% and presents an uncertainty of 3.4% against the uncertainty of reference value of 1.3%. The second set of Ni-63 values give another underestimation of 8% from reference value, with a scattering among data that gives an STD of 2%, that means that at least two separation processes are done in this set of data. The weighted average of Ni-63-2 for Lab#4 has an uncertainty of 3.4%, close to the one of Ni-63-1.

The values of Q-score are in figure 36 where it is observed that the bias of the values are lower than 20% in any case and lower than 10% if Cl-36 determination is excepted, (remind to the reader that Cl-36 is the nuclide with the lowest activity content and deviations are less relevant in this case)

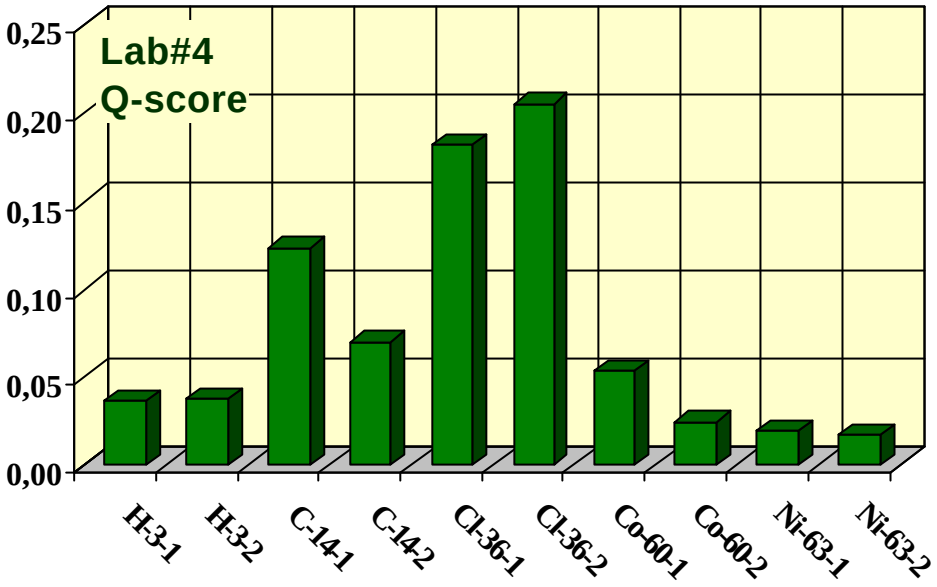

Figure 37. Q-score for Lab#4

The u-score (figure 38) gives the statistical evaluation of the lab#4 approach:

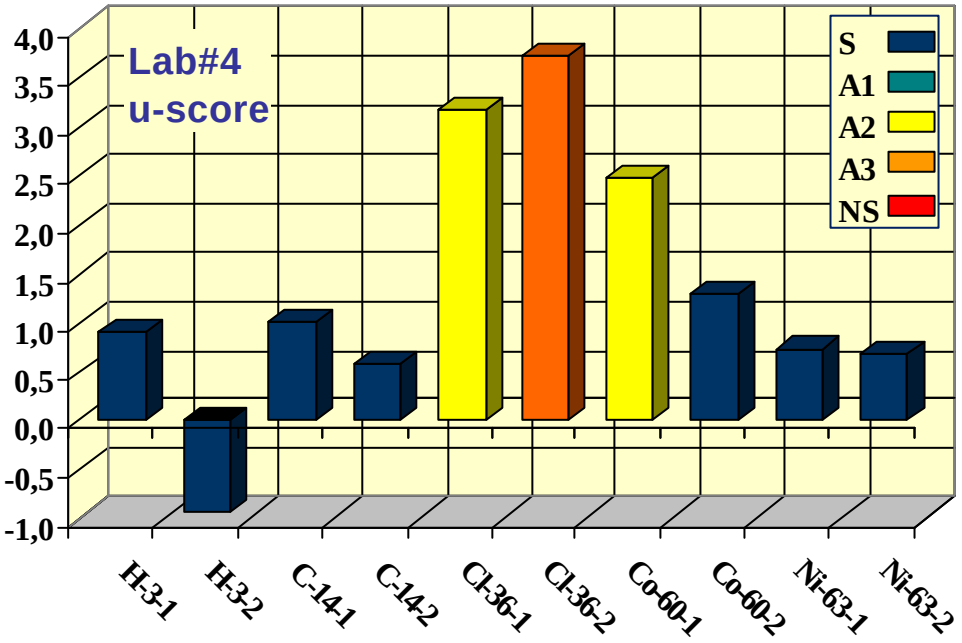

Figure 38. u-score for Lab#4

Lab#4 has evaluation as Satisfactory in 7 sets of 4 nuclides from 5 reporting with relative deviation lower than 10% in H-3(1 and 2 sets), C-14 (1 and 2 sets), Ni-63 (1 and 2 sets) and Co-60-2 set.

In the case of Co-60-1 quoted as Acceptable at level 2 due to the small uncertainty of the reference data, in fact the difference between both weighted averages regarding to one of Co-60-1 set (quoted as satisfactory) is lower than 3% that for systematic and random effects on uncertainty is considered the same value. Evaluator, consequently, do not suggest the revision of determination procedure.

The case of Cl-36 determination is already discussed in the point 4.3.3 where an advertisement of a higher deviation can be found in the determination of this nuclide due to the proximity of activity concentration of the sensitivity of the procedures regularly applied. In this nuclide lab#4 quoted as Acceptable at level 2 and acceptable at level 3 that means that a significance difference is found regarding to the reference value and felt into the 95% and 90% range of probability distribution around reference value. Nevertheless statistics needs further data to find the real deviation of the method applied.

The results of lab#4 are excellent with extremely good approach with low bias from reference values, high repetitively of data and procedures and high performance assessment of uncertainty. The results are in majority overestimate the reference value 7/10 ($\Sigma|Q|$/aliquot = 0.099) an the 3 values that underestimate the reference value are done also slighting ($\Sigma|Q|$/aliquot = 0.024).

4.4.5. Laboratory #5 Evaluation

Results of Lab#5 are summarized in table 22 and figure 39

Table 22. Data for Lab#5 evaluation

LAB# 2	x_i	x_{Ai}	2*Ui	X_A	$2*U_X$	SEP	DET	u score	qualify	Q score
H-3-1	3	1.02E+00	1.41E-02	1.00E+00	7.55E-02	COM	LSC	0.465	S	0.019
H-3-2										
C-14-1	3	1.04E+00	4.07E-01	1.00E+00	2.41E-01	COM	LSC	0.174	S	0.041
C-14-2										
Cl-36-1										
Cl-36-2										
Co-60-1	6	1.02E+00	4.08E-02	1.00E+00	2.33E-02	DIM	HRG	0.834	S	0.020
Co-60-2										
Ni-63-1										
Ni-63-2										

Lab#5 reported 3 nuclides of 5 in mandatory, supplied two sets of three determinations for C-14 and H-3 and one set of six result for Co-60 by non destructive assay.

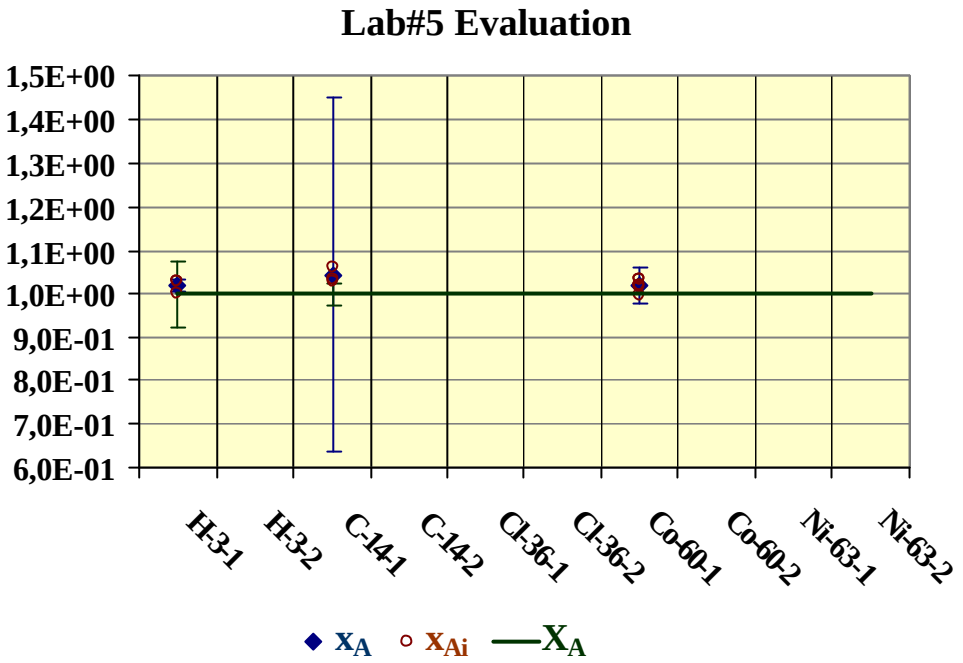

Figure 39. Results of Lab#5

The Analysis of the data in Figure 39 gives the following remarks:

- Tritium determination has been calculate with a set of 3 values with low scattering (STD =1.5%) calculating a weighted average that differs overestimating from reference value in 2% with an uncertainty of 1.4% against the uncertainty of reference value that is 3.1%.

- C-14 determination had also 3 data in one set with a standard deviation around mean of 1.6%. The deviation is quite similar to the tritium due to that the separation is performed in the same procedure than H-3. The weighted average has an uncertainty of 40%, (due to the individual uncertainty of the data submitted) and differs from reference value in 4%. This weighted average overestimates the reference value which uncertainty is 1.6% as is already mention.

- Cobalt-60 determination is reported in a set of six values which present low scattering with a STD of 1.3%. The calculated weighted average differs 2% from reference value

and quoted excellent taking into account both the 1.2% of uncertainty of reference value and the 2% of uncertainty of .weighted average.

The values of Q-score are in figure 40 where it is observed that the bias of the values are lower than 5% in any case.

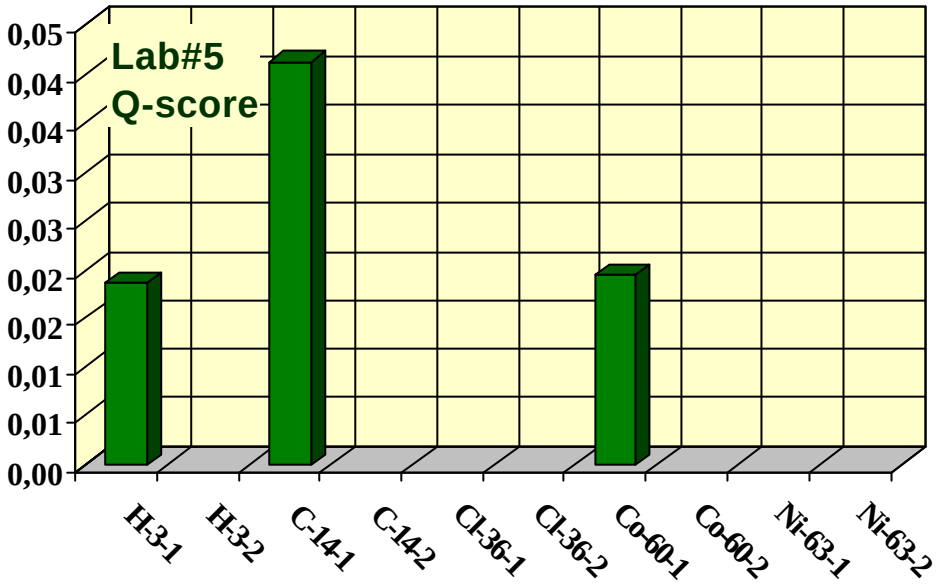

Figure 40. Q-score for Lab#4

The u-score (figure 41) gives the statistical evaluation of the lab#5 approach:

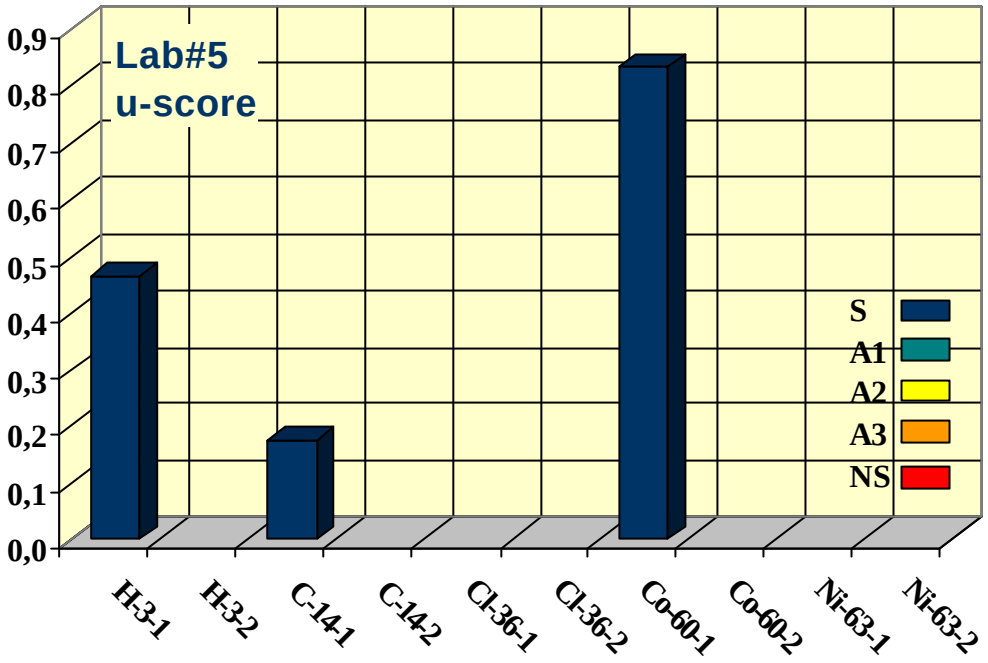

Figure 41. u-score for Lab#5

Lab#5 has every data reported evaluated as Satisfactory with relative deviation from reference value lower than 5% in every nuclide, in detail 2%, 4% and 2% for H-3, C-14 and Co-60. The accurate data submitted and the small scattering of this allows to a good quotation even with less than standard number of replicates submitted.

Lab#5 has no outliers and the weighted average always overestimate the reference value being the $\Sigma |Q|$/aliquot = 0.027 that means a average bias lower than 3% forall data submitted in the exercise.

The evaluator considers this a high degree expert lab for graphite characterisation and encourages it to put in operation or applied the methods for other important nuclides like Cl-36.

4.4.6. Laboratory #6 Evaluation

Results of Lab#6 are summarized in table 23 and figure 42

Table 23. Data for Lab#6 evaluation

LAB# 6	x_i	x_{Ai}	2*Ui	X_A	$2*U_X$	SEP	DET	u score	qualify	Q score
H-3-1	6	9.84E-01	4.02E-02	1.00E+00	7.55E-02	CAF	LSC	-0.286	S	0.016
H-3-2	6	9.29E-01	4.02E-02	1.00E+00	7.55E-02			-1.292	S	0.071
C-14-1	6	1.09E+00	8.89E-02	1.00E+00	2.41E-01	CAF	LSC	0.664	S	0.085
C-14-2	6	9.68E-01	8.89E-02	1.00E+00	2.41E-01			-0.245	S	0.032
Cl-36-1										
Cl-36-2										
Co-60-1	6	1.09E+00	2.34E-02	1.00E+00	2.33E-02	DIM	LRG	5.395	NS	0.089
Co-60-2	6	1.09E+00	2.35E-02	1.00E+00	2.33E-02			5.304	NS	0.088
Co-60-1										
Co-60-2										

Lab#6 reported 3 nuclides of 5 in mandatory, supplied two sets of six determinations per nuclide that were treated individually as different lab inputs. No outliers were found in the exercise for lab#6 so that all the 36 data were use for reference values calculations.

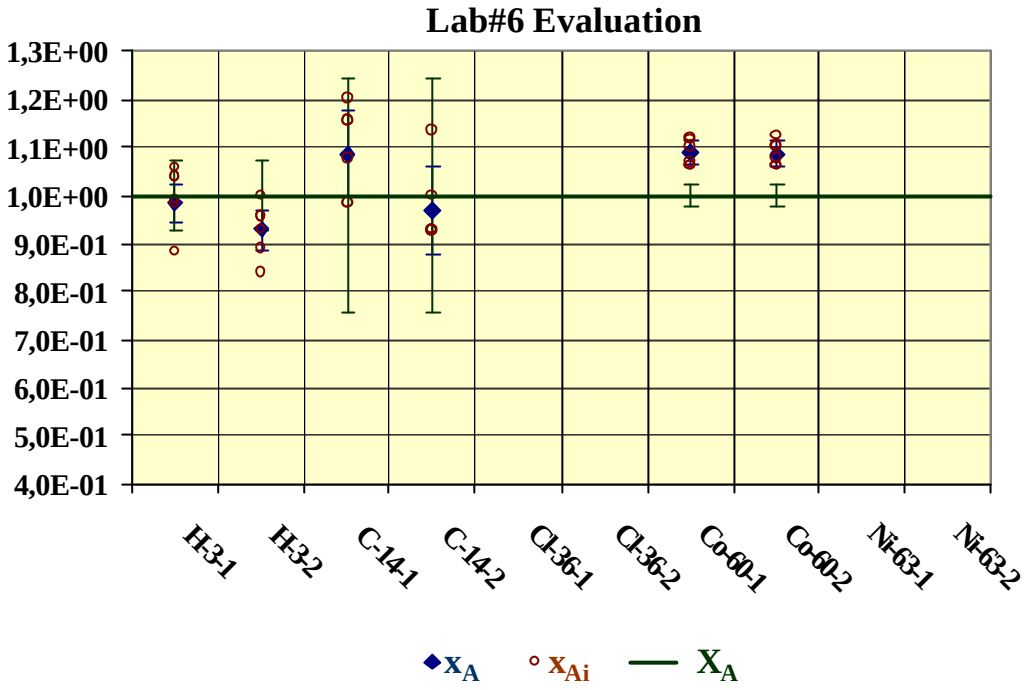

Figure 42. Results of Lab#6

The analysis of the data in Figure 42 suggests the following remarks:

- Tritium determination in the sample G-1 (H-3-1) presents a low scattered data (6% of STD) and the weighted average underestimate in 1% the reference value which has an uncertainty of 3.1%. The uncertainty associate to weighted average is 2%. The second set of data coming from G-2 sample gives a underestimation of the reference value in a 7.1%, data in the set H-3-2 is also concentrate with STD of 6% over the mean. The uncertainty associate with the weighted average for H-3-2 determination is 2.2%.

- Lab#6 submitted also two sets of data for C-14 determination. C-14-1 has a weighted average that overestimates the reference value in a 9.2% with a standard deviation among primary data of 9.2% around the mean value and an uncertainty of 4.1%. Similar results were calculated for the second set of C-14 determination data (C-14-2), the weighted average differs from reference value in a 3.2% in this case under estimating it, and the uncertainty of weighted average is 4.6% The data in the set are

lower scattered with an standard deviation of 8.6%. The uncertainty of reference data is always higher than the deviation observed in the results of Lab #4 for C-14 (12.1%).

- -Cobalt-60 determination is also reported in a double set of six values. Co-60-1 determination comes from another set of low scattered data (STD 2.4%) with a weighted average that differs 9% from reference value overestimating. it, being the associated uncertainty of the weighted average 1.1% and the one of reference value 1.2%. Co-60-2 set has a STD of 2.3% around mean value and overestimated value of weighted average regarding reference value in 9%. The evaluated uncertainty of the weighted average for Co-60-2 is 1.1%.

The values of Q-score are in figure 43 where it is observed that the bias of the values are lower than 9% in any case.

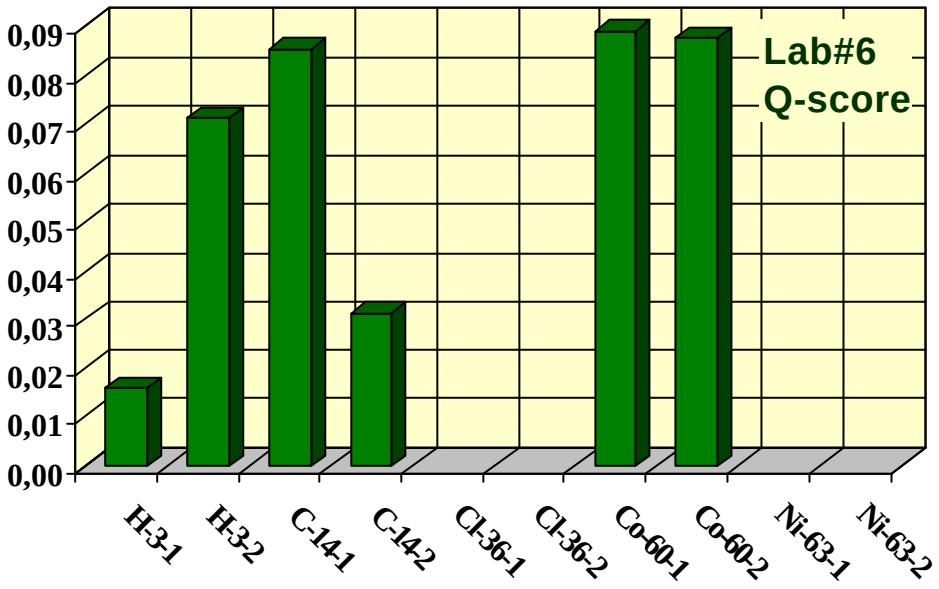

Figure 43. Q-score for Lab#6

The u-score (figure 44) gives the statistical evaluation of the lab#6:

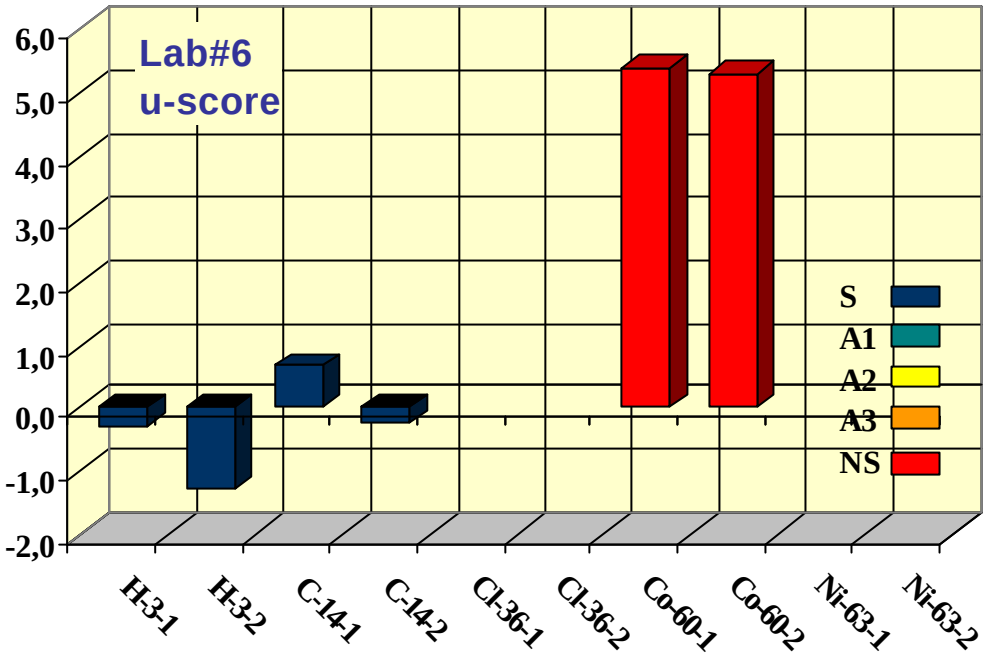

Figure 44. u-score for Lab#6

Lab#6 has evaluation as Satisfactory in 4 sets of 2 nuclides from 3 reporting with relative deviation lower than 9% in H-3(1 and 2 sets), C-14 (1 and 2 sets),

In the case of Co-60-1 and Co-60-2 the deviation is also lower than 9% but quoted as Non satisfactory. In the case of Lab#6 it has to considered two main factors. The first one is the accuracy of reference value as is mentioned in other lab evaluation that gives a large statistical weight any percentage of difference with reference value due to the small uncertainty obtained in the evaluation. On the other hand Lab#6 is the only one lab in the exercise that use Low resolution gamma spectrometry (INa(Tl) detector) that have less capability that High Resolution gamma spec for a more accurate calibration, even more Lab#6 use a directed measurement with experimental calibration. Consequently these factors the 9% deviation with reference value has to consider as excellent approach for Co-60 characterization in i-gaphite.

The results of lab#6 are excellent with extremely good approach with low bias from reference values, high repetitively of data and procedures and high performance assessment of

uncertainty. The results overestimate the reference value in 3/6 ($\Sigma|Q|$/aliquot = 0.087) and 3 values that underestimate the reference value ($\Sigma|Q|$/aliquot = 0.040).

Evaluator miss the other nuclides in the exercise from this lab, due to that the results submitted qualify the Lab as excellent and would have helpful for evaluation. Nevertheless encourage this lab to put in operation other methodologies for complete inventory of i-graphite

4.4.7. Laboratory #7 Evaluation

Results of Lab#7 are summarized in table 24 and figure 45

Table 24. Data for Lab#7 evaluation

LAB#7	x_i	x_{Ai}	2*Ui	X_A	$2*U_X$	SEP	DET	u score	qualify	Q score
H-3-1	5	9.31E-01	2.62E-02	1.00E+00	7.55E-02	CAF	LSC	-1.507	S	0.069
H-3-2	5	9.18E-01	2.59E-02	1.00E+00	7.55E-02	CAF	LSC	-1.797	A1	0.082
C-14-1	5	1.09E+00	5.39E-02	1.00E+00	2.41E-01	CAF	LSC	0.744	S	0.092
C-14-2	5	1.11E+00	5.47E-02	1.00E+00	2.41E-01	CAF	LSC	0.897	S	0.111
Cl-36-1	6	8.31E-01	1.32E-01	1.00E+00	5.02E-02	REF/TRP	LSC	-2.037	A1	0.169
Cl-36-2	6	1.26E+00	1.65E-01	1.00E+00	5.02E-02	REF/TRP	LSC	2.675	A2	0.258
Co-60-1	6	1.00E+00	2.54E-02	1.00E+00	2.33E-02	DIM/SG	HRG	0.232	S	0.004
Co-60-2	6	1.03E+00	2.61E-02	1.00E+00	2.33E-02	DIM/SG	HRG	1.839	A1	0.032
Ni-63-1	6	1.07E+00	4.37E-02	1.00E+00	3.65E-02	EXS/SPH	LSC	3.352	A2	0.098
Ni-63-2	6	1.07E+00	4.36E-02	1.00E+00	3.65E-02	EXS/SPH	LSC	3.255	A2	0.095
Sr-90-1	6	8.49E-01	3.48E-02	1.00E+00	4.43E-01	EXC/GRV	LSC	-0.666	S	0.151
Sr-90-2	6	8.30E-01	3.54E-02	1.00E+00	4.43E-01	EXC/GRV	LSC	-0.750	S	0.170

Lab#7 reported 68 determination of 6 nuclides, 5 in mandatory and additionally the determination of Sr-90 concentration. Data were supplied in a double set of 5, for tritium and radiocarbon, and a double set of 6 for the other nuclides reported

No outliers are found in the calculation of weighted average and the amount of sample delivered was enough for performing the analytical procedures.

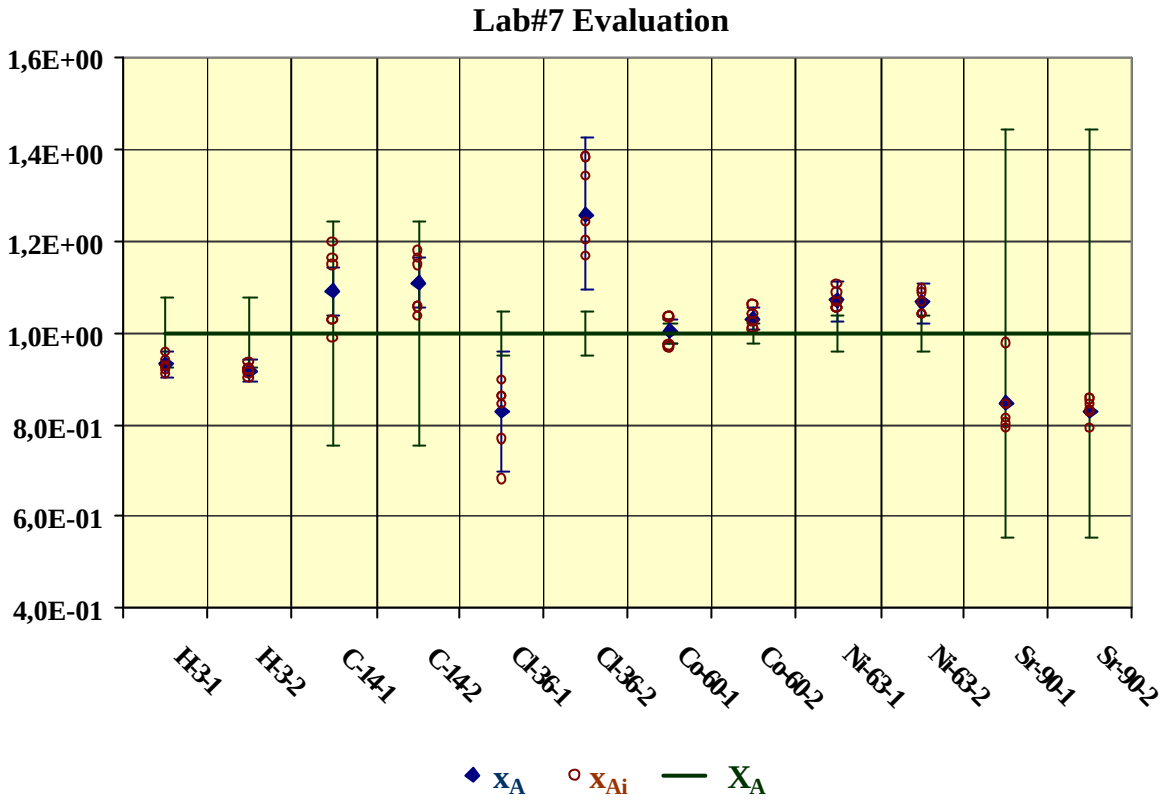

Figure 45. Results of Lab#7

Analyzing the data of Figure 45 can comment:

- Determination of tritium fom G-1 sample gives a high reproducibility of 2%. The weighted average of H-3-1 for lab#7 has an uncertainty of 1.4% and differs from reference value in -7%. The second set of data for H-3 determination has a STD of 1.3% among primary data of the set. The weighted average has an uncertainty of 1.4% and it underestimates the reference value in 8.2%. The reference value has an uncertainty of 1.2% very similar to the one of the weighted average calculated.

- C-14-1 determination has 5 data scattered with STD =8.3% . The uncertainty associate to the weighted average is 2.5%. The weighted average overestimates in 9.2% the reference value which has an uncertainty of 12.1%. The result for the G-2 sample, labelled C-14-2 is calculate for a less scattered (STD =5.75%) set of 5 inputs. The weighted average calculated has a uncertainty of 2.5% and, also, overestimates in a 11 % the reference value. The results can be considered good enough taking into account

all the factors, the bias of the weighted average the uncertainty of both reference and weighted averages values.

- Chlorine-36 determination presents 2 sets of 6 replicates. In the case of Cl-36-1 the values present a STD of 10.5% around the mean value. Weighted average of this set has an associated uncertainty of 8% and the bias with reference value is -16.9%. The second set of Cl-36 determinations scattered with a STD = 6.6% overestimating the reference value in 25.8%. The uncertainties associated with weighted average and reference value are 6.6% and 5% respectively. The data of Bias and uncertainties are in a good agreement for the evaluation of Cl-36 methodology applied.

- Cobalt-60 determination is also reported in double set of six values. In both cases overestimate the reference value whose uncertainty, as already mention in other lab studies, is 1.2%. Co-60-1 has a lightly dispersion among data with a STD of 3.2%. The uncertainty of the derived weighted average is 1.2% and the difference with reference value is 4%. In the second set the bias with reference value is 7% being the same the uncertainty associate with weighted average (1.3%) and the dispersion of the primary data around the mean measured by STD is 2.1% (less scattered that in Co-60-1).

- Nickel-63 evaluation is also given in two sets of six measurements or replicates. Ni-63-1 presents light scattering of the data (STD=2.1%) and the weighted average a uncertainty of 2%. The bias with reference value, whose uncertainty is 3.6%, is +7%. The second set of Ni-63 determinations has an STD = 3.4%.Weighted average (U = 2.%) overestimate reference value in 6.8%.

- Lab#7 submitted, additionally to mandatory nuclides, two sets of six values of strontium-90 determination in the sub-samples. Applying the evaluation scheme, with the limitation already mentioned about validation of reference values, the Sr-90-1 weighted average were built from a STD=9% of scattered data giving a weighted average with 2% of uncertainty that underestimates the reference value (U = 22%) in a 15.1%. In the case of the second set of Sr-90 data (STD =2.6%) the weighted average (U=2.1%) presents a difference with reference value of 17%. In both cases the weighted average are inside the reference value $\pm 2 \cdot U$ and is spected a good quotation.

All the results-pairs submitted by Lab#7, except for Cl-36, has a systematic tendency to overestimate or underestimate the reference value, and in all of these cases the scattering of primary data is lower than 9% around mean. The associated uncertainties to weighted averages are smaller or in the same order than the reference value uncertainty.

The case of Cl-36 is different due to the concentration of this nuclide in the samples are close to the sensitivity limit of the procedures and systems so that the variability of the results clos to the MDA is expected higher than in the other nuclides.

The values of Q-score (figure 46) where it is observed that the biases of the values are lower than 26%, 17% if Cl-36 evaluation is excepted

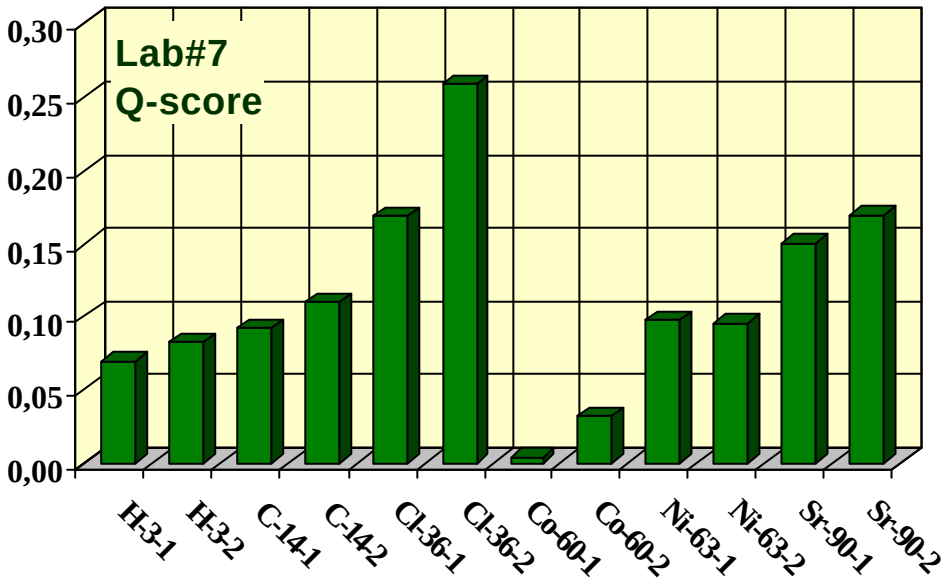

Figure 46. Q-score for Lab#7

The statistical evaluation of the results of Lab#7 is plotted in the u-score graph in figure 47

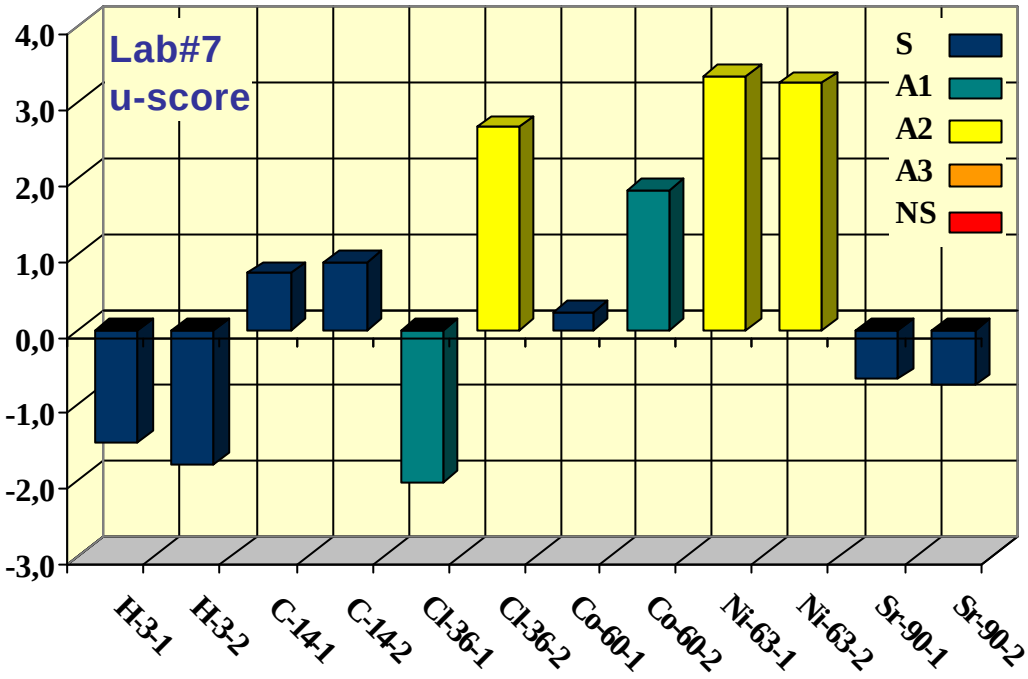

Figure 47. u-score for Lab#8

Results of H-3, C-14, Co-60 and Sr-90 are quoted as satisfactory. One set of Co-60 quoted as Aceptable at level 1 than means a probability higher than 99% of find real value in the sample by the method and due to the small value of uncertainty of reference value and the bias presented by this weighted average (3.2%) it is considered as satisfactory. These results show a Bias of 7% and 8% for H-3, 9% and 11 % for C-14 and 0.4% and 3.2% and Co-60 so that evaluation can be considered as excellent for these Lab.

Sr-90 quotation is also satisfactory but with the limitations of the consistency given by the number of inputs to construct the reference value (4 of 5). The bias is 15% and 17% from reference value.

Ni-63 is quoted as acceptable at level 2, which means a possible significant difference with reference value (Probability to find the weighted average in the reference value distribution is ≥95). The tendency of the method applied is to overestimate the reference value that pointed

out to calibration or cross contamination of the sample during the process. The deviations in both sets are practically the same 7%.

Cl-36 determination of Lab#7 quoted as acceptable at level 1 in the first set and acceptable at level 2 in the second. This results with bias of 17% and 25% respectively are enough good according to other results in the proficiency test, so that due to the precision showed in this RRT from lab#7 is recommended to upgrade the sensitivity of the method applied.

The results of Lab#7 in the exercise demonstrate that it is an expert lab in graphite characterisation, not outlier found in the 12 sets of measurements, accurate results, there are no quotes as non satisfactory either acceptable at level 3 that means a wide range of ability and a deep knowledge of the methodology and the matrix effect. The relative overestimate bias $\Sigma|Q|/\text{aliquot} = 0.099$) and the underestimate one is $\Sigma|Q|/\text{aliquot} = 0.128$.

4.4.8. Laboratory #8 Evaluation

Results of Lab#8 are in table 25 and figure 48

Table 25. Data for Lab#8 evaluation

LAB#7	x_i	x_{Ai}	2*Ui	X_A	$2*U_X$	SEP	DET	u score	qualify	Q score
H-3-1	6	1.01E+00	8.81E-01	1.00E+00	7.55E-02	CAF	LSC	0.156	S	0.011
H-3-2	6	6.21E-02	6.21E-02	1.00E+00	7.55E-02			-1.633	S	0.119
C-14-1	6	1.03E+00	8.45E-02	1.00E+00	2.41E-01	CAF	LSC	0.268	S	0.034
C-14-2	6	1.01E+00	8.28E-02	1.00E+00	2.41E-01			0.091	S	0.012
Cl-36-1	6	5.88E+00	7.73E-01	1.00E+00	5.02E-02	CAF	LSC	12.512	NS	4.878
Cl-36-2	6	3.76E+00	7.73E-01	1.00E+00	5.02E-02			7.067	NS	2.755
Co-60-1	6	1.07E+00	1.74E-02	1.00E+00	2.33E-02	DIS	HRG	4.507	NS	0.065
Co-60-2	6	1.05E+00	1.72E-02	1.00E+00	2.33E-02			3.541	A3	0.051
Ni-63-1	6	9.53E-01	8.56E-02	1.00E+00	3.65E-02	EXC/ICP	LSC	-0.473	S	0.023
Ni-63-2	6	9.34E-01	8.33E-02	1.00E+00	3.65E-02			-0.909	S	0.042
Sr-90-1	6	1.94E+00	8.50E-02	1.00E+00	4.43E-01	PREC/ICP	LSC	4.087	A2	0.939
Sr-90-2	6	1.90E+00	8.36E-02	1.00E+00	4.43E-01			3.939	A2	0.904

Lab#8 reported 72 determination of 6 nuclides, 5 in mandatory and additionally the determination of Sr-90 concentration. Data were supplied in a double set of 6 replicates for each nuclide.

Outliers are found in the Cl-36 data which will be discussed forward. The rest of the 60 data were used to calculate the reference values in the exercise.

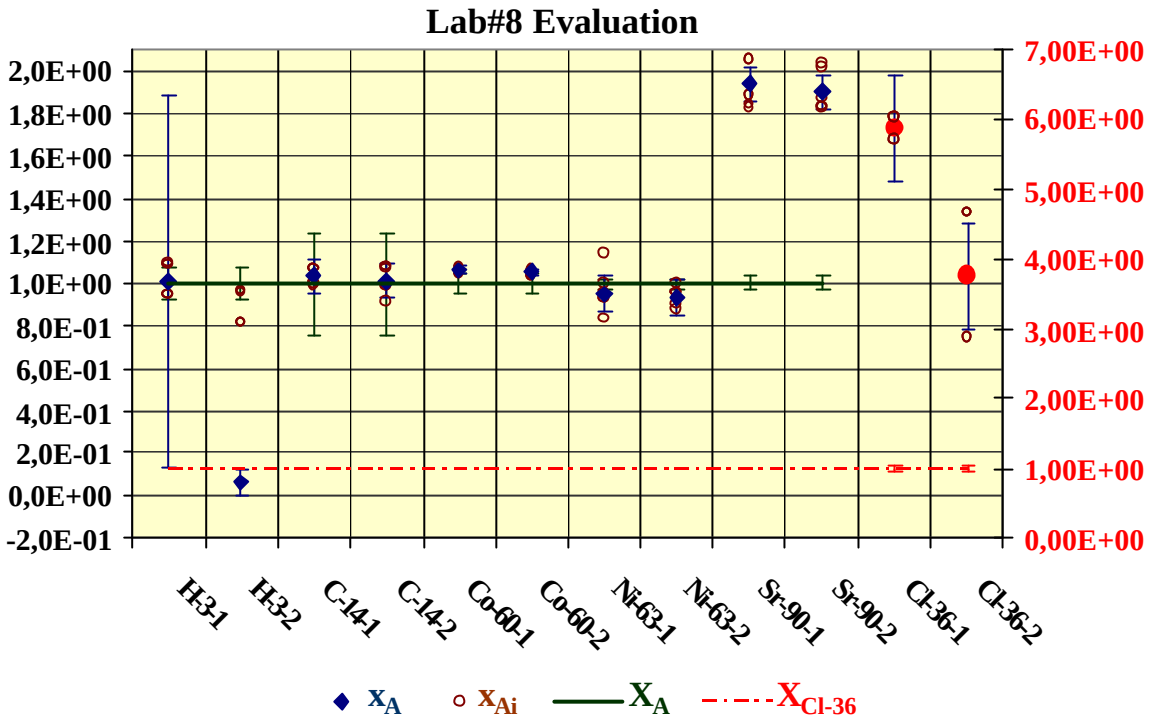

Figure 48. Results of Lab#8

Analyzing the data of Figure 48:

- Determination of tritium from G-1 sample gives a bi-mode distribution with two sets of 3 data each one. It seems to really fulfil the characterisation scheme proposed performing 3 replicates for two separation processes. Total standard deviation of six values is 7% and the weighted average calculated has an uncertainty of 3%. The bias regarding reference value (U=3.1%) is 1.1%. The second set of H-3 determination data is scattered with STD= 9%.also in a bi-mode distribution. The uncertainty of weighted average of H-3_2 is 3.5%, This underestimate the reference value in a 1.2%.

- C-14-1 determination has 6 data scattered with STD =4.2% . The uncertainty associate to the weighted average is in the same order of magnitude (4.1%). The weighted average overestimates in 3.4% the reference value which has an uncertainty of 12.1%. The result for the G-2 sample, labelled C-14-2 is calculate for a more scattered (STD =6.6%) set of 6 data. The weighted average calculated has a uncertainty of 4.1% and, also slightly overestimates the reference value in a 1.2 %. The results can be

considered excellent due to both the bias and the uncertainty associate to the weighted averages.

- Cobalt-60 determination is also reported in double set of six values. In both cases overestimate the reference value (U =1.2%). Co-60-1 has a dispersion evaluated through the STD of data in the set of 1%. The uncertainty of the derived weighted average is 0.8% and the difference with reference value is 6.5%. In the second set the bias with reference value is 5.1% and the uncertainty associate with weighted average is the same than in Co-60-1 (0.8%), the primary data around the mean has a STD =0.97%.

- Nickel-63 evaluation is also given in two sets of six measurements or replicates. Ni-63-1 presents STD = 10.4% in the scattering of the data. The weighted average has an uncertainty of 4.5% and this Ni-63-1 weighted average differs in a 4.7% from the reference value(U=1.8%) underestimating it, The second set presents a bias of 6.6% also underestimating the reference value, being the weighted average (U=4.5%) built up with six values whose STD around the mean is 4.8%.

- Evaluation of Lab#8 strontium-90 data has the same problems that the ones from Lab#2 and Lab#7: The consistence of the reference value, so that the data analyzing in this paragraph are only illustrative and not definitive as statistical evaluation of the methodology applied. The first set of data has a STD of 5.45. The uncertainty of the weighted average is 2.2%, similar results we find in Sr-90-2 with a STD among data of 4.8% and an uncertainty of 2.2%. The differences with reference value (U=22%) are 94% and 90% for Sr-90-1 and Sr-90-2 respectively.

- Chlorine-36 determination presents 2 sets of 6 replicates. MDA are reported in the first set of data and the evaluator considered these value as valid input for implement the evaluation, the MDA's treated with a STD of 2.8% build-up a weighted average which was rejected as outlier by inter-lab means. The weighted average (U=6.6%) presents a overestimation of reference value of factor 4.9, being the uncertainty of reference value of 2.5%. The second set of data presents again a bi-mode distribution with a set of 3 data submitted as MDA and another set of data quoted higher than MDA. Evaluator considered the possibility of treat the data higher than MDA value as the

input of Lab#8 but the attempt also reject the value as outlier by inter-lab mean (Grubbs test) and the quotation of Lab#8 was the same. The STD of the both set of 3 data together is 26% and the weighted average presents an uncertainty of 10.3%. The difference with reference value is an overestimation of factor 2.8.

The results submitted by Lab#8, except for Cl-36, and Sr-90, are accurate and precise; there are not systematic deviations from reference values.

The case of Cl-36 has a particular behaviour due to the concentration of nuclide in the sample and the sensitivity of the procedure that drive to submit 6 of 9 MDA data.

Sr-90 can not quantitatively evaluate due to the few data valid for built-up a consistent refrence value.

Q-score values (figure 49) gives the absolute bias of the weighted average. It is observed that (except for Cl-36 and Sr-90) the biases of the values are lower than 12%,

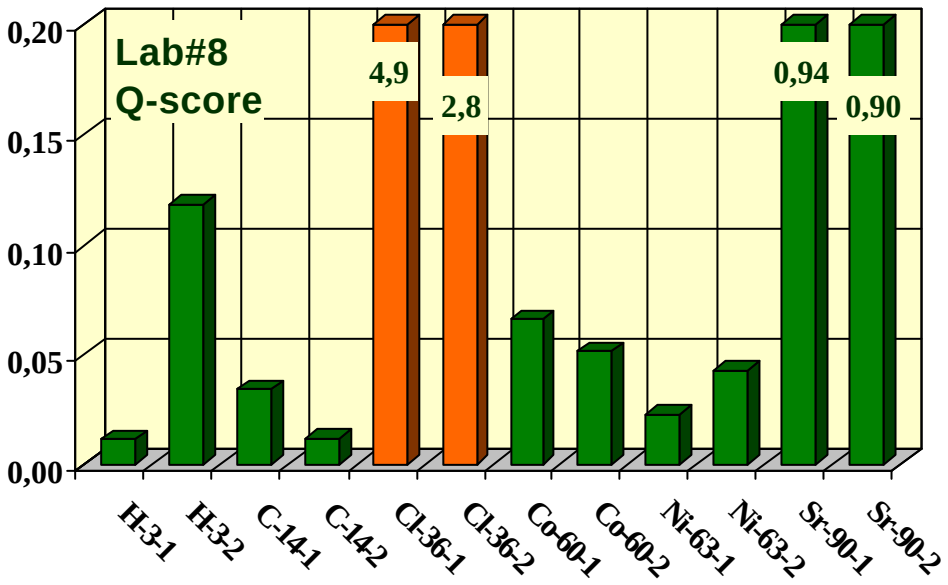

Figure 49. Q-score for Lab#8

The statistical evaluation of the results of Lab#8 is plotted in the u-score graph in figure 50

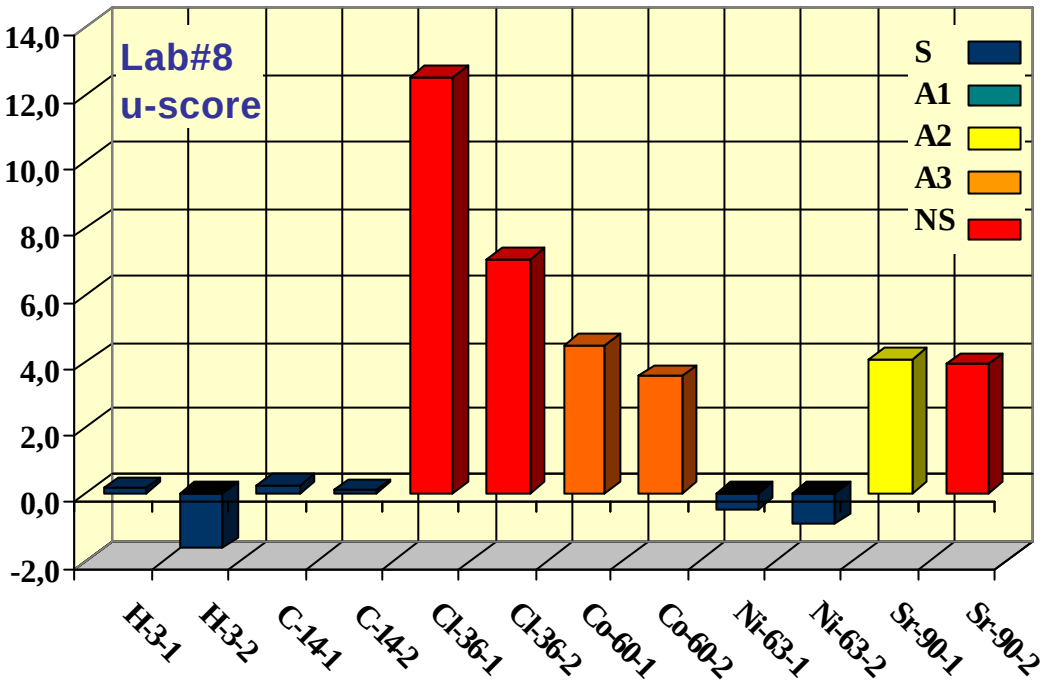

Figure 50. u-score for Lab#8

Results of H-3, C-14 and Ni-63 quoted as Satisfactory and no further explanations are needed, this values are logic seen the accurate and the precision of the results obtained.

Lab#8 quoted Acceptable at level 3 for Co-60 quoted as Acceptable at level 3. This statistical evaluation have to be combined with both the bias of the results 6.1% and 5.1% and the uncertainty of the Co-60 reference value 1.2% and then it is clear that is a high demanded in accuracy that the data collected from every lab obliges to individual data. Evaluator considered that this kind of deviation for this nuclide in radioactive waste is more than acceptable for inventory determination.

Sr-90 quotation is as acceptable at level 2 and Non satisfactory respectively for set 1 and 2 of measurements. The reasons are also explained and we can considered that the quoted in the

same order of magnitude of another lab (Lab#7) is enough for take a rough idea about the sensitivity of the method more than going into details of what is the defect or not of the determination process due to that there are not a robust reference value.

Cl-36 determinations by Lab#8 quoted as Non Satisfactory in both cases. The submission of MDA and the overestimation of activity drive to a sensitivity problem in the process. Lab#8 has to review and test all the process related with this kind of determination in this nuclide at least reasons for non systematic origin of deviation can be found for the case of this exercise.

The results of Lab#8 can be considered enough good with an exceptional mention of Cl-36 already discussed. The lab has the capabilities to face the characterisation of graphite and has the tools for the up-grading or tuning-up the method with low quote. The relative overestimate bias $\Sigma|Q|$/aliquot is 0.288, for 7 of 10 and the underestimate one is $\Sigma|Q|$/aliquot = 0.061 for 3 of 10 (excluding Cl-36 data).

4.4.9. Laboratory #9 Evaluation

Results of Lab#9 are summarized in table 26 and figure 51

Table 26. Data for Lab#9 evaluation

LAB#9	x_i	x_{Ai}	2*Ui	X_A	$2*U_X$	SEP	DET	u score	qualify	Q score
H-3-1	6	9.72E-01	1.99E-02	1.00E+00	7.55E-02	CAF	LSC	-0.647	S	0.028
H-3-2	6	9.22E-01	1.87E-02	1.00E+00	7.55E-02			-1.842	A1	0.078
C-14-1	6	1.17E+00	3.81E-02	1.00E+00	2.41E-01	CAF	LSC	1.359	S	0.166
C-14-2	6	1.16E+00	3.86E-02	1.00E+00	2.41E-01			1.291	S	0.158
Cl-36-1	6	9.97E-01	4.51E-02	1.00E+00	5.02E-02	DIS/EXT	LSC	-0.048	S	0.003
Cl-36-2	6	1.05E+00	4.87E-02	1.00E+00	5.02E-02			0.948	S	0.053
Co-60-1	6	9.02E-01	2.13E-02	1.00E+00	2.33E-02	DIM	HRG	-6.195	NS	0.098
Co-60-2	6	8.70E-01	2.06E-02	1.00E+00	2.33E-02			-8.366	NS	0.130
Ni-63-1	6	9.64E-01	4.38E-02	1.00E+00	3.65E-02	EXS/ICP	LSC	-0.384	S	0.011
Ni-63-2	6	9.67E-01	4.58E-02	1.00E+00	3.65E-02			-0.282	S	0.008

Lab#9 reported 10 sets of determinations of 5 of 5 in mandatory. It is submitted two sets of six replicate determinations per nuclide that were treated individually as different lab inputs. No outliers were found in the exercise for lab#9 so that the 60 data were use for reference values calculations.

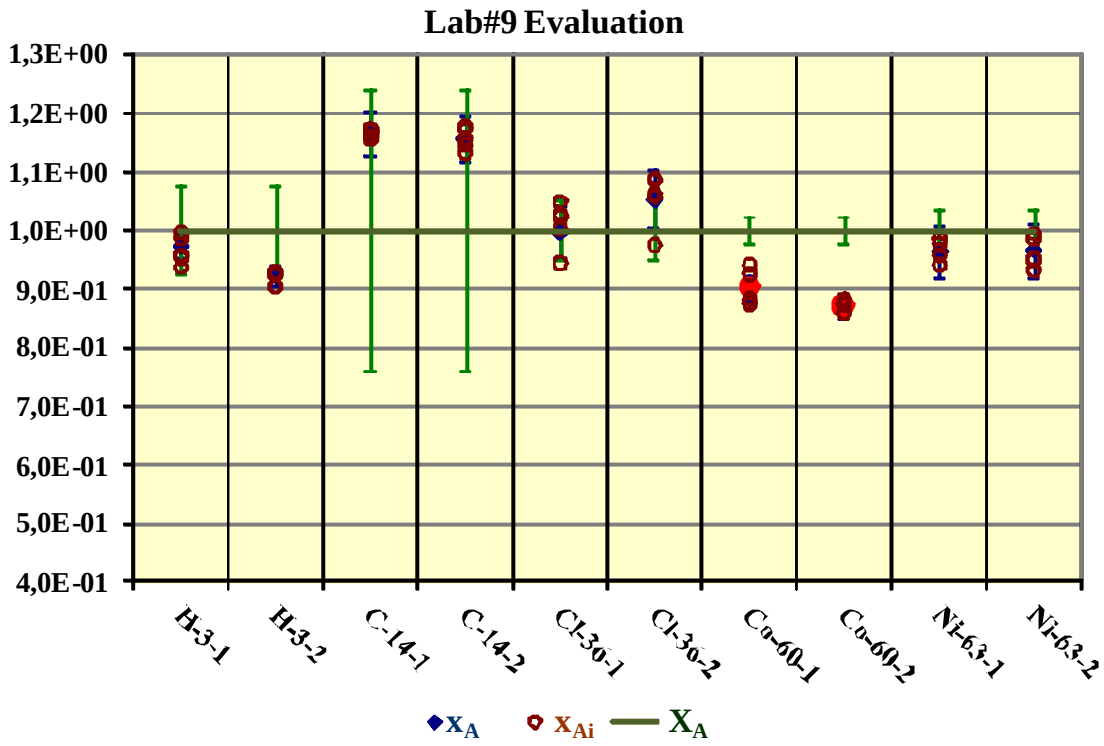

Figure 51. Results of Lab#9

Some remarks on the data of figure 51 are::

- Tritium determination in the sample G-1 (H-3-1) has six data scattered with a STD of 2.7%. the weighted average calculate with this set of data has an uncertainty of 1% and presents a deviation from reference value of – 2.8%, being the uncertainty of reference value for H-3 determination 3.2%. The accuracy of the weighted average and the same order of magnitude uncertainties will give a good approach. The second set of H-3 determination are slightly scattering (STD = 0.97%).The bias with reference value is 7.8% underestimate it. The weighted average has an uncertainty of 15 due to the precision of original data.

- Lab#9 also submitted two sets of data for C-14 determination. C-14-1 has a weighted average that overestimates reference value in 16.6% with a standard deviation among primary data of 0,65% around the mean value and an uncertainty of 1.6% in the set labelled C-14-2 it is found a little higher dispersion than in C-14-1, with a STD of

1,5%. The weighted average differs 15.8% from reference value (U=12.1%) overestimating it.

- First set of Chlorine-36 determination (Cl-36-1) has a STD of 4.25% among primary data. The calculated weighted average has a uncertainty associate of 2.3% and underestimates the reference value in a 2.6%, being the uncertainty of reference value of 2.5%. The second set for Cl-36 submitted by Lab#9 presented and STD among replicates of 3.9%. The weighted average (U=2.3% as in the Cl-36-1 set) differs from reference value in 5.3%. this accurate data for this specific nuclide that is in the lowest concentration in the exercise has the meaning of a very sensitive methodology and high level capability of the Lab.

- Cobalt-60 determination is also reported in a double set of six values. Co-60-1 determination comes from another set of low scattered data (STD 3.2%) with a weighted average that differs 9.8% from reference value overestimating it, being the associated uncertainty of the weighted average 1.2% and the one of reference value 1.25%. Co-60-2 is more precise than Co-60-1 set with a STD of 1.1% around mean value and a overestimated (13%) weighted average regarding reference value. The values of Co-60 from Lab#9 are not their best value within the measurements submitted in the exercise, in fact are the highest deviated ones even the method applied (Direct measurement by high resolution gamma spectrometry) is one of the most accurate and contrasted methods. Nevertheless the deviation registered is lower than 10% is a good quote for this nuclide.

- The replicates of Ni-63-1 set of data have a STD = 2.2%. This set of data gives a weighted average that underestimates the reference value in a 3.6% and presents an uncertainty of 2.3% against the uncertainty of reference value of 1.3%. The second set of Ni-63 values give another underestimation of 3.3% from reference value, with a scattering among data that gives an STD of 2.5%,. The weighted average of Ni-63-2 for Lab#9 has an uncertainty of 2.4%, in the same order of magnitude than Ni-63-1.

The values of Q-score are in figure 52 where it is observed that the bias of the values are lower than 17% in any case.

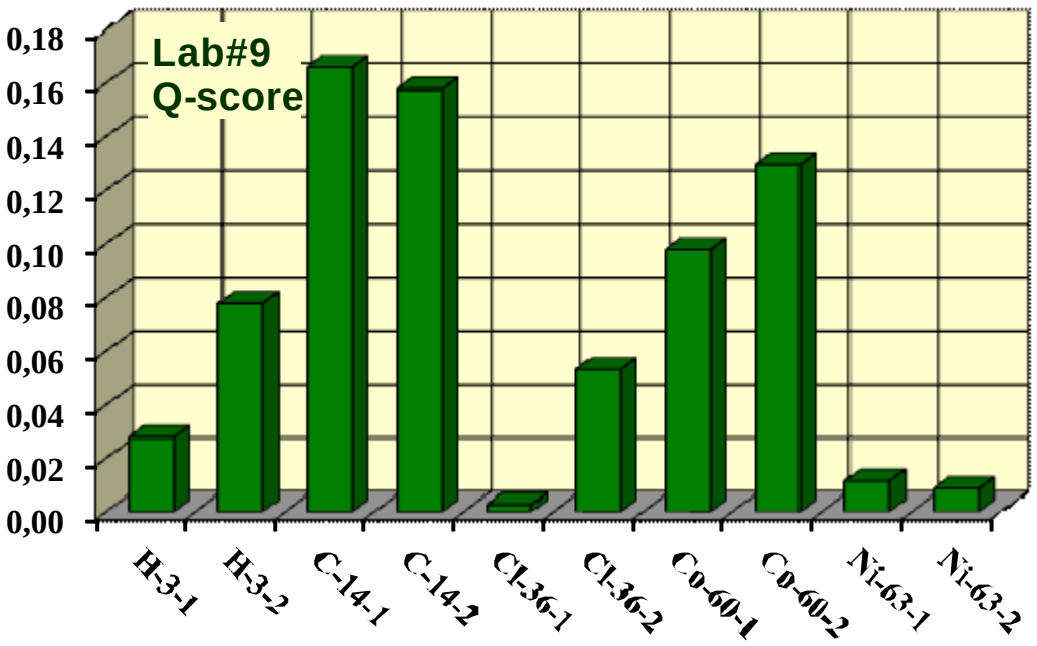

Figure 52. Q-score for Lab#9

The u-score (figure 53) gives the statistical evaluation of the lab#9 approach:

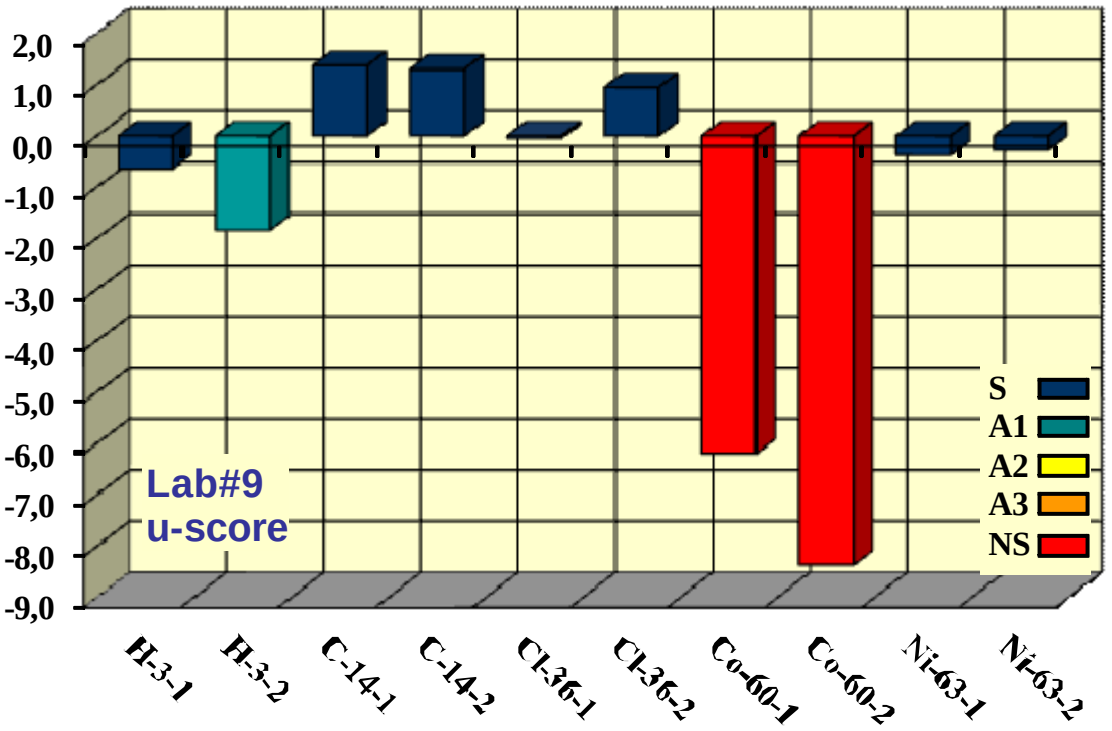

Figure 53. u-score for Lab#9

Lab#9 has evaluation as Satisfactory in 7 sets of 4 nuclides from 5 reporting with relative deviation < 3% in H-3(set 1), < 17% in C-14 (1 &2 sets), <5.5% for Cl-36 (1 &2 sets) and < 11% for Ni-63 (1 and 2 sets).

H-3-2 quote as acceptable at level 1 with a relative deviation of 8%. This bias and the results of H-3-1 indicate this value has the same validity that H-3-1 and the difference can be due to random effe ct of uncertainty.

In the case of Co-60 both sets quoted as Non- satis factory due to the small uncertainty of the reference data. Evaluator consider a problem in calibration as the explanation of deviation found (<11%).

The results of lab#9 indicates a high experience in graphite determination and accurate and contrast methodologies in the field. The results are in majority underestimate the reference value 7 of 10 ($\Sigma |Q|$/aliquot = 0.051) and the 3 values that overestimate the reference value are done also slighting ($\Sigma |Q|$/aliquot = 0.126).

4.4.10. Laboratory #10 Evaluation

Results of Lab#10 are summarized in table 27 and figure 54

Table 27. Data for Lab#10 evaluation

LAB#10	x_i	x_{Ai}	2*Ui	X_A	$2*U_X$	SEP	DET	u score	qualify	Q score
H-3-1	6	1.22E+00	1.62E-02	1.00E+00	7.55E-02	CAF	LSC	5.388	NS	0.221
H-3-2	6	1.13E+00	1.75E-02	1.00E+00	7.55E-02			3.216	A3	0.134
C-14-1	6	4.35E-01	1.81E-02	1.00E+00	2.41E-01	CAF	LSC	-4.668	NS	0.565
C-14-2	6	4.74E-01	1.96E-02	1.00E+00	2.41E-01			-4.344	NS	0.526
Cl-36-1	6	8.64E-01	6.61E-02	1.00E+00	5.02E-02	CAF/TRP	LSC	-2.270	A1	0.136
Cl-36-2	6	8.78E-01	4.81E-02	1.00E+00	5.02E-02			-1.945	A1	0.112
Co-60-1	6	8.89E-01	4.85E-02	1.00E+00	2.33E-02	DIM	HRG	-4.558	NS	0.122
Co-60-2	6	8.85E-01	4.83E-02	1.00E+00	2.33E-02			-4.145	NS	0.111
Ni-63-1	6	8.32E-02	3.62E-03	1.00E+00	3.65E-02	EXC/ICP	LSC	-48.627	NS	0.915
Ni-63-2	6	8.70E-02	4.06E-03	1.00E+00	3.65E-02			-48.360	NS	0.911

Lab#10 reported a pair of determinations set of 5 nuclides of 5 in mandatory. The two set per nuclide submitted have six replicate determinations. So that 60 data were treated individually as different lab inputs. Two outliers were found in the exercise for lab#10 so that 48 of the 60 data were use for reference values calculations.

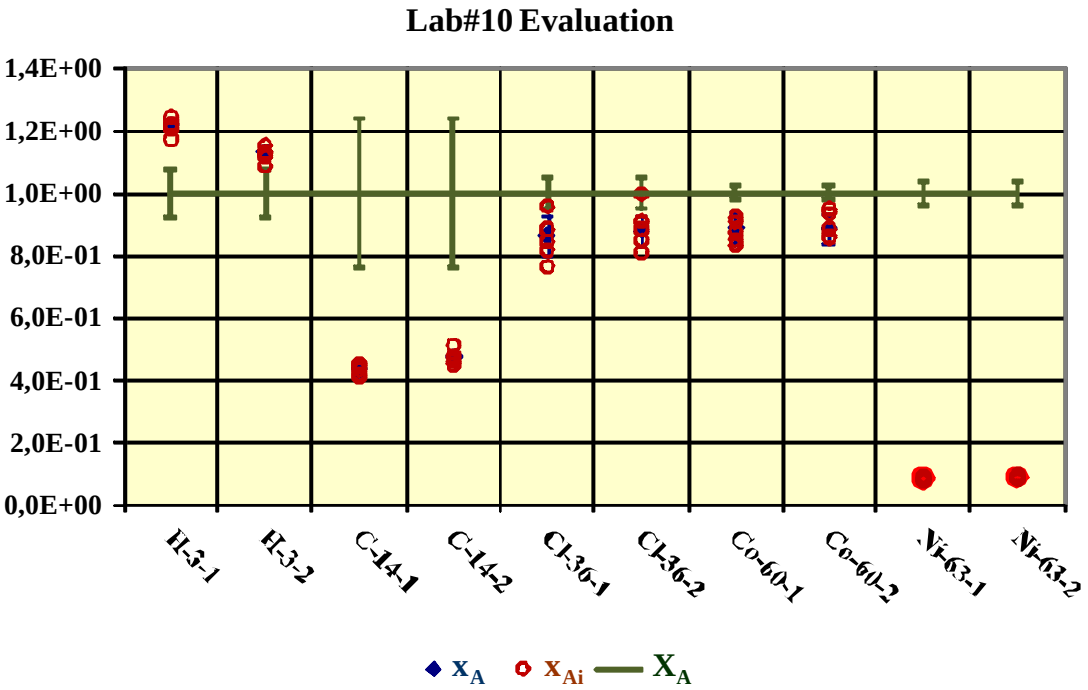

Figure 54. Results of Lab#10

Comments on data from Lab#10 in figure 54 are listed below:

- The two set of tritium determination has low scattered values around means, being the STD for set 1 3.0% and 3.3% for set 2. H-3-1 has a weighted average with an uncertainty of 0.7% and differs from reference value (U=3.8%) in +22%. The sec ond set has a weighted average whose uncertainty is 0.8% and the difference with reference value is 13.4% overestimating. In spite of the low uncertainty of weighted averages and the lower scattering of primary data the results are too high regarding the reference value. This systematic overestimation could be due to a calibration of LSC system or a cross contamination.

- C-14-1 set has 6 replicates with a STD = 4.4%. The uncertainty of the weighted average is 2.1%. The bias calculate is 56% lower than reference value (U= 12%). C-14-2 set of data has and STD of original data of 4.5%. The uncertainty of the weighted average is 2.1% and the difference with reference value is 52.6%. In both cases the

method underestimate the reference value, that means losses of material during separation process or defects in trapping system as most probably causes

- Lab#10 also submitted two sets of data for Cl-36 determination. Cl-36-1 has a weighted average that underestimates reference value in 13.6% with a standard deviation among primary data of 8,5% around the mean value and an uncertainty of 3.8%. It is found in the set labelled Cl-36-2 a dispersion of data with a STD = 7.3%. The weighted average differs 12.2% from reference value (U=2.5%) underestimating it. The values calculate for Cl-36 are in a moderate agreement with the reference value.

- Cobalt-60 determination is also reported in a double set of six values. Co-60-1 determination comes from another set of low scattered data (STD 3.8%) with a weighted average that differs 11.1% from reference value underestimating it, being the associated uncertainty of the weighted average 2.73% and the one of reference value 1.25%. Co-60-2 set has a STD of 2.7% around mean value and a underestimated (11.5%) weighted average regarding reference value. The values of Co-60 from Lab#10 are enough good with deviations in a 10% range.

- The replicates of Ni-63-1 set of data have a STD = 5.0%. This set of data gives a weighted average that underestimates the reference value in a 91.7%, however the uncertainty of weighted average is 2.7% against the uncertainty of reference value of 1.3%. The second set of Ni-63 values give another underestimation of 91% from reference value, with a scattering among data that gives an STD of 5.5%,. The weighted average of Ni-63-2 for Lab#10 has an uncertainty of 2.3%, in the same order of magnitude than the one of reference value of Ni-63-1.

The values of Q-score are in figure 55 where it is observed that the bias of the values are lower than 17% in any case.

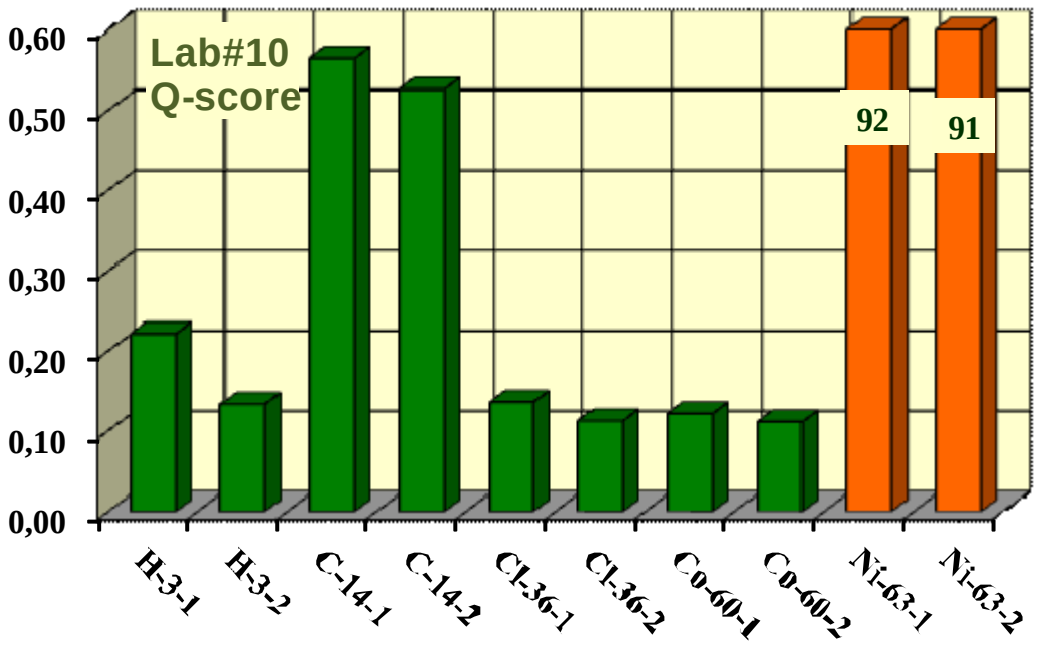

Figure 55. Q-score for Lab#10

The u-score (figure 56) gives the statistical evaluation of the lab#10 approach:

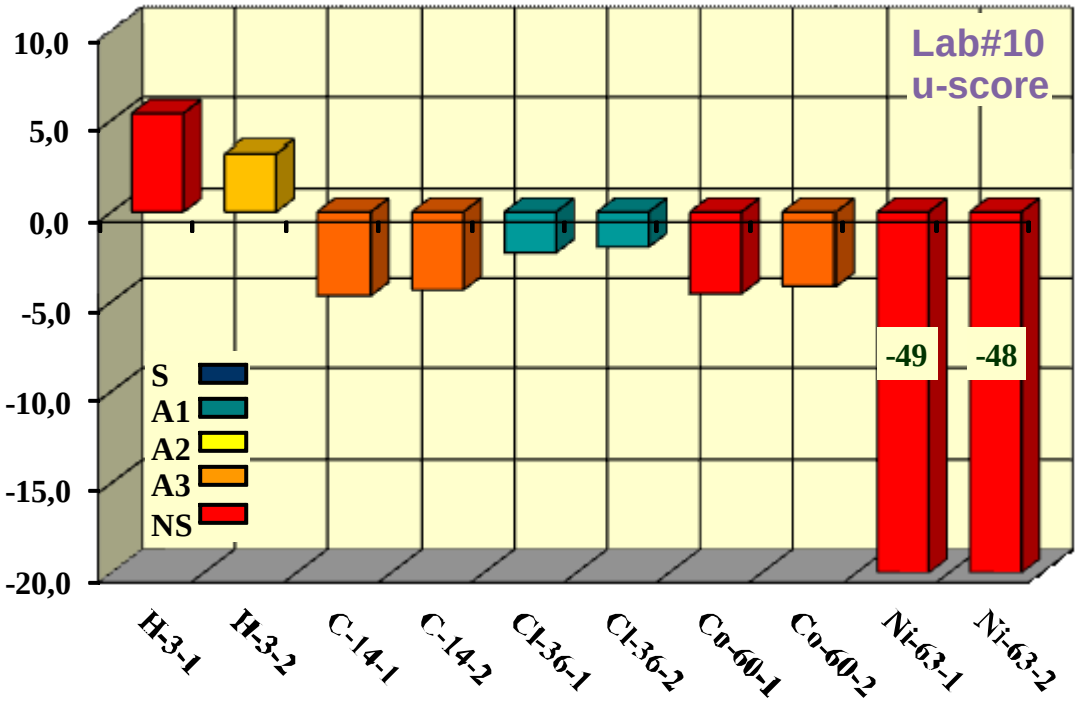

Figure 56. u-score for Lab#10

Lab#10 has evaluation as Acceptable at level 1 in the two data of Cl-36, that means the value has a probability >99% to find the real value existing a possibly significant difference with reference value. The bias of this sets of values are 13.6 and 11.2 % respectively for Cl-36-1 and Cl-36-2. This coincidence between Q-score and u-score qualify the method for chlorine determination as enough good.

Evaluation tritium present a u-score as non satisfactory and Acceptable at level 3 in the case of H-3-2. The respective Q-score are 22 and 13%, so that the evaluation of H-3 content in the sample has not enough quality even the precision of the data submitted. The overestimation suggest a cross contamination in the process but the Lab have to check the methodology with standards in the matrix in order to qualify the desired accuracy.

C-14 quoted as Non Satisfactory in both sets the Q-score quote 56% and 53% underestimating the reference value, so that both tests indicate that there are a lack of material control during the process that the lab has to be checked and turning-up again with enough quality assurance controls.

In the case of Co-60 both sets quoted as Non- satisfactory due to the small uncertainty of the reference data. Evaluator consider no problem in calibration due to the range of Q-score (11-12%).

Ni-63 determination quoted also non-satisfactory with deviations close to factor 2 from reference value. Both sets were rejected as outliers by inter-lab means. That indicates again losses of material during the process as in the case of C-14, It is needed a new setting-up of the method to re-evaluate the analytical results.

The results of lab#10 indicate the necessity of setting some methods again for i-graphite. Gamma spectrometry and Cl-36 measurement are enough accurate and precise. In general all

results present a good precision that means a routine operation with good practices, so that the effort has to concentrate in the establishment of recovery factor in an appropriate way.

The results are in majority underestimate the reference value (excluding Ni-63) 6 of 8 ($\Sigma |Q|$/aliquot = 0.425) and the 2 values that overestimate the reference value are done also slighting ($\Sigma |Q|$/aliquot = 0.178).

4.4.11. Laboratory #11 Evaluation

Results of Lab#11 are summarized in table 28 and figure 57

Table 28. Data for Lab#11 evaluation

LAB# 2	x_i	x_{Ai}	2*Ui	X_A	$2*U_X$	SEP	DET	u score	qualify	Q score
H-3-1	6	1.26E+00	1.04E-02	1.00E+00	7.55E-02	CAF	LSC	6.526	NS	0.256
H-3-2										
C-14-1	6	1.09E+00	1.58E-02	1.00E+00	2.41E-01	CAF	LSC	0.709	S	0.086
C-14-2										
Cl-36-1										
Cl-36-2										
Co-60-1	6	9.27E-01	2.37E-02	1.00E+00	2.33E-02	DIM	HRG	-4.426	NS	0.073
Co-60-2										
Ni-63-1										
Ni-63-2										

Lab#11 reported 3 nuclides of 5 in mandatory, supplied one set of six determinations per nuclide

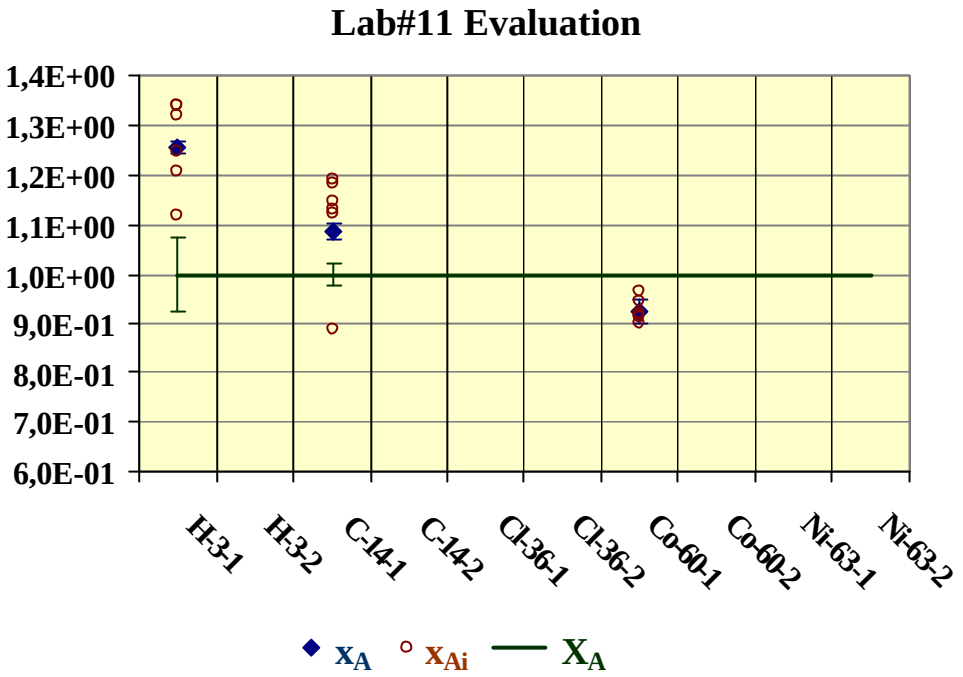

Figure 57. Results of Lab#11

The Analysis of the data in Figure 57 gives the following remarks:

- Tritium determination has been calculate with a set of 6 values scattered with a STD =7%. With these 6 values is calculated a weighted average that differs 25.6%, overestimating the reference value with an uncertainty of 0.4% against the uncertainty of reference value that is 3.1%. The bias of the result is un order of magnitude than the uncertainties, this use to drive to a poor quotation

- C-14 determination has also 6 data in one set with a standard deviation around mean of 10%. The deviation regarding to reference value is 8.6% and the uncertainty associated to weighted average is 0.73%. The reference value has an uncertainty of 12%. In this case deviation and uncertainty are in similar order of magnitudes (in relative terms) so that the values use to quote good in the evaluation.

In both cases, H-3 and C-14, the weighted averages overestimate the reference value and the dispersion of original data and the uncertainty of the values managed are also similar, but the

other lab quotes and the uncertainty of reference value made the contribution of Lab#11 more influence in the case of C-14 and consequently produce a lower bias

- Cobalt-60 determination is reported in a set of six values which present low scattering with a STD of 2.5%. The calculated weighted average differs 7% from reference value and being excellent approach but taking into account the 1.2% of uncertainty of reference value and the 1.3% of uncertainty of .weighted average and on the other hand the deviations of other labs in the exercise the difference found in Lab#6 will be a not good quotation.

The values of Q-score are in figure 58.

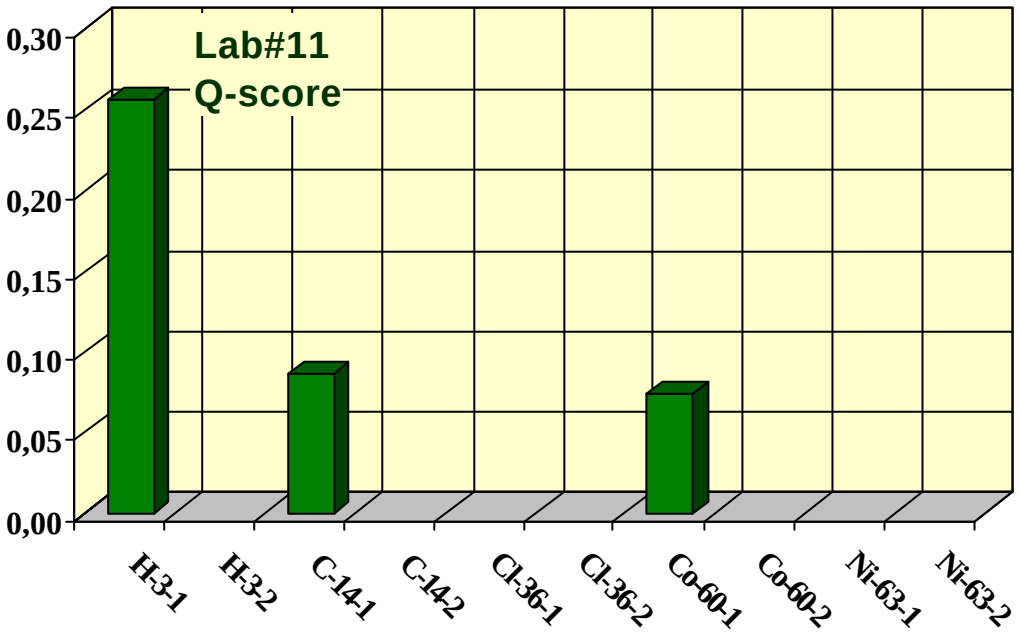

Figure 58. Q-score for Lab#11

The u-score (figure 59) gives the statistical evaluation of lab#11:

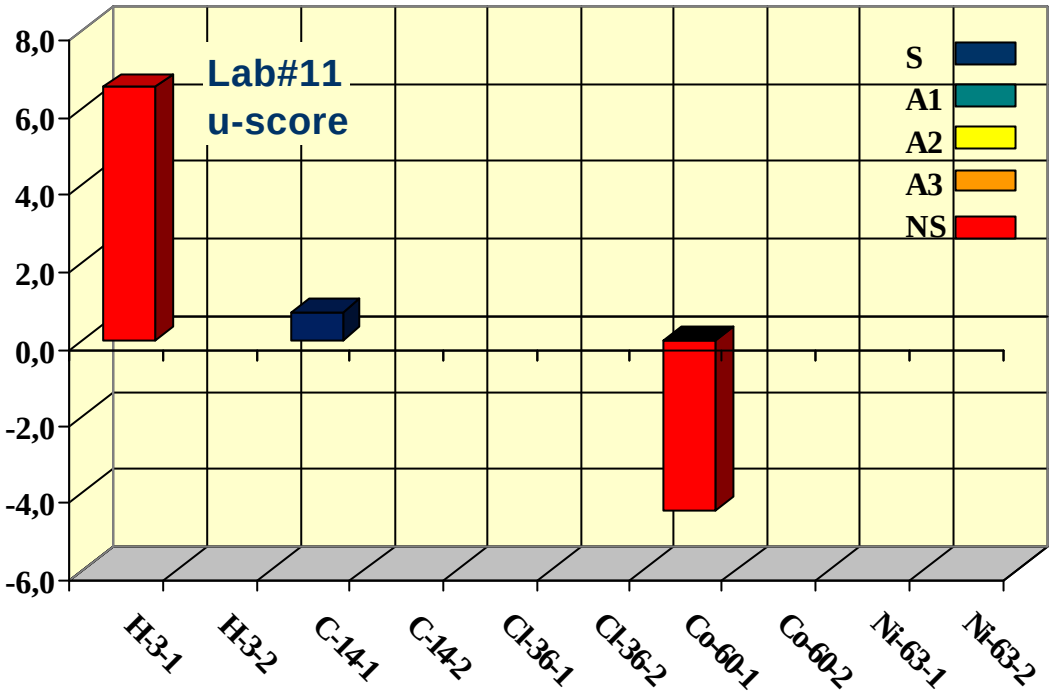

Figure 59. u-score for Lab#11

Tritium determination of Lab#11 quote as Non Satisfactory and the bias is 25.6%. Evaluator suggest to review and tuning-up de H-3 determination.

C-14 determination gives, nevertheless, quotes as satisfactory with similar numbers in the statistical data of the sample. The Q-score is is 8.6%

Co-60-1 is quoted as Non Satisfactory. Even the low level of bias (q-score = 7.3%) the difference of weighted average and the 2·U area surrounded the reference value gives bad quotations by u-score.

Lab#11 needs to review the H-3 characterisation procedure in order to find the source of contamination that increases the mass recovery of H-3 in the process.

5. GENERAL CONLCUSIONS AND REMARKS

The aim of the exercise is to qualify the participant labs to perform accurate and precise radiological characterisation of the main nuclides in irradiated graphite. The methodologies applies has been checked and the Labs has a toll for the surveillance of the effectiveness of their procedures the sensitivity level and alternatives in order to upgrade, improve or put in operation methods to determine tritium, radiocarbon, chlorine-36, nickel-63, cobalt-60 and other gamma emitters and an approach of strontium-90 determination in graphite.

Samples were prepared from powder of i-graphite and delivery in such a way that fulfil the transport and particular safety requirements with the help and cooperation of any Radiation Protection departments of the participant labs in an effective way.

The election of this samples, in steat of traced samples, has an extra difficulty that is the calculation of reference value by consensus with the labs input, but it has an extra advantage: The evaluation is more reliable due to that we find the same matrix effect interferences than in real cases and allows to tuning-up the analysis methodologies.

The samples homogeneity has been checking by statistical approach by ANOVA (F-Snedecor test) with gamma lines of Co-60, Cs-137 and Eu-154 lines and post evaluation with the results of tritium, radiocarbon and again cobalt-60 data coming from the labs results in order to check the distribution of the activity within the expert labs and to confirm the homogeneity of the samples distribution and consequently there were not necessary a correction factor by sample homogeneity in the results.

The inputs for the exercise are in table 29:

Table 29. Primary data treated by nuclide

	primary data #	weighted average #	outliers-C	outliers-G
H-3	91	16	1	0
C-14	94	17	0	0
Cl-36	69	12	2	1
Co-60	111	19	2	0
Ni-63	72	12	1	2
Sr-90	27	5	1	0
TOTAL	464	81	10	

464 x 4 primary data values (specific activities, uncertainties, MDA and evaluation date) were used for calculating 81 weighted average (eq.3) and their uncertainty (eq. 4 or eq.5) and derived 6 reference value (eq 6) and their uncertainty (eq.7)

The outliers were 12.3% of the total data treated being this ratio maximum (1/4) for Ni-63 and Cl-36. 70% of the outliers were dropped for reference value calculation by intra-lab variance (precision in the replicates results) and 30% for inter-lab mean (extremes out of normal distribution of the means).

The statistical evaluation by relative bias (Q-score) is in the sector diagrams of figure 60.

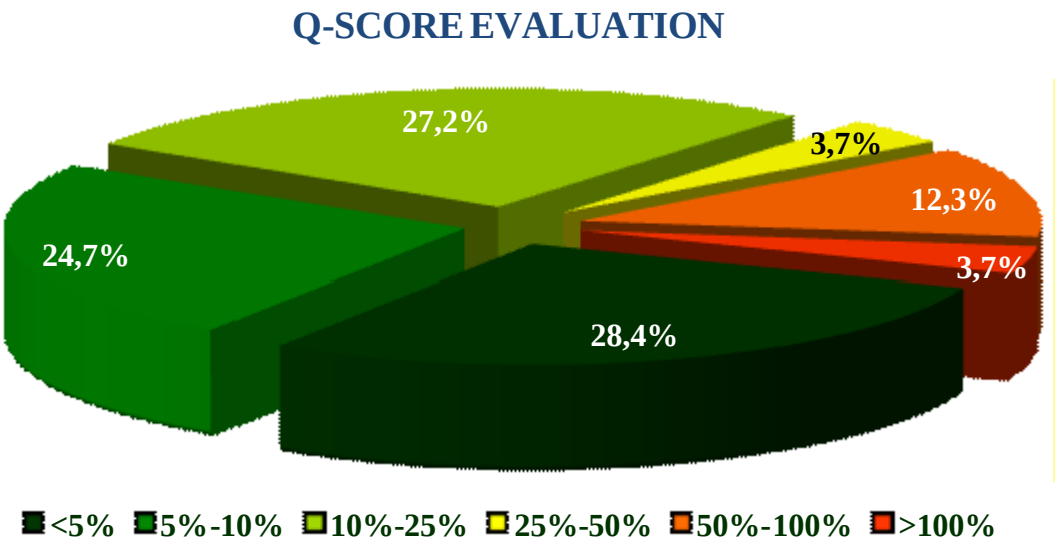

Figure 60. Q-score evaluation

53,1% of the results have a relative deviation lower than 10%, 27,2% of the results has a deviation between 10 and 25% and 19,7% of the Q-score have a deviation higher than 25%. The results by nuclide are in figure 61.

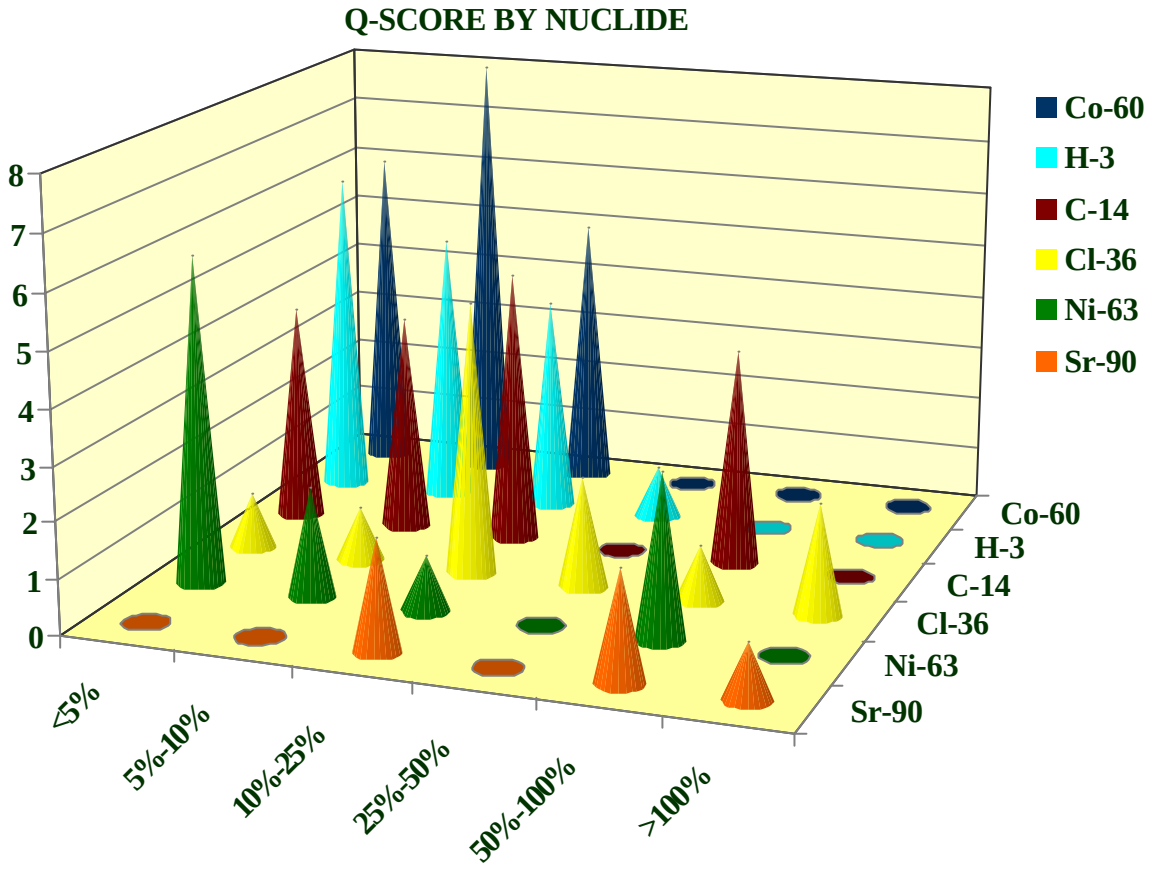

Figure. 61. Q-score by nuclide

A study by nuclide and global exercise of the Q-mean and |Q| as well as Qmax and Q min is represented in figure 62, where we can observed that excepted Sr-90 evaluation with only 5 input data, the Q-mean of the exercise is 8.4% (29% with Sr-90 evaluation) being |Q| mean of the exercise 25.3% (46.1% with all determinations).

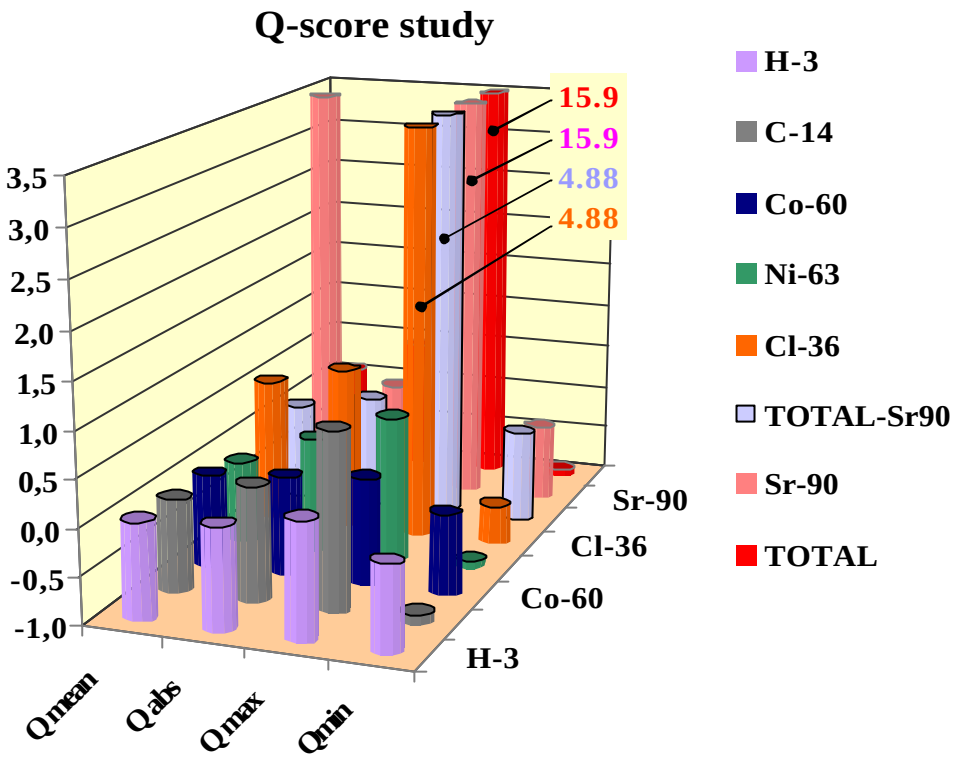

Figure 62. Q-score Study for Total exercise and by nuclide

U-score give a statistical approach of individual data by nuclide or by lab with more than an quantitative deviation that Q-score gives but a probabilistic accuracy of any result according to the tests. In figure 63 is observed the quote of the labs in the exercise.

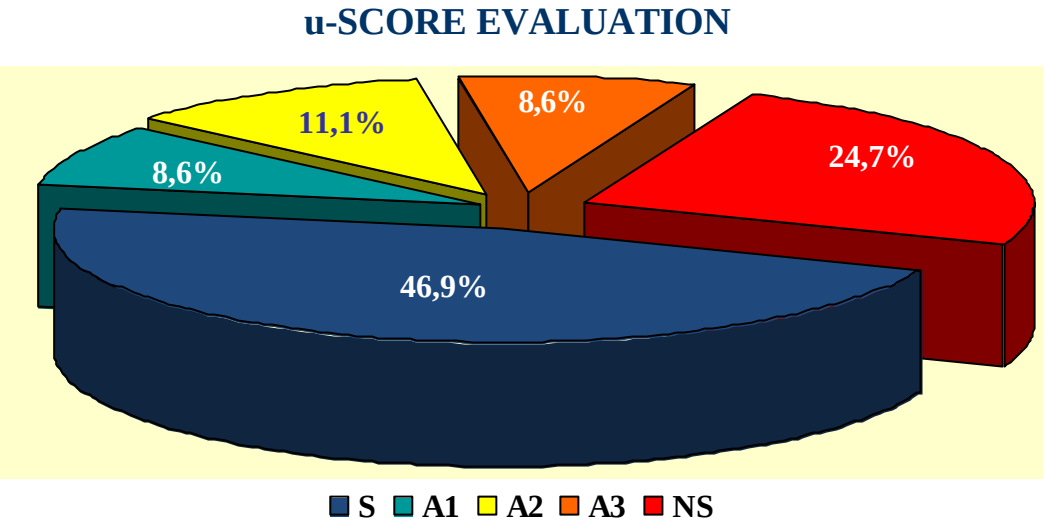

Figure 63. u-score Evaluation in the CWRRT

According to the graphic we obtain a ~47% of the data that has a probability ≥99.9% to find the reference value, even more 2/3 of the data are in the range of probability ≥ 95% to find reference value. 25% of the data quoted as Non-satisfactory (probability =90%) but taking into account that the narrow distribution of Co-60 in the exercise that follows a normal distribution centred in 1 with a $\sigma = 0.012$, the ratio of real Non-satisfactory quotes are 13.6%.

Figure 64 shows the u-score by nuclides where is clear that the majority of the quotes are satisfactory or acceptable at level 1, only Co-60 due to the nature of the distribution function of reference value presents a different frequency diagram shape that the other nuclides and analyses of Cl-36 that due to the concentration of this nuclide in the sample present quote distribution the nuclides

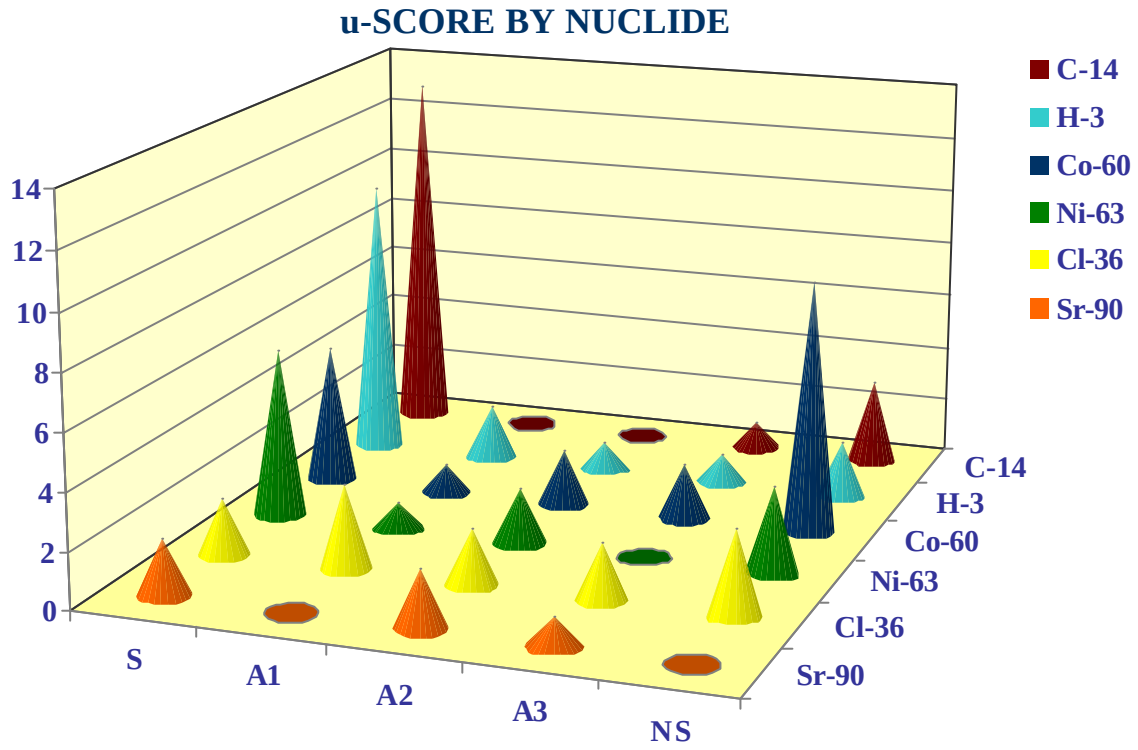

Figure 64. u-score Evaluation by nuclide

The evaluation by nuclides is detailed in section 4.3 but some specific remarks can extracted as summary:

- Tritium and radiocarbon are excellent determine by the participants with very similar procedures. With 70% of the data quoted as Satisfactory and 58% with a deviation less than 10%

- Ni-63 determination are also quoted excellent by the consortium. The methodologies applied are based in the same principle with different approaches, and 50% of the results quoted as Satisfactory, having two thirds of the results a relative difference lower than 10%.

- Co-60 evaluation by u-score quote a 26% of Satisfactory but 475 of non satisfactory by the shape of the distribution of reference value as is already explained. If the Q-score is observed 74% of the data present a bias lower than 10% and 100% lower than 15%. So that the conclusion is that all participant labs has the ability to determine the Co-60 in a enough accurate way using the methods applied in the CWRRT.

- Cl-36 determination is the most difficult one in the exercise, due to the lower concentration (in some cases close to detection limit) presents a u-score frequency diagram more close to rectangular distribution than a normal distribution, Only 2 of 12 values quoted as Satisfactory and they are the same that quoted with a bias lower than 10%. On the other hand 25% of the data quoted as Non-Satisfactory. In the case of Cl-36 some of the data obtained suggest to take into account as reference and other the evaluation indicates to review in order to understand the source of deviation finded.

- Sr-90 also has a bad quotation in the exercise but taking into account the number of Labs that submitted data of this nuclide (5) the evaluation is only useful as individual reference more than a evaluation of the capability of the methods. Nevertheless the 40% of the values quoted as Satisfactory with a deviation ranging between 15-17% and no labs quoted as Non Satisfactory,

The analysis by individual Lab is not summarized and no conclusions are presented in this section in order to avoid any ranking that is not the aim of this inter-comparison test.

Some general view of lab results is performed:

- There are 6 labs that reported 5 of 5 nuclides (3 of them also reported Sr-90)
  - 5 of the six quoted as satisfactory or acceptable at level 1 in the range of 50-70% of the data and Non satisfactory between 0 and 30% of the data. The absolute Q- means of the labs ranging from 7.2% to 79.7%
  - 1 lab of six quoted as satisfactory or acceptable at level 1 in 20% of the data and Non-satisfactory in 70% of the data being its absolute Q- means in CWRRT of 38%

- There is one lab that reported 4 of 5 nuclides that has 20% of satisfactory or acceptable at level 1 data and 60% of Non satisfactory. The Absolute Q mean is 39%

- There are 4 labs that reported 3 nuclides (tritium, radiocarbon and cobalt-60)
  - The Satisfactory and Acceptable at level 1 quotes ranging from 100% to 20% and the Non Satisfactory data are in the range 0-67%. The absolute Q mean varies from 6% to 20%.

Majority of Labs have and excellent quotation in both or in combination evaluations (Q and u scores) and they do not need major changes in the procedures. Some values promote a signal to discuss or question the performance of the lab in this nuclide and it is tried to explain in the individual lab evaluation being a intra-lab work to perform the identification of lacks that generate this statistical signal in the proficiency test.

6. LITERATURE

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