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INTERLABORATORY RADIOCHEMICAL ANALYSIS COMPARISON ON A PRIMARY WASTE FLUX

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EXECUTIVE SUMMARY

An accurate knowledge of the inventory of long-lived and radiotoxic alpha, beta and gamma-emitting radionuclides present in radioactive wastes from Nuclear Power Plants is a critical parameter for a reliable categorisation of the waste in compliance with the existing disposal site regulations. Therefore it is very important to have access to reliable radiochemical and radioanalytical procedures which provide results with a high accuracy. The objective of the project was to perform an interlaboratory radiochemical analysis campaign on the destructive measurement of radiotoxic and long-lived radionuclides in a primary waste flux. The aims of the inter-comparison test were to:

- determine the accuracy and reliability of the different analytical methods applied in the different participating laboratories belonging to "European Network of Testing Facilities for the Quality Checking of Radioactive Waste Packages",

- compare, validate and harmonise the analytical methods used,

- detect discrepancies and shortcomings in routine analysis, which will help to identify whether a separation or measurement method needs further improvement.

The project has been structured around six work packages:

Work package 1. - Definition phase. The consortium agreed on the specifications of the samples to be compared i.e. type, volume, range of activity; transport time schedule; time period for the characterisation; data evaluation procedures and results presentations.

Work package 2. - Sampling. Two different waste stream samples, agreed by the consortium, were analysed: one spent cation exchange resins and one evaporator concentrate. Representative samples of the resin and concentrate were homogenised, sorted, prepared and distributed under the responsibility of El Cabril-ENRESA. The representativity of each sample prior to its delivery was checked by gamma spectrometry. Real samples from LWR's were prepared. The transport of the samples was organised by ENRESA, according to applicable regulations.

Work package 3. - Analysis of samples. The analyses of the different radionuclides were carried out in the laboratories belonging to the different contractors with the procedures used on a routine base. The nuclides analysed were ^{3}H, ^{14}C, ^{55}Fe, ^{63}Ni, $^{89/90}Sr$, ^{99}Tc, ^{129}I, ^{238}Pu, $^{239/40}Pu$, ^{241}Pu, ^{241}Am, ^{242}Cm, ^{244}Cm, ^{234}U and ^{238}U. The procedures were carried out on two aliquots from the initial resin sample and the separations were done on three different solutions collected from each aliquot. At the end, six results per nuclide were obtained.

Work package 4. - Results. The results were reported in a spreadsheet, giving the specific activities in sample material, the confidence levels and the uncertainties due to statistics and processes, in a predefined way from Work Package 1. A full description of all-destructive techniques, separation procedures and measurement techniques used for the analyses of the different alpha, beta and gamma emitting radionuclides were reported.

Work package 5. - Statistical evaluation of results. All institutes according to a predefined list, reported the analysis of the results of the "interlaboratory comparison". The results were sent to CIEMAT where the statistical evaluation was carried out. The statistical approach has been fully described and is based on the evaluation of all quantitative and measured parameters. An example of uncertainty evaluation was written and distributed to harmonise the implementation of quality assurance procedure for activity determination in the framework of this project. Laboratory means of up to 15 radionuclides from 11 expert's laboratories were compared with reference values and target uncertainty obtained in an appropriate manner. Outliers were identified according to the Cochran test and Grubbs test and eliminated. The consistency of laboratory means and reference values was checking according to *u score*.

Work package 6. - Conclusions. The results obtained in Work Packages 2, 3, 4 and 5 were discussed and problems and discrepancies reviewed after detailed examination of the experimental data and the radioanalytical procedures and techniques. The exchange of views on radioanalytical procedures can provide the platform for a consensus on the qualification of the methods used by each laboratory participant. It will enable, where necessary, each laboratory to effectively review and transform its procedures.

The origin of the results obtained throughout the project will not be attributed to specific laboratories in the public reports.

1. OBJECTIVES AND STRATEGIC ASPECTS

An accurate knowledge of the inventory of long-lived and radiotoxic alpha, beta and gamma emitting radionuclides present in radioactive waste from Nuclear Power Plants is a critical parameter for a reliable categorisation of the waste in compliance with the existing disposal site regulations. In the case of a near surface disposal facility the accepted activity limits for alpha emitting radionuclides are lower than those for beta and gamma emitting radionuclides, due to the long half-life and higher radiotoxicity of the alpha emitters. Therefore, it is very important to have access to reliable radiochemical and radioanalytical procedures which provide results with a high accuracy.

The destructive measurement of the different alpha, beta and gamma emitting radionuclides present in the radioactive waste arising from Nuclear Power Plants implies a complex process starting with the sampling up to obtaining the final result. It includes several steps such as mineralisation 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.

The radiochemical separation will be based on liquid-liquid extraction, ion exchange chromatography, precipitation, extraction chromatography, etc.

Measurement techniques commonly applied are alpha and gamma spectrometry, beta-scintillation counting, mass-spectrometry, etc.

The reliability of the final result at the end of the process cannot be evaluated in a simple way. The uncertainty of this result 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 analysis and different techniques,
- Carrying out control analysis with a reference matrix, or
- Participation in interlaboratory comparisons.

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

The collaboration of scientists and, the exchange of information on waste samples and radioanalytical methods among the different partners identifies the scope of application, the strengths and weaknesses of the methods and provides opportunities for improvement, harmonisation, validation and finally qualification of selected methods within the European Community. The international character of the research programme also leads 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 for the disposal facilities, the Regulatory Body and public opinion. Besides, as a result, 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 more reliable and accurate measurements.

2. SCIENTIFIC AND TECHNICAL DESCRIPTION OF THE RESULTS

2.1. WORK PACKAGE 1. DEFINITION PHASE

The consortium defined the specifications of the samples, time schedule and deadline for the delivery of the sample and time period available for characterisation.

- The consortium decided on a sample with the following activity range:

	RESIN		CONCENTRATE	
	$A_{minimum}$ (Bq/g)	$A_{maximum}$ (Bq/g)	$A_{minimum}$ (Bq/g)	$A_{maximum}$ (Bq/g)
^{60}Co	6,0E+02	1,0E+06	1,0E+03	4,0E+04
^{137}Cs	3,0E+02	6,0E+05	3,0E+02	5,0E+03

Finally, two samples were chosen: one spent cation exchange resin and one evaporator concentrate from the Spanish Nuclear Power Plant (NPP), Cofrentes. This NPP sent to ENRESA-El Cabril Verification Laboratory 400 g of resin and 4 litres of concentrate. The radioactive concentrations declared by the NPP are as follows:

ISOTOPIC ANALYSIS		
	RESIN A (Bq/g)	**CONCENTRATE A (Bq/g)**
^{60}Co	4,46E+03	2,55E+03
^{137}Cs	3,29E+02	9,10E+02
^{134}Cs	8,50E+01	1,46E+02
^{65}Zn	1,53E+03	1,06E+02

The concentrate chemical composition indicated by the NPP is:

CONCENTRATE CHEMICAL ANALYSIS			
	SOLUBLES (ppm)	**INSOLUBLES (ppm)**	**TOTAL (ppm)**
Iron	216	649	865
Copper	0,55	102	102,55
Calcium	8059	1082	9141
Magnesium	2448	329	2777
Phosphates	3750	4000	7750
Chloride	12000	-	12000
Sulphates	67000	3500	70500
Sodium	19100	710	19810

Results were normalised by the evaluator to 01/09/2000 taking into account the determination date given by partners.

2.2. WORK PACKAGE 2. SAMPLING AND DISTRIBUTION

2.2.1. Sampling

Samples were prepared within the particular radiological requirements of each partner and its homogeneity was checked in ENRESA-El Cabril Radioactive Waste Verification Laboratory (LVCR). The procedure performed in order to test the homogeneity of the prepared samples was as follows:

2.2.1.1. Resin

1. The whole resin sample was filtered in order to ensure the same water content in each aliquot.
2. The whole resin sample was mixed.

3. In accordance with the requests of the different participating laboratories, the following aliquots were prepared:

Partner	Resin (g)	Contact dose rate (μSv/h)	1 m dose rate (μSv/h)
CIEMAT	30,3495	80	0,5
ENRESA-EL CABRIL	21,9779	68	0,4
CEA	22,0711	77	0,4
SCK-CEN	29,6584	92	0,5
NRG	21,0548	60	0,4
FZJ	65,1301	133	0,5
Belgoprocess	28,0856	88	0,4
University of Helsinki	18,7331	67	0,4
NNC	38,8281	107	0,5
TUM	29,0181	85	0,5
ENEA	32,7391	100	0,5

4. Each aliquot was transferred to the containers sent to the partners.
5. The resin in each container was homogenised and three test portions were taken.
6. In the three portions, the gamma lines of ^{60}Co and ^{137}Cs were analysed.
7. The data obtained were evaluated according to a Technical Report of IUPAC "The International Harmonised Protocol for the Proficiency Testing of (Chemical) Analytical Laboratories" resulting from the Symposium on Harmonisation of Quality Assurance Systems in Chemical Analysis (May, 1991) as follows:

   - An estimate (s_s^2) of the sampling variance and an estimate (s_a^2) of the analysis variance by one-way analysis of variance, without exclusion of outliers, were formed.
   - Values of **0, s_s, s_a, n** and the result of the **F-test** were reported.
   - Once the analysis of variance was performed, the critical value of F (tabulated value) is compared with the calculated F-value.
   - According with the protocol when the critical value of F is higher than the calculated F-value, the test means that the material is sufficiently homogeneous in order to assure that all prepared aliquots have comparable activity in statistical terms.

The analyses of variance performed indicate that the aliquots prepared were sufficiently homogeneous.

2.2.1.2. Evaporator concentrate

1. The whole concentrate sample was shaken in a beaker while the aliquot was taken.
2. In accordance with the requests of the different participating laboratories, the following aliquots were prepared:

Partner	Concentrate (g)	Contact dose rate (µSv/h)	1 m dose rate (µSv/h)
CIEMAT	309,0	90	3
ENRESA-EL CABRIL	155,5	45	1,6
CEA	-	-	-
SCK-CEN	639,2	150	3
NRG	139,4	50	0,7
FZJ	163,1	57	1
Belgoprocess	628,2	150	1
Helsinki University	164,9	55	0,5
NNC	620,4	140	1,3
TUM	612,1	150	1,6
ENEA	318,9	90	0,7

3. Each aliquot was transferred to the containers sent to the partners.
4. The concentrate in each container was homogenised and three test portions were taken.
5. In the three portions, the gamma lines of ^{60}Co and ^{137}Cs were analysed.
6. The data obtained were evaluated in the same way as the resin.

The analyses of variance performed indicate that the aliquots prepared were sufficiently homogeneous.

2.2.2. Distribution of samples

The logistics of the transport chosen were:

- By road from El Cabril (ENRESA) to CIEMAT and to Barajas (Madrid) airport using an authorised van,
- By plane from Madrid to the airport of the different countries involved in the project: Marseilles, Milan, Frankfurt, Brussels, Amsterdam, London and Helsinki,
- By road from the airport to the different facilities CEA, ENEA, FZJ, TUM, NRG, SCK·CEN, Belgoprocess, NNC and University of Helsinki using an authorised van in "exclusive use".

The packaging radiological data were:

LABORATORY	DOSE CONTACT RATE μSv/h	DOSE 1m RATE μSv/h
CIEMAT	42	1,00
CEA	20	0,35
SCK·CEN	55	1,20
NRG	27	0,40
FZJ	60	1,20
BELGOPROCESS	75	1,80
HELSINKI UNIVERSITY	30	0,45
NNC	54	1,20
TUM	60	1,20
ENEA	50	1,00

These packages, according to the timetables of the flights, were received in the different laboratories on the following dates, all in 2001:

CIEMAT (Madrid): **February 19th**
CEA (Cadarache): **February 26th**
SCK·CEN (Mol): **February 22nd**
NRG (Petten): **February 22nd**
Helsinki University: **February 23rd**
NNC-WQCL (Winfrith): **February 22nd**
TUM/RCM (Garching): **February 23rd**
ENEA (Saluggia): **February 22nd**

2.3. WORK PACKAGE 3. ANALYSES OF SAMPLES

A brief summary of the work performed by each partner regarding the analyses of the samples follows. A fuller description of all methods is reported in the "Procedures report" produced in May 2002.

The procedures were performed on two aliquots from the initial resin and concentrate samples and the separations were done on three different solutions taken from each aliquot. At the end, six results per nuclide were obtained.

2.3.1. CIEMAT

2.3.1.1. Resin

Sample aliquots of resin were first dried at a temperature of 60 ± 1ºC for 48 hours.

Dissolution: Two aliquots from the original wet sample were taken and dissolved by oxidation with hydrogen peroxide in acid medium (pH = 2), and heating under reflux. In the solutions obtained ^{3}H, ^{99}Tc and ^{129}I were analysed. Then, another two aliquots were taken and similarly dissolved by oxidation, but in this case, because of the presence of metallic oxides, it was necessary to dissolve them by acid treatment with conc. HCl, conc. HNO_3, 70% $HClO_4$ and 1:1 H_2F_2. In the solutions obtained ^{55}Fe, ^{63}Ni, ^{89}Sr and ^{90}Sr, ^{238}Pu, $^{239/40}Pu$, ^{241}Am, ^{242}Cm, ^{244}Cm, ^{234}U and ^{238}U have been analysed.

Tritium: The procedure is based on the double tritium distillation. ^{3}H is determined by the measure of its beta emission once the possible gamma interferences are checked by gamma spectrometry.

Carbon-14: The procedure is based on the oxidation of any biological samples and most materials (wet and dry) and conversion of the sample to a gaseous state. When the original sample burned at 900ºC in an oxygen stream, the bulk of the material is converted to carbon dioxide and water. Metals, salts, oxides and materials with very high melting points remain without reacting. ^{14}C is determined by the measurement of its beta emission once the possible gamma interferences are checked by gamma spectrometry.

Iron-55: The procedure to analyse ^{55}Fe is based on the precipitation of ferric ions as hydroxides by ammonia. ^{55}Fe is determined by liquid scintillation counting by the measurement of Auger electrons, which are a consequence of radioactive decay by electron capture. The measurement is carried out once the possible gamma interferences are checked by gamma spectrometry. The chemical yield is determined by spectrophotometry.

Nickel-63: The procedure to analyse ^{63}Ni is based on the selective liquid-liquid extraction of the complex nickel-dimethylglyoxime. ^{63}Ni is determined by the measurement of its beta emission by liquid scintillation counting once the possible gamma interferences are checked by gamma spectrometry. The chemical yield is determined by spectrophotometry.

Strontium-89/90: The procedure to analyse $^{89/90}Sr$ is based on the strontium adsorption on an Eichrom Sr-Resin specific column after conversion of the solution to the nitrate form. $^{89/90}Sr$ is determined by the measurement of its beta emission by liquid scintillation counting once the possible gamma interferences are checked by gamma spectrometry. Two counts are made, one immediately after the separation and the other one with a minimum time interval of 8-10 days to correct the influence of ^{89}Sr. The chemical yield is determined by gravimetry.

Technetium-99: The procedure is based on the selective extraction of the anion TcO_4^- with dibenzo 18-crown 6(DB18-C6) in a toluene-acetone mixture. ^{99}Tc is determined by the measurement of its beta emission by liquid scintillation counting once the possible gamma interferences are checked by gamma spectrometry. The chemical yield is determined by adding ^{99}Tc as an internal standard.

Iodine-129: I is isolated by co-precipitation with hydroxides and hexachloroplatinum (IV) acid and measurement by X-ray spectrometry with a low-energy-photon-detector. The chemical yield is determined by adding ^{129}I as an internal standard.

Actinides isotopes: The procedure for **Pu isotopes** is based on an oxidation-reduction step with $NaNO_2$ and NH_2OH and the separation from fission products, rare earths and another actinides using anion exchange chromatography. The alpha isotopes of plutonium are determined by the measurement of its alpha emission. ^{241}Pu is determined by the measurement of its beta emission. The chemical yield is determined by adding ^{242}Pu as tracer.

The procedure for **Am and Cm isotopes** is based on the separation from fission products, rare earths and another actinides using anion exchange chromatography and liquid-liquid extraction. The isotopes of americium and curium are determined by the measurement of its alpha emission. The chemical yield is determined by adding ^{242}Am as tracer.

The procedure to determine **^{234}U and ^{238}U** is based on the separation by liquid-liquid extraction using TBP (n-hexane), anion exchange chromatography using a Dowex 1x8 resin and electrodeposition. Uranium isotopes are determined by the measurement of its alpha emission.

2.3.1.2. Evaporator concentrate

Dissolution: Due to the many undissolved species present in the concentrate, the sample has been analysed as a whole, solid and liquid. The same solubilisation procedure as for the resin has been carried out.

For all radionuclides, the same separation procedures as for the resin have been carried out.

2.3.2. <u>ENRESA-EL CABRIL</u>

2.3.2.1. Resin

Digestion by fusion: An aliquot (1.5 g) of sodium carbonate is mixed with an aliquot of wet resin in a platinum melting pot. It is covered with another aliquot of sodium carbonate. This mixture is burned in a furnace at 925ºC, for 30 minutes. Afterwards, the platinum melting pot is moved and put in cold water to separate the sample. Hydrochloric acid is added to dissolve the sample, and it is poured into a beaker. It is dried, mixed with nitric acid, dried and mixed again with nitric acid.

Tritium and Carbon-14: ^{3}H and ^{14}C are separated by Catalytical Combustion in the Combustion Oven. An aliquot of the sample is introduced in the combustion chamber of the oven at 900ºC

where N_2 and O_2 gas pass through this chamber. The combustion products pass through a series of catalysts at 680ºC and carbon dioxide and tritiated water are trapped in two different vials containing trapping solutions, one for ^{14}C and one for ^{3}H. Finally, the vials are measured by LSC.

Iron-55: An aliquot of sample from acid digestion is taken. To it are added carriers, nitric acid, and hydrochloric acid and it is heated. Afterwards, ammonia solution is added to pH 10 and a precipitate of Fe is obtained, which is centrifuged. The precipitate is dissolved with HCl and passed through a column of Dowex Resin (previously prepared with 4N HCl). The column is cleaned with 4N HCl to eliminate interferences, and then Fe is eluted with 0.1N HCl. This eluate is mixed with 0.1N HCl and heated. Finally, from this final solution, two aliquots are taken: 1.-measured by LSC, 2.- measured by Inductively Coupled Plasma Spectrometry to determine the separation yield, together with the measurement of the original aliquot of the sample before separation.

Nickel-63: An aliquot of sample from acid digestion is taken. To it are added carriers, nitric acid and ammonia solution to pH 10. It is centrifuged and precipitated with dimethylglyoxime. This precipitate is centrifuged again and it is dissolved with HCl and ethanol. DMG is added again, filtered and extracted with chloroform and then with HCl. The aqueous phase obtained is heated and mixed with HNO_3. From the final solution, two aliquots are taken: 1.-measured by LSC, 2.- measured by Inductively Coupled Plasma Spectrometry to determine the separation yield, together with the measurement of the original aliquot of the sample before separation.

Strontium-90: An aliquot of sample from acid digestion is taken. Carriers and nitric acid are added. The solution obtained is heated. An extraction with TBP (tri-n-butyl phosphate) is carried out and the aqueous phase is discarded. The organic phase is mixed with nitric acid and this is extracted with water. Nitric acid is added to the aqueous phase and, from this final solution, two aliquots are taken: 1.- measured by LSC, 2.- measured by Inductively Coupled Plasma Spectrometry to determine the separation yield, together with the measurement of the original aliquot of the sample before separation.

Technetium-99: ^{99}Tc is extracted by chromatography using a column of Eichrom resin. Two similar acid digestions are done at the same time. The first one is only the sample and carriers and the second one is the sample, carriers and an aliquot of ^{99}Tc tracer to determine the chemical yield of the process. After the two digestions, an aliquot of each is heated with H_2O_2 to oxidise all Tc, at 90ºC for 1 hour. These aliquots are passed through two different columns of TEVA Spec resin (previously prepared with 0.1M HNO_3), adding Cs carrier. The column is cleaned three times with 0.01M HNO_3 and the third aliquot of nitric acid is measured by Gamma Spectrometry to check interferences of isotopes. Afterwards, the Tc is stripped from the two columns with 12M HNO_3 and measured by LSC.

Iodine-129: To separate iodine it is necessary to make a digestion of the sample in a different way to the previous digestion. An aliquot of original sample and carriers are mixed in a flask and this is connected to four beakers containing 1st water, 2nd and 3rd sodium thiosulphate and 4th water. Next, the sample is attacked with nitric acid, hydrochloric acid and hydrogen peroxide. Several extractions, first with toluene and then with nitric acid are made in the solutions in the beakers. The organic phase is mixed with toluene and an aliquot of this solution is taken and illuminated with UV until it is totally discoloured. Finally, an aliquot is measured by LSC.

Actinides isotopes: Different carriers and ^{236}Pu, ^{243}Am tracers are added to an aliquot of sample and an acid digestion is made. An aliquot is taken and passed through a Dowex Resin column (previously prepared with 8N HNO_3). The column is washed with 8N HNO_3 and Am-Cm will be determined from this dissolution. The column is washed with 10N HCl and then **^{238}Pu and $^{239/40}$Pu** are eluted with 0.36N HCl-0.01N HF. This elution is evaporated to 25 ml and electrodeposited. Finally, the electrodeposited sample is measured by alpha spectrometry to determine ^{238}Pu, $^{239/40}$Pu. ^{236}Pu is also determined in order to obtain the process efficiency.

The procedure for the analysis of **Am-Cm isotopes** is performed in the dissolution of 8N HNO_3 from Dowex Resin that is evaporated and mixed with 300 ml H_2O. Calcium carrier and oxalic acid are added, heated, and adjusted to pH 1.5 to precipitate Calcium Oxalate. This precipitate is centrifuged and dissolved with 2N HNO_3. A fresh dissolution of 0.8N Ascorbic Acid is added to discolour the sample. This mixture is passed through a TRU.Spec column (previously prepared with 2N HNO_3). The column is washed with 9N HCl and Am-Cm are eluted with 4N HCl. Finally, this elution is electrodeposited and measured by alpha spectrometry to determine ^{241}Am, ^{242}Cm, ^{244}Cm. ^{243}Am is also determined in order to obtain the process efficiency.

In order to determine **^{241}Pu**, different carriers are added to an aliquot of sample and an acid digestion is made. The sample from digestion is taken and passed through a Dowex Resin column (previously prepared with 8N HNO_3). The column is cleaned with several dissolutions: 8N HNO_3; 10N HCl; 1N HNO_3 – CH_3OH 90%; 0.1N HCl - CH_3OH 80%- 0.5N NH_4SCN. ^{241}Pu is eluted with 0.36N HCl- 0.01N HF. This elution is evaporated to 25 ml and an aliquot is measured by LSC. Also, gamma isotopes and ^{55}Fe are determined on aliquots from elution to check that there are not interferences in ^{241}Pu measurement.

2.3.2.2. Evaporator concentrate

Acid digestion: Different carriers (Ni, Fe, Sr, Y, Co, Cs) and nitric acid are added to a homogenised aliquot of sample. The solution is heated with hydrogen peroxide and a mixture of nitric-hydrochloric acid until the end of the reaction. It is dried and mixed with 8N HNO_3.

For all radionuclides, the same separation procedures as for the resin have been carried out.

2.3.3. CEA

Sample aliquots of resin were first dried at a temperature of 60 ± 1 °C for 48 hours. Then, specific dissolution and separation procedures were carried out on dried resins prior to the measurement step. The principles of these procedures are described below:

Tritium: Dissolution of dry sample aliquots by conc. H_2SO_4 in an open microwave digester and oxidation with H_2O_2; Trapping of ^{3}H in an acidic solution (H_2SO_4); Distillation of ^{3}H and Measurement by Liquid Scintillation Counting

Carbon-14: Dissolution of dry sample aliquots by conc. H_2SO_4 in an open microwave digester and oxidation with H_2O_2; Trapping of ^{14}C in an alkaline solution (NaOH); Oxidation of carbon to CO_2 in an acid and oxidising medium; Distillation and trapping of carbon into Carbosorb and Measurement by Liquid Scintillation Counting.

Iron-55: Dissolution of dry sample aliquots by conc. H_2SO_4 in an open microwave digester and oxidation with H_2O_2; Precipitation of iron hydroxide; Dissolution in hydrochloric acid; Separation through an ion exchange resin; Dry evaporation and dissolution in HCl and Measurement by Liquid Scintillation Counting.

Nickel-63: Dissolution of dry sample aliquots by conc. H_2SO_4 in an open microwave digester and oxidation with H_2O_2; Separation of nickel in the form of a bis-dimethylglyoxime - nickel complex; Extraction of the complex by chloroform before back-extraction by hydrochloric acid and Measurement by Liquid Scintillation Counting.

Strontium-89/90: The principle is based upon the separation of Ca/Sr, by precipitating the strontium nitrate with concentrated nitric acid in the presence of a carrier (natural Sr). Ba and Y as well as rare earth are also precipitated in an ammoniacal medium, in the presence of Fe III. Finally, the strontium carbonate is precipitated and redissolved by adding nitric acid. The ^{89}Sr and ^{90}Sr measurement is performed by Liquid Scintillation Counting.

Technetium-99: Desorption from dry sample aliquots by 14M HNO_3; Filtration and elimination of the insoluble residue; Addition of Re (tracer); Heating and oxidation with H_2O_2; Extraction chromatography on TEVA·Spec resin; Elution with 7M HNO_3 and Measurement by Inductively Coupled Plasma – Mass Spectrometry.

Iodine-129: Digestion of dry sample aliquots by a mixture of HNO_3 – $HClO_4$ in a closed microwave oven under controlled pressure; Dilution in HNO_3 – $HClO_4$ – $KMnO_4$ to stabilise iodide species in the iodate form and Measurement by Inductively Coupled Plasma – Mass Spectrometry.

Actinides isotopes: Dissolution of the resin is made in H_2SO_4 / H_2O_2 medium. Alpha emitters are coprecipitated in ammoniacal medium by ferric hydroxide. The precipitate is dissolved with HNO_3 and a valence adjustment is made with NH_2OH / HCl. An extraction on an impregnated support with TBP/CMPO isolates actinides and purifies the solution from the main gamma emitters and from the iron. At this step an aliquot is taken for electrodeposition and **curium isotopes** measurement.

Americium and plutonium isotopes contained in the second aliquot are separated on an anion exchange resin in HNO_3 then HCl medium. Fractions containing plutonium and americium are treated by electrodeposition for alpha measurement. Plutonium electrodeposition plate is dissolved in HNO_3 medium for ^{241}Pu measurement.

The dissolution method used for the determination of **^{234}U and ^{238}U** consisted in a mineralisation of ~0.2 – 0.3 g dry resins aliquots by a mixture of concentrated nitric and perchloric acids in a closed microwave system under controlled pressure. In the present case, no separation method was carried out for ^{234}U and ^{238}U measurement. After dissolution of the two resin samples, the solutions were split into three aliquots and diluted by a factor of 10 in a mixture of HNO_3 – $HClO_4$ – $KMnO_4$ in order to reach acceptable conditions for ICP-MS analyses.

2.3.4. SCK·CEN

2.3.4.1. Resin

Dissolution: The delivered resin sample was well mixed with the water that had been formed on top of the sample. A small amount of the wet resin was weighed on a glass dish and dried for 48 hours at 60°C to determine the water content. Simultaneously an amount of wet resin was weighed in a glass reactor and destructed with H_2O_2 using $Fe_2(SO_4)_3$ as a catalyst in HNO_3. Undissolved particles were filtered off and dissolved with a K_2CO_3 fusion. Both solutions were combined afterwards. During the acid dissolution the released $^{14}CO_2$ in the off-gasses was trapped in 4M NaOH. Some of the tritium was also trapped in the water and alkaline flasks and were measured separately.

Gamma-spectrometry measurements: Three measurement samples of 20 ml from each dissolution were taken and measured by gamma-spectrometry.

Tritium: Tritium is distilled under reduced pressure as water in the form of HTO or T_2O. Due to the difference between boiling temperatures of H_2O, HTO and T_2O, the concentration of Tritium will differ a little from the original solution but this difference is negligible. Vacuum distillation: when the liquid is exposed to a vacuum environment, the water vapour will occupy all the room. A cooling trap, placed at a certain distance of the sample, will condense the vapour. The cooling trap is a glass flask immersed in a mixture of acetone and solid CO_2 achieving temperatures of -60°C to -70°C. So water will continuously evaporate at room temperature.

Carbon-14: To separate the carbon-14 from our radioactive waste samples they are dissolved with acids. This way most of the carbon is oxidised and released as $^{14}CO_2$ in the off-gas. The off-gas is lead through a cascade of wash bottles filled with 4-8 M NaOH where the $^{14}CO_2$ is trapped. Next about 25 ml of the combined NaOH wash-solution is used to separate a second time the $^{14}CO_2$. The technique is called Acidolysis. The NaOH sample is placed in a closed glass system, were all gases are evacuated with a vacuum pump. To the sample perchloric acid is slowly added to acidify and release the trapped $^{14}CO_2$. The re-released $^{14}CO_2$ is cooled down with one trap of acetone/solid carbon dioxide at -70°C and two traps cooled with liquid N_2 at -210°C. In the last two traps the $^{14}CO_2$ is frozen. After the acidification all $^{14}CO_2$ is sublimated to the last trap. Next the frozen $^{14}CO_2$ is mixed with Carbosorb, a commercial organic solvent which absorbs the carbon dioxide when defrosted. This solvent has the benefit of being well mixable with liquid scintillation cocktail for beta measurement with LSC.

Iron-55: Iron is separated from other radioactive isotopes (mostly Nickel and Cobalt) in the solution using a DOWEX 1-X8 column. The purified solution is concentrated by evaporation and a small aliquot is evaporated on a stainless steel counting disc. After fixation the X-rays of ^{55}Fe are measured on a Low Level Proportional Counter. The chemical yield is determined by ICP/MS.

Nickel-63: To the solution a known amount of Ni carrier is added, also a small amount of Co and Cs carrier. The solution is first cleaned with an anion resin. Most of the Iron (^{55}Fe) and Cobalt (^{60}Co) are retained on the column. Nickel will flow through. Next a second separation is carried out by precipitation of the nickel with DMG as its complex. The complex is redissolved with nitric acid. The DMG is broken down with hydrogen peroxide. The solution matrix is adjusted to a low acid concentration and the chemical separation yield is measured by ICP/MS analysis. The ^{63}Ni is measured by a Liquid Scintillation Counter.

Strontium-90: Strontium is absorbed from a 6 M HNO_3 solution on an Eichrom Sr•Spec® column. Interfering radionuclides are not retained and are washed from the column. Strontium-90 is eluted with water and is left for a longer period to allow the daughter ^{90}Y to grow in. After a period of 7 - 10 days, enough ^{90}Y has been formed to be measured. The ^{90}Y is separated by 2 precipitation steps and counted on a glass fibre filter with a LLPC. From the measurement result the original ^{90}Sr concentration is calculated taking into account the ^{90}Y ingrowth and the ^{90}Y decay.

Actinides isotopes: The actinides are precipitated from the solution and redissolved. Pu is separated on an anion exchange column while U, Am and Cm are separated with an Eichrom TRU•Spec® column. Each eluent is subjected to electrodeposition so that the actinides are collected on a stainless steel planchet. The activities on the planchets are counted by an alpha spectrometer.

2.3.4.2. Evaporator concentrate

The delivered sample was a brownish viscous slurry containing a large amount of residue. In order to make it easier to handle, it was diluted with water. The residue was separated from the liquid phase by centrifugation. The residue was then dried and milled to a fine powder. The liquid phase still contained some very fine solid particles but these could easily be homogenised by shaking the solution before sampling. About 1g of dried residue was dissolved in a glass reactor in the presence of an equivalent amount of liquid phase. When adding concentrated HNO_3 and HCl and boiling for several hours, most of the residue was dissolved. The undissolved residue was filtered and treated with a K_2CO_3 fusion technique. Both the acid and melt solutions were combined. As with the resin destruction, the released ^{14}C was trapped as $^{14}CO_2$ in an alkaline solution of 4 M NaOH. However, during the dissolution of the concentrate sample the release of acid fumes from the reactor was very high and resulted in an acidification of the hydroxide solutions. Therefore for the determination of **^{14}C**, the acid dissolutions were repeated using 8 M NaOH for the collection of the off-gasses.

Tritium: The procedure used is the same as the mentioned for the analysis of the resin but in this case the original solution was used in order to avoid losses and dilution factors.

Gamma-spectrometry measurements: Three measurement samples of 20 mL from each dissolution were taken and measured by gamma-spectrometry.

For the other radionuclides, the same separation procedures as for the resin have been carried out.

2.3.5. NRG

2.3.5.1. Resin

Two sub-samples of about 2 grams were taken at the same time for both ^{3}H-analyse and $^{89,90}Sr$, ^{55}Fe, ^{63}Ni analyses. The sub-sample for ^{3}H was not dried but directly used in the distillation procedure to determine this radionuclide. The value for the dry weight will be derived from the second sub-sample. This second sub-sample was dried for 48 hours at 60^{o} C. After drying the sample was refluxed for 48-72 hours at 140^{o}C and afterwards boiled to dryness. After taking up in 200 ml 2M nitric acid, the sample solution was split up for the different analyses. After the determination of ^{3}H, $^{89,90}Sr$, ^{55}Fe and ^{63}Ni there was still some sample solution left for actinide analysis.

Tritium: To obtain the tritium activity in these samples there is no pre-treatment necessary. Add to a weighted amount of the sample 70 ml demi water. For the resin, leave overnight at room temperature. The distillation of the resin is carried out to dryness to ensure complete transfer of the tritium. The evaporator concentrate is "soluble" in water, so the distillation can be carried out directly. To remove volatile elements the sample is heated on a sand bath for about 10 minutes and then distilled. From a sufficient amount of distillate pipette 10 ml into a glass vial, add 10 ml liquid scintillation counting cocktail and count with the correct counting protocol for tritium. Counting time depends on the count rate. After counting calculate the tritium activity in the sample considering the quenching in the sample.

Iron-55: An appropriate amount of sub-sample is treated with concentrated acids in order to dissolve it and subsequently is made up in 8M HNO_3. A known amount of stable iron is added to determine the chemical yield of the procedure. A sub sample (initial sample) is taken and later analysed by spectrophotometry. The iron isotopes are then separated from other elements by repeated coprecipitation of iron hydroxide. After the last precipitation the sample is checked for the presence of interfering isotopes (^{134}Cs, ^{137}Cs, ^{54}Mn) by means of gamma spectrometry. If necessary the precipitations must be repeated. The final sample is then split up into two fractions determined by weight. One fraction is measured by LSC to determine the amount of ^{55}Fe. The other fraction (final sample) is analysed together with the initial sample by means of spectrophotometry to determine the chemical yield.

Nickel-63: An appropriate amount of sub-sample is treated with concentrated acids in order to dissolve it and subsequently is made up in 8M HNO_3. A known amount of stable nickel is added to determine the chemical yield of the procedure. A sub sample (initial sample) is taken and later analysed by spectrophotometry. The nickel isotopes are then separated from other elements by several series of liquid/liquid extractions. After the last extraction the sample is checked for the presence of interfering isotopes (^{134}Cs, ^{137}Cs, ^{54}Mn) by means of gamma spectrometry. If necessary the extractions must be repeated. The final sample is then split up into two fractions determined by weight. One fraction is measured by LSC to determine the amount of ^{63}Ni. The other fraction (final sample) is analysed together with the initial sample by means of spectrophotometry to determine the chemical yield.

Strontium-89/90: After a pre-treatment of the sample with concentrated nitric acid and hydrogen peroxide the residue is dissolved in 8 M HNO_3. A weighted aliquot is neutralised to pH 7 with concentrated ammonia and after addition of inactive strontium carrier, calcium, strontium et. al. are precipitated as oxalates. This is followed by the separation of strontium from calcium using fuming nitric acid. Barium, caesium and lead isotopes are removed by chromate precipitation and other potential fission products including yttrium by coprecipitation on ferric hydroxide. Finally strontium is precipitated as carbonate, filtered and counted several times on a low-level beta-counter until there is no increase in count rate.

Actinides isotopes: After weighing an appropriate amount of sub-sample yield tracers are added. The sub-sample is treated with concentrated acids in order to dissolve it and subsequently is made up in 8 molar nitric acid. Sequentially, plutonium, uranium and americium (and curium) are separated from the bulk sample using three anion exchange columns. In order to separate uranium from iron a liquid-liquid extraction has to be performed with methyl iso-butyl ketone. The fraction containing plutonium is split up into two portions determined by weight: one for alpha spectroscopy and another for liquid scintillation counting. Finally, before electroplating on stainless steel discs, the different fractions (washings) are taken up in a sodium sulphate sulphuric acid solution.

2.3.5.2. Evaporator concentrate

For all radionuclides, the same separation procedures as for the resin have been carried out.

2.3.6. FZJ

2.3.6.1. Resin

0.2 g of dried resin were weighed in a teflon autoclave and dissolved with 6 mL HNO_3 conc. and 2 mL H_2O_2 (35%).

Tritium and Carbon-14: The combustion of both wet samples is performed in a furnace with a catalyst bed of CuO at 800 °C. Tritium is captured in a gas trap filled with diluted nitric acid. This solution is distilled and the ^{3}H is measured with LSC. The formed CO_2 containing the ^{14}C is absorbed in sodium hydroxide solution. This solution is directly measured by LSC. The results of the ^{3}H measurements were also compared with a direct distillation of the wet samples.

Iron-55: Both samples are totally dissolved with microwave decomposition. Counting samples for the x-ray measurements are prepared from aliquots of the dissolved solutions by drying and evaporation on a teflon plate. Stainless steel plates cannot be used for the determination of ^{55}Fe. The samples are measured with a low energy Ge-detector.

Nickel-63: Both samples are totally dissolved with microwave decomposition. To this solution Cobalt, Caesium and Nickel tracer solutions are added. These tracer solutions ensure the precipitation of Nickel without co-precipitation of Cobalt and Caesium. The solution is adjusted to pH 6 and afterwards the Nickel is precipitated with a 1 % dimethylglyoxime solution (alcoholic solution). The red precipitate is filtered, washed several times with warm water and finally dissolved in 3 M HNO_3. An aliquot of this solution is measured by LSC.

Strontium-89/90: Both samples are totally dissolved with microwave decomposition. To this solution a Strontium tracer solution is added and in a next step the solution is adjusted to 8 M HNO_3. The $^{89/90}Sr$ is separated on Sr resin column (Eichrom). The column is loaded with the solution, washed with 8 M HNO_3 and eluted with 0.05 M HNO_3. A measurement is performed by LSC and the chemical yield of this procedure is determined by ICP-AES.

Technetium-99: Both samples are totally dissolved with microwave decomposition. The solution is adjusted to 0.05 M HNO_3. The ^{99}Tc is separated on TEVA resin column (Eichrom). The column is loaded with the solution, washed with 0.05 M HNO_3 and eluted with 8 M HNO_3. A measurement is performed by LSC.

Iodine-129: For a first method both samples are suspended in water, $^{127}I_2$-Carrier solution is added and the I_2 is extracted with toluene. The organic phase is measured by γ-spectrometry. It was proved with ^{129}I standard solutions that the exchange of the isotopes ^{127}I and ^{129}I was quantitative. In a second method the samples are suspended in toluene. A carrier solution of CdI_2 is added and the I^- ions are oxidised with H_2O_2 to I_2 and extracted by the organic phase. The organic phase is separated and the I_2 is reduced with an ascorbic acid solution back to I^-. Now the aqueous phase can be measured by LSC. An aliquot of the undissolved samples was also used for a direct γ-measurement.

Actinides isotopes: Before the dissolution, tracer solutions of ^{243}Am, ^{236}Pu and ^{232}U were added. The liquid-liquid extraction of actinides is performed with an organic extracting agent TOPO (Tri-octylphosphinoxide) dissolved in n-heptane. This organic TOPO-heptane phase extracts Uranium and Plutonium from an acid liquid solution, and after neutralisation Americium and Curium are extracted from an almost neutral solution. Counting samples for alpha spectroscopy in a grid chamber are prepared from both extractions by drying and evaporation. Uniform counting layers are obtained from the TOPO solutions by controlled heating of the planchet from the rim.

2.3.6.2. Evaporator concentrate

1 mL of the homogenised evaporator concentrate was completely dissolved with 5 mL concentrated HNO_3, 2 mL HBF_4 (40%) and 1.5 mL H_2O_2 (35 %).
For all radionuclides, the same procedures used in the analysis of the resin have been performed.

2.3.7. <u>Belgoprocess</u>

2.3.7.1. Resin

The chemical destruction of the ion exchange resin is the transformation of the resin and other solids of the sample of the ion exchange resin into the liquid form by a stepwise addition of the proper chemicals to the heated sample.

Tritium: ^{3}H has been analysed, based on the counts in the range of 0 to 18.6 keV of the β-spectrum of the measured liquid.

Iron-55, Nickel-63 and Strontium-90: ^{55}Fe has been analysed based on the counts in the β-spectrum of the sample at a mean energy of ≅ 6 keV. The eventual activity of ^{41}Ca, ^{59}Ni, ^{109}Cd and ^{241}Pu, which are situated in nearly the same region of the β-spectrum, has been attributed to ^{55}Fe. ^{63}Ni has been analysed, based on the counts in the β-spectrum of the sample at a mean energy of ≅ 17 keV. The eventual activity of ^{93}Zr and ^{151}Sm, which are situated in nearly the same region of the β-spectrum, has been attributed to ^{63}Ni. The activity of ^{90}Sr is set equal to the activity of its daughter ^{90}Y, which has been analysed based on the counts in the β-spectrum of the sample at a mean energy of 935 keV.

Strontium-89, Iodine-129 and Americium-241: The measurement is made directly on a sub-sample of the original sample of the resin or the evaporator concentrate and on a destruction of a sub-sample of the evaporator concentrate. ^{89}Sr has been analysed, based on its peak at an energy of 909.1 keV and with a yield of 0.015% in the γ-spectrum of the sample. ^{129}I has been analysed, based on its peaks at an energy of 29.7 keV (yield = 57.1%), 39.6 keV (yield = 7.5%) and 33.7 keV (yield = 12.8%) in the γ-spectrum of the sample. ^{241}Am has been analysed, based on its peak at an energy of 59.5 keV (yield – 35.7%) in the γ-spectrum of the sample.

Actinides isotopes: ^{238}Pu, $^{239/40}Pu$, ^{234}U and ^{235}U are measured by α-spectrometry, applied on a "hexone extract" of the destruction of a sub-sample of the original sample of the ion exchange resin or the evaporator concentrate. The extraction with hexone or methylisobutylcetone (MIC) is used in order to obtain a solution that contains exclusively the U- and Pu-isotopes and which is free from salts as much as possible.

2.3.7.2. Evaporator concentrate

Two techniques of chemical destruction of the samples of the evaporator concentrate have been applied:

- Boiling in concentrated nitric acid.
- Alkaline melt. The sample is mixed with K_2CO_3 and heated for 1 hour at 1000°C. By quickly cooling down of the heated mixture, a cracked glassy product is obtained. That solid is then intensively mixed with demineralised water for 3 hours. Finally, nitric acid is added in order to obtain a measurable solution.

For all radionuclides, the same separation procedures as for the resin have been carried out.

2.3.8. Helsinki University

2.3.8.1. Resin

The resin is stirred to homogenise it and then it is divided into three aliquots (one aliquot in storage). The aliquot is dried at 60ºC for 48 hours to constant weight. Then the resin sample is leached with increasing acid concentrations of HNO_3 and HCl. Then the resin is dried and ashed at 1000ºC, leached with increasing concentrations of HNO_3 and HCl and finally the solution is combined with the original one.

Iron-55: Stable iron as a yield carrier was added to an aliquot of dissolved resin. Iron was separated from other radionuclides by iron hydroxide precipitations, by liquid-liquid extraction and by ion exchange. ^{55}Fe was then measured by LSC. Yield was determined by AAS (Flame).

Nickel-63: Stable nickel as a yield carrier was added to an aliquot of dissolved resin. Nickel was separated from other radionuclides by carbonate and dimethylglyoxime (DMG) precipitations and by ion exchange. ^{63}Ni was then measured by LSC. Yield was determined by AAS (Graphite furnace).

Strontium-89/90: Extraction chromatography was used to separate strontium from interfering radionuclides. The daughter nuclide ^{90}Y was isolated after ingrowth. The total beta activity and ^{90}Y were measured by LSC. ^{85}Sr was used as a yield tracer for strontium separation. Yield for yttrium separation was assumed to be 100%. The activity of ^{89}Sr was determined from the total beta activity by subtracting the activity of ^{90}Sr and ^{90}Y.

Actinides isotopes: In order to determine **plutonium isotopes**, ^{242}Pu as a yield carrier was added to an aliquot of dissolved evaporator concentrate or resin. Plutonium was separated from other radionuclides by ion exchange. ^{238}Pu and $^{239/40}$Pu were then measured by alpha spectrometry. **^{241}Pu** was then measured by liquid scintillation counting. Yield was determined by alpha spectrometry and liquid scintillation counting.

In order to determine **americium and curium isotopes**, ^{243}Am as a yield carrier was added to an aliquot of dissolved evaporator concentrate or resin. Americium and curium were separated from other radionuclides by ion exchange. They were then measured by alpha spectrometry. Similar chemical behaviour of americium and curium was assumed.

In order to determine **uranium isotopes**, ^{232}U as a yield carrier was added to an aliquot of dissolved evaporator concentrate or resin. Uranium was separated from other radionuclides by repeated cerium hydroxide coprecipitations. Uranium was then measured by alpha spectrometry.

2.3.8.2. Evaporator concentrate

After shaking the concentrate to homogenise it, it is divided into three aliquots (one aliquot for storage). The aliquots are dissolved with concentrated HNO_3 and HCl heated under reflux and finally filtered.

Tritium: The evaporator concentrate was dissolved in acid under reflux cooling. Tritium was distilled to remove the salts and other interfering radionuclides. Tritium was measured by LSC.

For the rest of radionuclides, the same separation procedures as for the resin have been carried out.

2.3.9. NNC

2.3.9.1. Resin

Two weighed sub-samples of about 5g of homogenised wet resin were taken and dried in a muffle furnace at 60°C for 48 hours. The weights of the dried resins were used to determine the water content of the original resin sample.

Two weighed sub-samples of about 3g of homogenised wet resin were taken and dissolved in a 2:1 mixture of concentrated H_2SO_4 and 30% H_2O_2. The solutions were then made up to 250ml in calibrated volumetric flasks with deionised water.

Separate solutions were prepared for I-129 analysis by refluxing further wet resin sub-samples with 6M NaOH, and making up to 100ml.

For all analyses, reagent blank solutions for analysis were prepared from the supplied blank resin sample.

Tritium: Tritium is extracted as tritiated water from the sample solution by distillation after first being treated with an alkaline reducing agent to prevent volatilisation of radioisotopes of iodine or ruthenium. A measured aliquot of the distillate is added to a liquid scintillation cocktail. The sample is shaken and allowed to equilibrate prior to analysis by liquid scintillation counting. The counting efficiency of the sample is determined by internal standardisation using a ^3H reference standard solution. The method efficiency is determined from a measured aliquot of ^3H reference standard solution analysed as per the samples.

Carbon-14: A measured aliquot or weight of sample is mixed with potassium dichromate, and refluxed with a mixture of concentrated sulphuric and concentrated orthophosphoric acids. Any inorganic or organic carbon present in the sample is converted to $^{14}CO_2$. Air is passed through the reaction flask and the $^{14}CO_2$ is bubbled through 0.1 M nitric acid to remove impurities. The $^{14}CO_2$ is then bubbled through Carbosorb, where it is absorbed. The Carbosorb is transferred to a calibrated volumetric flask, and made up to a known volume with fresh Carbosorb. A measured aliquot of the Carbosorb volume is added to a liquid scintillation cocktail. The sample is shaken and allowed to equilibrate prior to analysis by liquid scintillation counting. The counting efficiency of the sample is determined by internal standardisation using a ^{14}C reference standard solution. The method efficiency is determined from a measured aliquot of ^{14}C reference standard solution analysed as per the samples.

Iron-55: The sample solution is mixed with iron, nickel and cobalt carriers, 30% hydrogen peroxide and solid ammonium chloride, and heated in a water bath. Concentrated ammonia solution is added to precipitate iron hydroxide, which is removed by centrifugation, leaving impurities in solution. The precipitate is dissolved in 8M HCl, and shaken with di-isopropyl ether to extract the iron. The ether phase is shaken with deionised water to extract the iron. The aqueous phase is heated in a water bath to remove any residual di-isopropyl ether, and concentrated ammonia solution is added to precipitate iron hydroxide, which is removed by centrifugation. The precipitate containing the ^{55}Fe is dissolved in 2M orthophosphoric acid, transferred to a calibrated volumetric flask, and made up to a known volume with deionised water. A measured aliquot of the acid volume is added to a liquid scintillation cocktail. The sample is shaken and allowed to equilibrate prior to analysis by liquid scintillation counting. The counting efficiency of the sample is determined by internal standardisation using a ^{55}Fe reference standard solution. The method efficiency is determined from a measured aliquot of ^{55}Fe reference standard solution analysed as per the samples.

Technetium-99: The sample solution is mixed with iron carrier, 30% hydrogen peroxide and concentrated nitric acid, and heated in a water bath. This ensures that the Tc is in the pertechnetate form. Concentrated ammonia solution is added to precipitate iron hydroxide, co-precipitating impurities, which is removed by centrifugation. The solution is acidified with concentrated sulphuric acid, and shaken with 5% $^{V}/v$ tri-n-octylamine in xylene to extract the ^{99}Tc. A measured aliquot of the organic volume is added to a liquid scintillation cocktail. The sample is shaken and allowed to equilibrate prior to analysis by liquid scintillation counting. The counting efficiency of the sample is determined by internal standardisation using a ^{99}Tc reference standard solution. The method efficiency is determined from a measured aliquot of ^{99}Tc reference standard solution analysed as per the samples.

Iodine-129: The sample solution is mixed with iodide carrier, and neutralised with nitric acid and ammonia solution. Iron and cobalt carriers are added, and the sample is heated in a water bath. Concentrated ammonia solution is added to co-precipitate impurities with iron hydroxide, which is removed by centrifugation. Sodium hydroxide solution is added to co-precipitate impurities with cobalt hydroxide, which is removed by centrifugation. Sodium hypochlorite solution is added to ensure that iodine in solution is in the periodate form. The iodine in the solution is then reduced to the iodide form by the addition of concentrated nitric acid, 1M hydroxylamine hydrochloride solution, and then 1M di-sodium disulphite solution. The solution is adjusted to pH 6.5 – 7 with ammonia solution and nitric acid prior to passing through an anion exchange column to adsorb the iodide from the solution. Impurities are washed from the column with deionised water, and 2M sodium chloride solution. The ^{129}I is eluted from the column with sodium hypochlorite solution into a calibrated volumetric flask, and made up to a known volume with deionised water. The whole sample is transferred to a 50 ml counting pot prior to analysis by low energy gamma and x-ray spectrometry capable of measuring energies in the range 3 – 100 keV. The method efficiency is determined from a measured aliquot of ^{129}I reference standard solution analysed as per the samples.

Actinides isotopes: The sample solution is mixed with iron carrier, and ^{243}Am, ^{242}Pu and ^{232}U reference standard solutions. Conc. ammonia solution is added to co-precipitate actinides with iron hydroxide. The iron is extracted from 8 M HCl with di-isopropyl ether. After evaporation to dryness, the residue is dissolved in 8 M HCl, and conc. HNO_3, and passed through an anion exchange column to adsorb Pu and U radioisotopes. The Am and Cm fraction passes through, and is absorbed on a second column with 8 M HNO_3 and methanol. Am and Cm radioisotopes are eluted with 8 M HNO_3. U radioisotopes are eluted from the initial column with 3 M HNO_3, and Pu radioisotopes are then eluted with 2% HI in HCl. The actinides are electrodeposited on to stainless steel discs, and counted by alpha spectrometry. After counting, Pu radioisotopes are stripped with 8 M HNO_3 and HCl, and evaporated to dryness. The residue is dissolved in an aliquot of 1 M HNO_3, mixed with liquid scintillation cocktail, and analysed by LSC for ^{241}Pu. The counting efficiency of the sample is determined by internal standardisation using a ^{241}Pu reference standard solution.

2.3.9.2. Evaporator concentrate

Two measured sub-samples of about 5ml of homogenised evaporator concentrate were taken and dissolved in a solution of $Fe_2(SO_4)_3$ and 30% H_2O_2. at pH 2.1. Dissolution was completed by the addition of other acids, and the solutions were then made up to 250ml in calibrated volumetric flasks with deionised water.

Separate solutions were prepared for ^{129}I analysis by refluxing further evaporator concentrate sub-samples with 6M NaOH, and making up to 100ml.

For all radionuclides, the same separation procedures as for the resin have been performed.

2.3.10. TUM

2.3.10.1. Resin

Tritium and Carbon-14: The resin sample was slowly heated up to 1400 °C (O_2 atmosphere), the thermal combustion products were additionally oxidised and finally analysed by means of liquid scintillation spectrometry.

Iron-55: The hydrochloric acidic digestion solution was concentrated and oxidised (H_2O_2 addition). Afterwards Fe-III was extracted by means of methyl isobutyl ketone. After re-extraction to aqueous media ^{55}Fe was measured by means of liquid scintillation spectrometry. The chemical yield was performed by Fe quantification in the digestion solution and the liquid scintillation sample.

Nickel-63: After Fe extraction and ^{60}Co decontamination ^{63}Ni was precipitated as Ni dimethyl glyoxime. The cleaned precipitate was dissolved, ^{63}Ni was measured by means of liquid scintillation spectrometry.

Strontium-89/90: Some stable Sr (100 mg as $Sr(NO_3)_2$) was added to the digestion solution as chemical carrier. Before ^{55}Fe and ^{63}Ni separation the Sr/^{90}Sr was precipitated as $SrSO_4$. Then the sulphate was transformed to $SrCO_3$. After removal of impurities (washing, digestion, precipitation), ^{90}Sr was measured by means of liquid scintillation spectrometry. The chemical yield was determined by balancing the natural, and added Sr (by ICP-OES).

Technetium-99: The dried sample material was spiked with HNO_3, and ^{99m}Tc was added as a chemical yield tracer. After the separation of interfering nuclides, ^{99}Tc/^{99m}Tc was adsorbed on a Tc selective resin. After the ^{99m}Tc gamma spectrometry measurement for chemical yield calculation the resin material was allowed to stand for one month for complete the ^{99m}Tc decay. The ^{99}Tc activity was measured by means of liquid scintillation spectrometry.

Actinides isotopes: Prior to the subsequent ashing a known amount of nuclide tracer for the actinides to determine the chemical yield correction (^{236}Pu, ^{232}U, ^{243}Am) was added to the dried sample material. The **Pu and U isotopes** were separated by extraction techniques (TBP/Dodecane) and ion exchange. The **Am and Cm** isotopes were separated by element selective resins (CMPO). The chemical yield was determined by measuring the added tracer nuclides with alpha spectrometry. In order to get a counting sample, the nuclides were separated by electrodeposition. The alpha emitting nuclides were measured by alpha spectrometry (vacuum chambers, semiconductor detectors), the ^{241}Pu was measured by liquid scintillation spectrometry using pulse shape analysis. The aim of the chemical preparation procedure was to get a clean acidic solution containing the desired actinide only in order to achieve a high resolution alpha spectrum rather then reaching a high chemical yield. Therefore, the chemical yield was comparably low (ca. 20 %).

2.3.10.2. Evaporator concentrate

Tritium and Carbon-14: The aqueous sample phase was distilled to dryness, the distillate was analysed by means of liquid scintillation spectrometry. The dry residue was heated up to 1400 °C (O_2 atmosphere), and the thermal combustion products were additionally oxidised and finally analysed by means of liquid scintillation spectrometry.

For the rest of the radionuclides, the same separation procedures as for the resin have been carried out.

2.3.11. ENEA

2.3.11.1. Resin

Tritium: The method of dosage of the activity, due to this radioisotope, is based on the separation of tritium, that may be distilled (together with H_2O) as HTO and/or T_2O, from aqueous solution that contain tritium together with other radioisotopes that would interfere in the measurement. The distillation allows the isolation of Tritium by obtaining an aqueous distillate where the concentration of HTO and/or T_2O, due to the small difference of boiling temperature that exist between H_2O, HTO and T_2O, are in practice equal to that of the solution to be analysed. The concentration is determined by LSC measurement on an aliquot of distillate.

Iron-55: Iron-55 is separated using Eichrom's TRU Resin column. Iron is loaded on the column in 8 M HNO_3 and is removed with 2 M HNO_3.

Nickel-63: Nickel is precipitated as a nickel/dimethylglyoxime complex on the Eichrom Nickel Resin column. The Nickel/dimethylglyoxime complex is then removed with a minimum amount of 3 M HNO_3. The strip solution can be measured for ^{63}Ni by LSC. If ^{55}Fe and actinides are present in the sample, they should be separated prior to loading the sample on the NICKEL column. This could be accomplished by using a TRU column that separates iron and actinides from nickel.

Strontium-90: This separation is carried out with Sr·Resin (EiChrom) chromatographic column. The column is washed with a volume of a 0.05M solution of $H_2C_2O_4$ in 8M HNO_3 and with 8 M HNO_3. The Strontium is recovered from the resin with 0.05 M HNO_3. The concentration is determined by the Liquid Scintillation Counting technique, measuring the aqueous solutions eluted from the chromatographic column, within 4 hours of the purification process.

Technetium-99: This separation is carried out with suitable ion-exchange resins, highly selective for Technetium, named TEVA-Spec. These resins strongly retain Technetium under acidic conditions from 0.1M HNO_3. The active sites of the resin are made of quaternary ammonium salts. The mobile phase is an HNO_3 solution of suitable concentration. Technetium, as pertechnetate anion (TcO_4^-), is strongly retained when the eluent is a diluted solution of nitric acid. When the concentration is raised up until 8M, TcO_4^- is easily eluted. The concentration is determined by the Liquid Scintillation Counting technique.

Actinides isotopes: The separation is carried out with the **UTEVA** column, and the column is washed with 3M HNO_3. The solutions are set aside for the separation of Americium-Curium from Plutonium. The **UTEVA** column is rinsed with 9M HCl and, in order to remove any Neptunium and Thorium from the column, 5M HCl and 0.05M $(COOH)_2$ are passed through the column. The Uranium is then stripped with 0.01M HCl. On the other hand, the **TRU** column is equilibrated with 2M HNO_3 and 0.1M $NaNO_2$. Sodium nitrite oxidises Plutonium from the trivalent to the tetravalent state and enhances the Pu/Am separation. 0.5M HNO_3 is passed through the column to lower the nitrate concentration prior to conversion to the chloride system. 9M HCl is passed through the **TRU** column. Americium and Curium are recovered from the column by passing through 4M HCl. Before the elution of Plutonium, a rinse with 4M HCl and 0.1M HF removes selectively any residual Thorium. Plutonium is recovered from the **TRU** column with 0.1 M $NH_4HC_2O_4$. The activity of alpha emitters is measured by alpha spectrometry and the activity of ^{241}Pu is measured by the liquid scintillation counting technique.

2.3.11.2. Evaporator concentrate

For all radionuclides, the same separation procedures as for the resin have been carried out.

2.3.12. Synoptic view

The following table indicates the radionuclides analysed by each partner as shown:

NUCLIDE	CIEMAT	ENRESA EL CABRIL	CEA	SCK·CEN	NRG	FZJ	BELGO-PROCESS	HELSINKI UNIVERSITY	NNC	TUM	ENEA
^{3}H	X	X	X	X	X	X	X	X*	X	X	X
^{14}C	X	X	X	X		X			X	X	
^{55}Fe	X	X	X	X	X	X	X	X	X	X	X
^{63}Ni	X	X	X	X	X	X	X	X		X	X
$^{89/90}$Sr	X	X**	X	X**	X	X	X	X		X	X
^{99}Tc	X	X	X			X			X	X	X
^{129}I	X	X	X			X	X		X		
^{238}Pu	X	X	X	X	X	X	X	X	X	X	X
$^{239/40}$Pu	X	X	X	X	X	X	X	X	X	X	X
^{241}Pu	X	X	X	X	X			X	X	X	X
^{241}Am	X	X	X	X	X	X	X	X	X	X	X
^{242}Cm	X	X	X	X	X	X		X	X	X	X
^{244}Cm	X	X	X	X	X	X		X	X	X	X
^{234}U	X		X	X	X	X	X	X	X	X	X
^{238}U	X		X	X	X	X	X	X	X	X	X

* Only from evaporator concentrate; possibilities for determination depend on sample composition.
** Only ^{90}Sr

2.4. WORK PACKAGE 4. REPORTING OF RESULTS

A preliminary format where it was indicated what was necessary to fill in the "reference document with a full description of all destructive techniques used for the analyses of the different alpha, beta and gamma emitting radionuclides" has been prepared. The contents of that format are as follows:

1. Title of the procedure

2. Scope

3. Terms and definitions

For the purposes of the methods, terms and definitions applied.

4. Principle

5. Instrumentation

6. Operating procedure

6.1. Separation method

Description of the method by a flow chart and indicating the main steps of the procedure

6.2. Chemical yield method

Description of the method used to determine the chemical yield, by a flow chart and indicating the main steps of the procedure

6.3. Measurement efficiency method

To indicate how the procedure is performed in order to determine the measurement efficiency

6.4. Preparation of the samples for measuring

7. Calculations and expression of results
7.1. Chemical yield
7.2. Measurement efficiency
7.3. Activity concentration
7.4. Uncertainties
7.5. Detection limit and Minimum Detectable Activity
8. Interference
9. References

All partners completed the format and the mentioned report was sent to the European Commission in May 2002.

2.4.1. Data reporting

2.4.1.1. Introduction

The aim of this work package was to establish the best way to report the results obtained for each laboratory [Lab] in the inter-comparison exercise. The analysis and the results should be done and reported in such a way that the statistical assessment could be performed in order to decide or point out the reliability of each individual determination of the specific activity content in both supplied samples: spent resins [R] and evaporator concentrate [C].

2.4.1.2. Split level and replications

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

It was determined that a minimum of three aliquots of sample, with similar amount of mass or volume, was needed. 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 meant loss of information.

Each treated aliquot must be divided into three equal aliquots for performing the separation procedure for each nuclide, which means six (6) sub-aliquots per nuclide and Lab.

A sample of inactive resin and chemical composition data of the evaporator concentrate were supplied to prepare blank samples to subtract matrix effects for each determination and to perform a good estimation of minimum detectable activity in order to evaluate the determination capabilities of each procedure.

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 An uncertainty will be calculated through the *quasi-variance* of the sample:

$$\mu_N = N \quad \Rightarrow \quad \mu'_N = \overline{N} = \frac{1}{n}\sum_{i=1}^{n} N_i$$

$$\sigma_N = \sqrt{\frac{N}{t}} \quad \Rightarrow \quad \sigma'_N = \sqrt{\frac{\sum_{i=1}^{n}\left(N_i - \overline{N}\right)^2}{n-1}}$$

Where:

N: Count rate of the sub-aliquot or blank

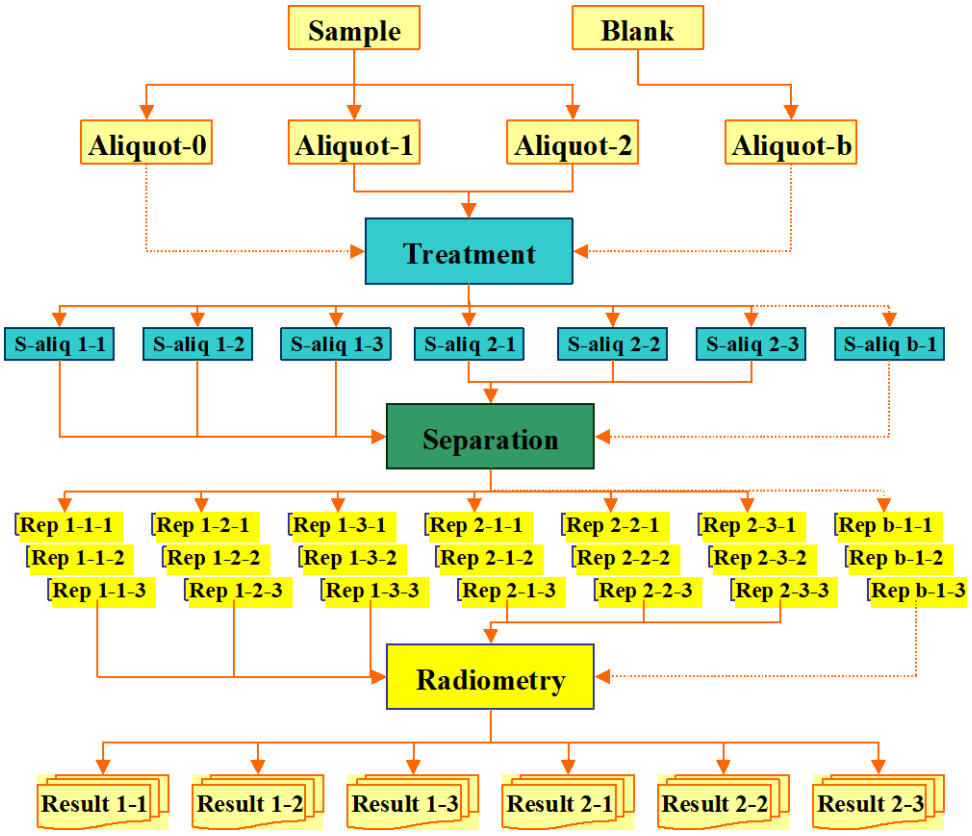
N_i: Count rate of i replicant of any sub-aliquot or blank

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

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

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

The process can be summarised in the following flow chart:



2.4.1.3. Data spreadsheet for reporting

A data spreadsheet was designed and distributed to the partner Labs in order to organise the receipt of results and the communication between the evaluator and responsible scientist for the results given.

A **code number** for each Lab was assigned randomly in order to ensure the confidentiality of results in the evaluation and avoid the establishment of any kind of ranking among the partners in the consortium since that is not the aim of this proficiency test.

The spreadsheet, with the following main contents, was created in MS Excel 97:

- **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**
  - **Specific activity per sub-aliquot**
  - **Specific MDA per sub-aliquot**
  - **Type A uncertainty**
  - **Type B uncertainty**

Activity and MDA calculation equations

Equations used for calculating specific activity and MDA, as detailed as possible, have to be reported for each nuclide in order to check results and evaluate the consistency of type B uncertainties, which is fundamental in the statistical assessment. An example of ^{90}Sr activity calculation is given in the following equations:

$$A_e = \frac{N}{Eff \cdot CY \cdot M}; \quad N = R - B; \quad CY = \frac{m_f}{m_i}; \quad M = \frac{m_{alq} \cdot DF_2}{DF_1};$$

$$Eff = \frac{N_{RS}}{A_{RS}} \cdot \left[1 - EXP\left(-\lambda_{Y-90} \cdot \Delta t\right)\right]; \quad N_{RS} = R_{RS} - B$$

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

A list of terms and symbols are given in the data sheet in order to harmonise the equation reporting, and any other symbol needed by any partner for the correct definition of activity and MDA calculations have to be included in the list supplied.

Concept	Symbol	Concept	Symbol
Activity of reference source/standard	$\mathbf{A_{rs}}$	Initial mass of carrier	$\mathbf{m_i}$
		Mass of aliquot	$\mathbf{m_{alq}}$
Blank Count Rate	**B**	Mass of sample	**M**
Chemical Yield	**CY**	Measurement Time	**t**
Decay Constant	$\boldsymbol{\lambda}$	Minimum Detectable Activity	**MDA**
Decay time	$\boldsymbol{\Delta t}$	Net Count Rate	**N**
Dilution/concentration factor	**DF**	Specific Activity	**A**
Efficiency	**Eff**	Total Blank counts	**b**
Final mass of carrier	$\mathbf{M_f}$	Total Gross counts	**I**
Gross Count Rate	**G**	Total Net counts	**n**

Table I. Symbols and concepts to be used in equations definition

Report of specific activity, MDA and uncertainties

Results of specific activity and MDA will be filled in for any sub-aliquot of any aliquot from each sample, and the reference parameter in the case of resins is the mass of the sample (results in Bq/g) of dry material at a drying temperature of 60ºC for 48 hours and in the case of concentrate is the volume (results in Bq/mL).

Type A (statistics on counting) and overall (combined type A and B uncertainties) uncertainty must be calculated as detailed as possible in order to make a correct statistical study of results that leads to the correct relative and absolute evaluation of any method applied. An example of an uncertainty evaluation was written and distributed within the consortium to harmonise the implementation of quality assurance procedure for activity determination in the framework of this project.

An example of the final spreadsheet for reporting activity is given in **Table II**.

^{m}X					Uncertainties			
ID. KEY	**Sample**	**Nuclide**	**Aliquot – replicates**	**A (Bq/g)**	**Type A (%)**	**Overall (Bq/g)**	**MDA (Bq/g)**	**Determ. date**
27	**R-1**	**^{m}X**	**1-1**					
27	**R-1**	**^{m}X**	**1-2**					
27	**R-1**	**^{m}X**	**1-3**					
27	**R-1**	**^{m}X**	**2-1**					
27	**R-1**	**^{m}X**	**2-2**					
27	**R-1**	**^{m}X**	**2-3**					
Sep. Method								
Meas. System								
Activity equation								
MDA equation								

Table II. Reporting table for a nuclide for a resin sample

2.5. WORK PACKAGE 5. EVALUATION OF RESULTS

2.5.1. Statistical evaluation

A specific report with all the results obtained by all partners has been prepared together with this final report. For that reason, only general information about the way that the evaluation has been performed and general conclusions about the results are given.

2.5.1.1. Introduction

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

Reference values and the 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.

The first option is not in the scope of this project for two reasons:

1.- The most highly qualified labs in the E.U., for these types of measurements, are part of the consortium and

2.- to devote a large budget for the evaluation in labs outside the E.U. was not the aim of the share-costed project of the EC.

The second option is the one to be adopted with the restrictions and the limits that agreement values mean for the statistical evaluation.

2.5.1.2. Reference values

The evaluation of each individual Lab data for each nuclide (j) is done by the weighted average of 6 replicate values given (m), which is the weighted factor of the reported combined (type A and B) variance (u^2 (^jx_m)).

$$ {}^{j}x_i = \frac{\sum_{m=1}^{6}\left(\frac{{}^{j}x_m}{u^2\left({}^{j}x_m\right)}\right)}{\sum_{m=1}^{6}\left(1/u^2\left({}^{j}x_m\right)\right)} $$

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

$$ u\left({}^{j}x_i\right) = \sqrt{1/\sum_{m=1}^{6} 1/u^2\left({}^{j}x_m\right)} $$

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

$$ s\left({}^{j}x_i\right) = \sqrt{\frac{\sum_{i=1}^{m}\frac{\left({}^{j}x_m - {}^{j}x_i\right)^2}{u^2\left({}^{j}x_m\right)}}{(m-1)\sum_{m=1}^{6} 1/u^2\left({}^{j}x_m\right)}} $$

It is agreed that the estimation of the population mean (μ) as the reference value of specific activity (^jX) for each nuclide (j) is calculated by the weighted average from data supplied (^jx_i) by each Lab (i) which is the weighting factor of the variance calculated for each Lab as above (u^2 (^jx_i)).

$$ {}^{j}X = \frac{\sum_{i=1}^{k}\left(\frac{{}^{j}x_i}{u^2\left({}^{j}x_i\right)}\right)}{\sum_{i=1}^{k}\left(1/u^2\left({}^{j}x_i\right)\right)} $$

The uncertainty associated with this value is calculated by:

$$u\left({}^{j}X\right)=\sqrt{\frac{1}{\left(\sum_{i=1}^{k}\left(\frac{1}{u^{2}\left({}^{j}x_{i}\right)}\right)\right)}}$$

2.5.1.3. Outliers

It is generally thought 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 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:

Cochran test

Firstly, apply the Cochran outlier test (1-tail test at P = 1%) and remove any laboratory whose critical value exceeds a tabular value given. This test computes the within-laboratory variance.

Grubbs tests

Apply the single-value Grubbs test (2-tail) and remove any outlying laboratory; and if no laboratory is flagged, then apply the pair-value test (two values at the same end and one value at each end, P = 1% overall). Remove any laboratories flagged by these tests using the corresponding table but stop the removal if more than 22.2% (2 of 9 laboratories) would be removed.

Finally, the reference values are recalculated after the laboratories flagged by the mentioned procedure have been removed.

2.5.1.4. 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), with X the real value or the assigned value as the best estimate of the 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

Q-score

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

$$Q = \frac{x - X}{X}$$

This type of score relates to the 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, and in fact must be where the estimation of the true value is all the partners means.

Q-score gives the direct measure of the bias associated with the determination, but its 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

z-score

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

$$z = \frac{x - X}{\sigma}$$

The 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 validated 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 was normal, then z would be a normal distribution centred on zero [$z \rightarrow N(0,1)$].

The main characteristics of z for interpreting data are:

- z is standardised, so it is useful for a comparison 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 does not allow the cancellation of different sign values with the same magnitude.
  - **Sum of absolute values** of scores, SAZ = $\Sigma |z|$; and it is useful if there are extreme outliers or many outlying labs.

The meaning of the z-score can be immediately appreciated:

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

u-*score*

Another type of evaluation is the use of the u-score which is defined as the deviation of the reference value with regards to the combined uncertainty between the one coming from the reference value calculation and the one coming from the individual determinations:

$$ {}^{j}u_i = \frac{{}^{j}x_i - {}^{j}X}{\sqrt{u^2\left({}^{j}X\right) + u^2\left({}^{j}x_i\right)}} $$

The advantage of this evaluation method relative to the others is that, on one hand you do not need well-defined target values of the mean and standard deviation as in the case of the z-score, and on the other hand this statistical parameter follows a well-known distribution and is sensitive to the outliers in order to detect inconsistencies in the declaration of activity and uncertainties, as opposed to the Q-score parameter.

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

|u| Value	P (%)	Evaluation of x vs X	Qualification
|u| < 2.015	99.9	**Values are not significantly different**	**Satisfactory (S)**
2.015< |u| <2.571	99.0	**Possibly Significant** Doubts are cast on X, further evidence is needed for rejection	**Acceptable (A1)**
2.571< |u| <4.032	95.0	**Significant** X could have significant differences with x, further data is needed	**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)**

Table III. Evaluation parameters established for Interlab-analysis project

2.5.2. Summary

The results of **15 radionuclides** were received:

- **7** from alpha emitting radionuclides and
- **8** from beta emitting radionuclides

1579 results and their corresponding **uncertainties** were managed:

- **754** from concentrate sample (**382** from alpha and **372** from beta emitters)
- **825** from resin sample (**413** from alpha and **412** from beta emitters)

A detailed study of the results of each radionuclide is presented in the deliverable "Statistical evaluation report" which is reported together with this Final Report. For this reason, only a summary of Q-score and u-score obtained in each one of the participating laboratories both in beta and alpha emitting radionuclides and in resin and concentrate is included here.

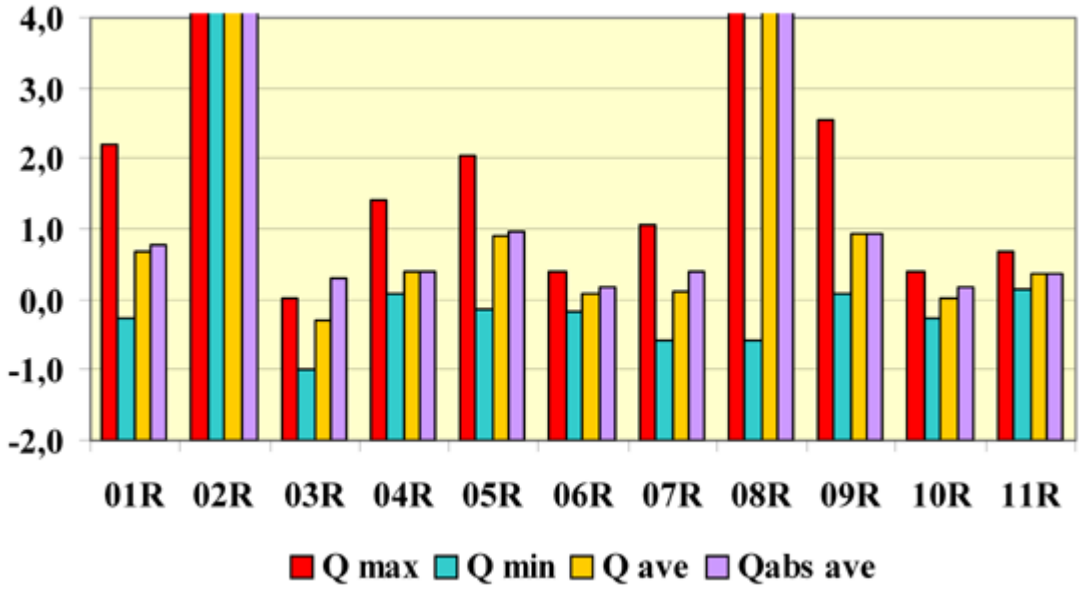


Fig. 1. Q-score of beta emitters in resin

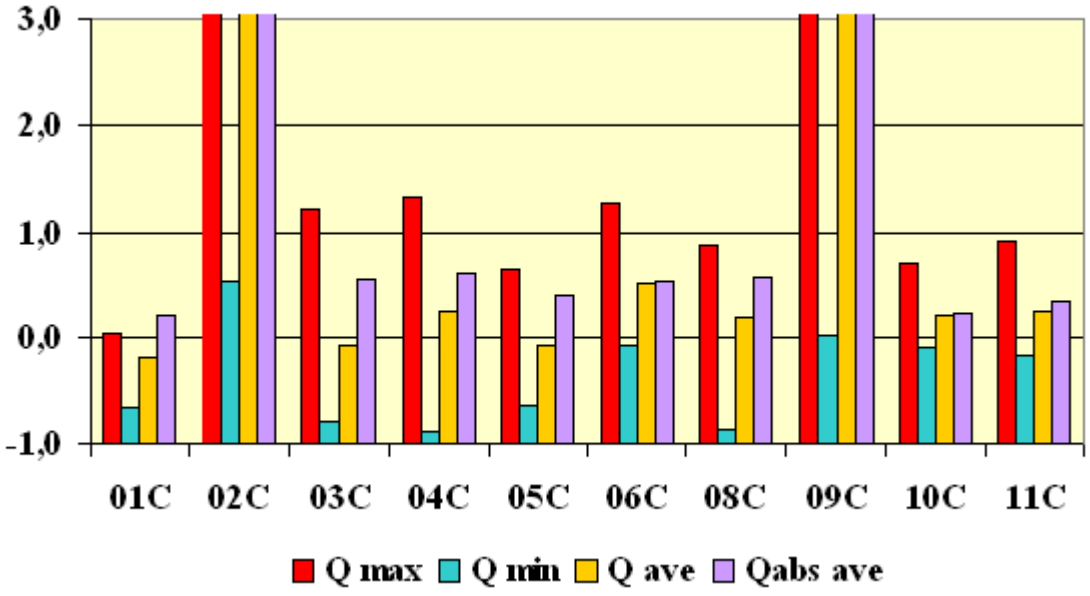


Fig. 2. Q-score of beta emitters in concentrate

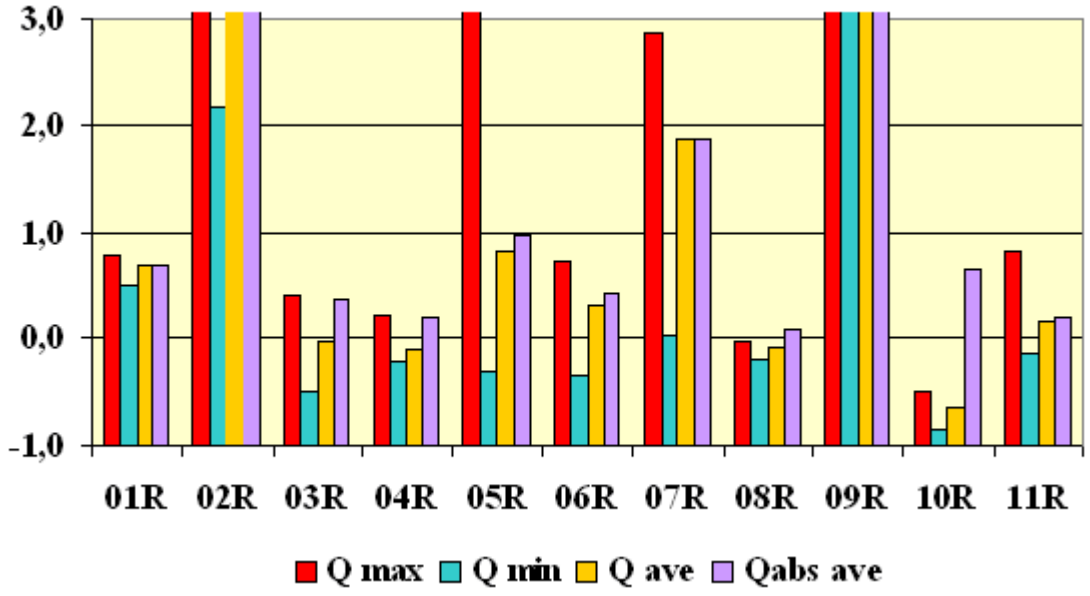


Fig. 3. Q-score of alpha emitters in resin

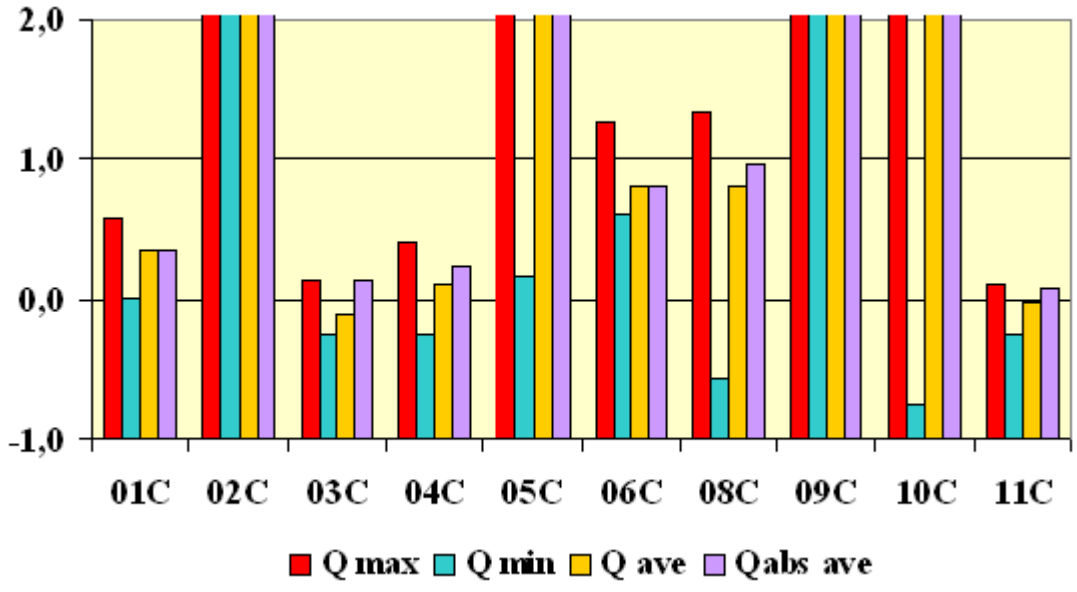


Fig. 4. Q-score of alpha emitters in concentrate

					Dropped							
	Sample	Data Report.	Evaluated	MDA	MDA	M/V	S	A1	A2	A3	NS	Average
KEY CODE-1	RESIN	5	5	0	0	1	2	0	0	3	0	A2
KEY CODE-2	RESIN	6	5	1	0	6	0	0	0	1	4	NS
KEY CODE-3	RESIN	4	4	0	0	1	3	0	0	0	1	A1
KEY CODE-4	RESIN	7	5	2	0	0	3	0	2	0	0	A1
KEY CODE-5	RESIN	6	4	1	0	2	1	0	2	1	0	A2
KEY CODE-6	RESIN	8	6	2	0	0	5	1	0	0	0	S
KEY CODE-7	RESIN	8	6	4	1	1	5	0	1	0	0	S
KEY CODE-8	RESIN	7	6	0	0	1	2	1	1	0	2	A2
KEY CODE-9	RESIN	5	4	2	0	2	1	1	0	1	1	A2
KEY CODE-10	RESIN	8	6	2	1	0	6	0	0	0	0	S
KEY CODE-11	RESIN	5	5	0	0	0	2	0	2	1	0	A1
TOTAL		69	56	14	2	14	30	3	8	7	8	A1
%				25,0	28,6		53,6	5,4	14,3	12,5	14,3	

Table IV. Evaluation of beta emitters presents in the resin. Summary u-score

					Dropped							
	Sample	Data Report.	Evaluated	MDA	MDA	M/V	S	A1	A2	A3	NS	Average
KEY CODE-1	CONCENTR.	5	5	1	1	0	4	1	0	0	0	S
KEY CODE-2	CONCENTR.	6	5	1	0	6	0	0	0	1	4	NS
KEY CODE-3	CONCENTR.	5	5	0	0	2	2	1	0	0	2	A2
KEY CODE-4	CONCENTR.	7	5	3	1	0	2	0	2	0	1	A2
KEY CODE-5	CONCENTR.	6	4	2	0	0	4	0	0	0	0	S
KEY CODE-6	CONCENTR.	8	6	3	1	1	4	1	1	0	0	S
KEY CODE-8	CONCENTR.	7	6	0	0	1	1	2	1	1	1	A2
KEY CODE-9	CONCENTR.	5	4	2	0	2	1	1	1	0	1	A2
KEY CODE-10	CONCENTR.	8	6	2	0	0	4	2	0	0	0	S
KEY CODE-11	CONCENTR.	5	5	0	0	0	2	0	1	1	1	A2
TOTAL		62	51	14	3	12	24	8	6	3	10	A1
%				27,5	29,4		47,1	15,7	11,8	5,9	19,6	

Table V. Evaluation of beta emitters presents in the concentrate. Summary u-score

					Dropped							
	Sample	Data Report.	Evaluated	MDA	MDA	M/V	S	A1	A2	A3	NS	Average
KEY CODE-1	RESIN	6	4	2	0	2	3	0	0	0	1	A1
KEY CODE-2	RESIN	6	4	6	1	3	0	0	0	0	4	NS
KEY CODE-3	RESIN	7	5	2	0	0	4	0	1	0	0	S
KEY CODE-4	RESIN	7	5	2	0	0	4	1	0	0	0	S
KEY CODE-5	RESIN	7	5	4	1	1	1	0	3	0	1	A2
KEY CODE-6	RESIN	5	5	1	0	0	4	0	1	0	0	S
KEY CODE-7	RESIN	7	5	2	1	4	2	0	1	2	0	A2
KEY CODE-8	RESIN	7	5	0	0	0	4	1	0	0	0	S
KEY CODE-9	RESIN	5	3	5	1	2	0	0	0	0	3	NS
KEY CODE-10	RESIN	7	5	0	0	2	4	0	1	0	0	S
KEY CODE-11	RESIN	7	5	2	0	0	4	0	1	0	0	S
TOTAL		71	51	26	4	14	30	2	8	2	9	A1
%				51,0	35,3		58,8	3,9	15,7	3,9	17,6	

Table VI. Evaluation of alpha emitters presents in the resin. Summary u-score

	Sample	Data Report.	Evaluated	MDA	Dropped MDA	Dropped M/V	S	A1	A2	A3	NS	Average
KEY CODE-1	CONCENTR.	6	6	0	0	0	6	0	0	0	0	S
KEY CODE-2	CONCENTR.	6	6	5	0	6	0	0	0	0	6	NS
KEY CODE-3	CONCENTR.	7	7	1	0	0	6	0	1	0	0	S
KEY CODE-4	CONCENTR.	7	7	3	2	0	3	2	2	0	0	A1
KEY CODE-5	CONCENTR.	7	7	1	1	2	0	3	1	1	2	A2
KEY CODE-6	CONCENTR.	5	5	1	0	1	5	0	0	0	0	S
KEY CODE-8	CONCENTR.	7	7	0	0	1	1	0	1	1	4	A3
KEY CODE-9	CONCENTR.	5	5	5	3	2	0	0	0	0	5	NS
KEY CODE-10	CONCENTR.	7	7	0	0	2	6	0	0	0	1	A1
KEY CODE-11	CONCENTR.	7	7	1	0	0	7	0	0	0	0	S
TOTAL		64	64	17	6	14	34	5	5	2	18	A2
%				26,6	31,3		53,1	7,8	7,8	3,1	28,1	

Table VII. Evaluation of alpha emitters presents in the concentrate. Summary u-score

An overview of the beta and alpha emitters' evaluation is given here in order to put in context the details of the different labs and procedures responsible for the determination of important nuclides in the two matrices. A more detailed statistical evaluation report leading to the results hereafter has been produced.

2.5.2.1 Summary of Beta emitters evaluation

Pure beta and beta-gamma emitting nuclides determinations submitted lead to the calculation of 131 weighted average values from two samples (C and R) and eight nuclides.
Because ^{99}Tc and ^{129}I are in a concentration lower than the detection limits of the procedures applied by the labs, 107 results were used for the proficiency test (81%) from which 10 of the data managed are MDA results treated as up to the detection limit data for evaluation.

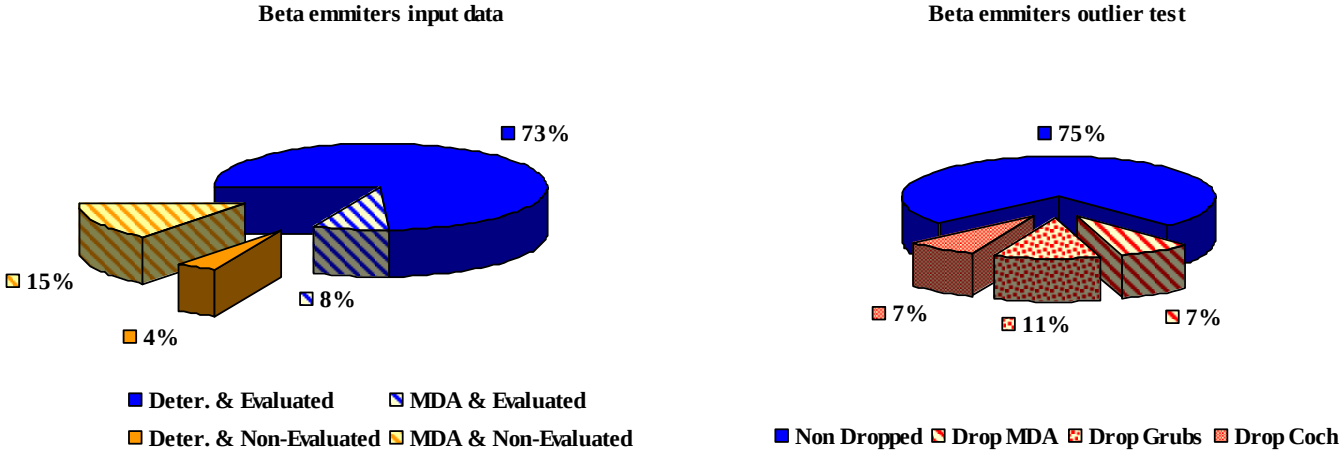


Fig. 5. Input Data and outlier summary for beta emitters evaluation

Outliers test dropped from the reference value calculation were 28 weighted averages (25% of valid input data): 8 due to MDA reporting, 12 by inconsistent weighted average with regards to the others and 8 by high variance in the data submitted by each lab. (Figure 5).

Qualification of beta emitters in the resin sample by u-score gives a 73% total of good results from the experts' labs: satisfactory (54%), acceptable at level 1(5%) and acceptable at level 2 (14%) values. The same percentage (74%) with an accuracy lower than 50% with regard to the reference value (43% lower than 20% deviation) is observed in the Q-score evaluation in the resin sample such as is plotted in figure 6.

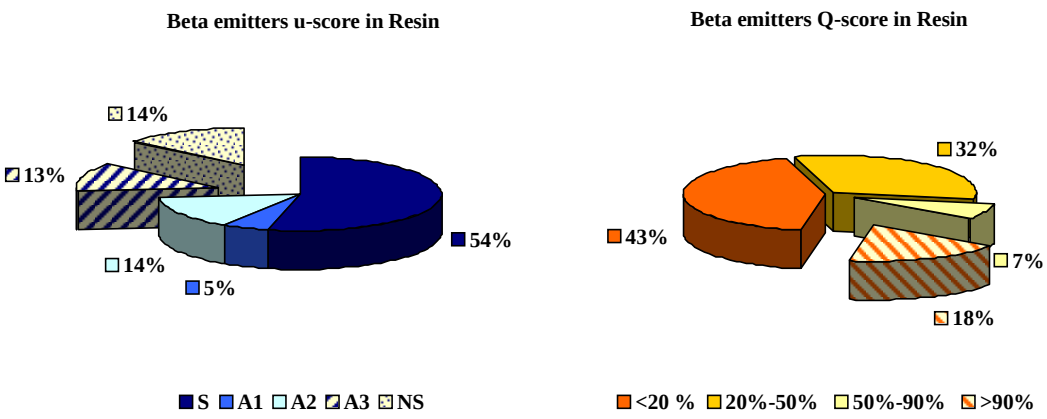


Fig. 6 Beta emitters evaluation in resin sample

Beta emitters in the concentrate sample by u-score shows a 74% total of good results from the experts labs: satisfactory (46%), acceptable at level 1(16%) and acceptable at level 2 (12%) values. A lower ratio (53%) with an accuracy lower than 50% with regard to the reference value (33% lower than 20% deviation) is observed in the Q-score evaluation in the concentrate sample as plotted in figure 7.

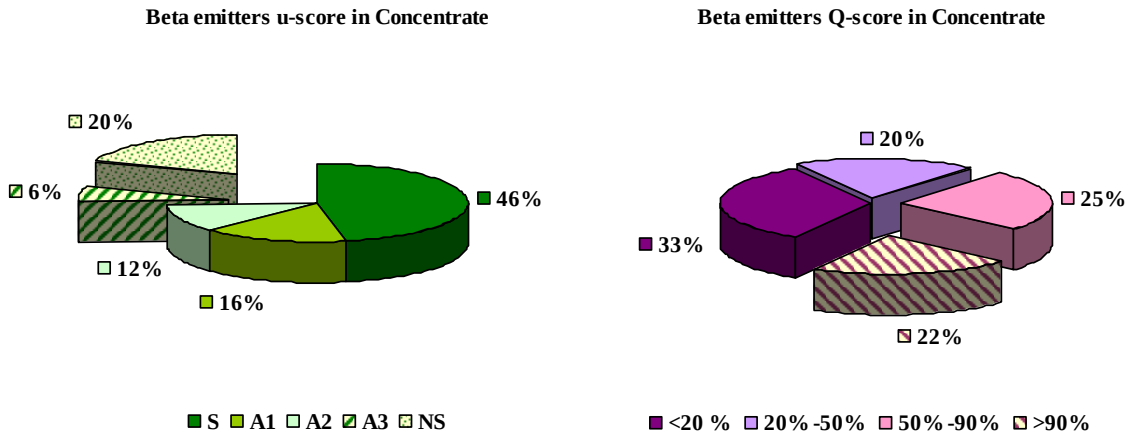


Fig. 7 Beta emitters evaluation in concentrate sample

The evaluation by lab of u-score test is summarised in figure 8 where we find the frequency pile-up distribution per lab. Excellent results in u-score are observed for CN1, CN3, CN6, CN7 and CN10 (>60% of submitted results quoted satisfactory or acceptable at level 1). Very good results for CN4 and CN5 with more than 85% of results quoted acceptable at level 2 or satisfactory. Labs with good results are CN8, CN9 and CN11 (>60% of data better than acceptable at level 2). Only one lab CN2 has no results better than acceptable at level 3.

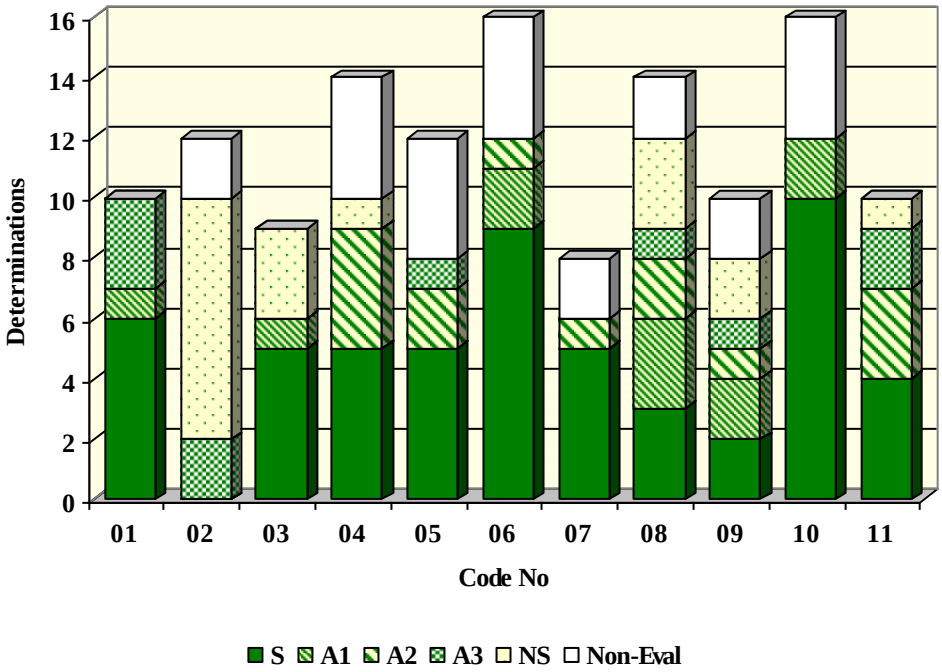


Fig. 8 Beta emitters u-score evaluation per Lab

Evaluation results per lab in accuracy terms are plotted as Q-score qualification in figure 9. Labs CN1, CN3, CN6, CN7 and CN10 present an accuracy lower than 20% of the reference value in more than 55% of the evaluated nuclides submitted. Labs CN4, CN5 give this accuracy level for more than 35% of results. CN8, CN9 and CN11 give an accuracy lower than 50% in a ratio of the submitted results higher than 50%. CN2 presents an accuracy level higher than 90% in more than 95% of the results submitted.

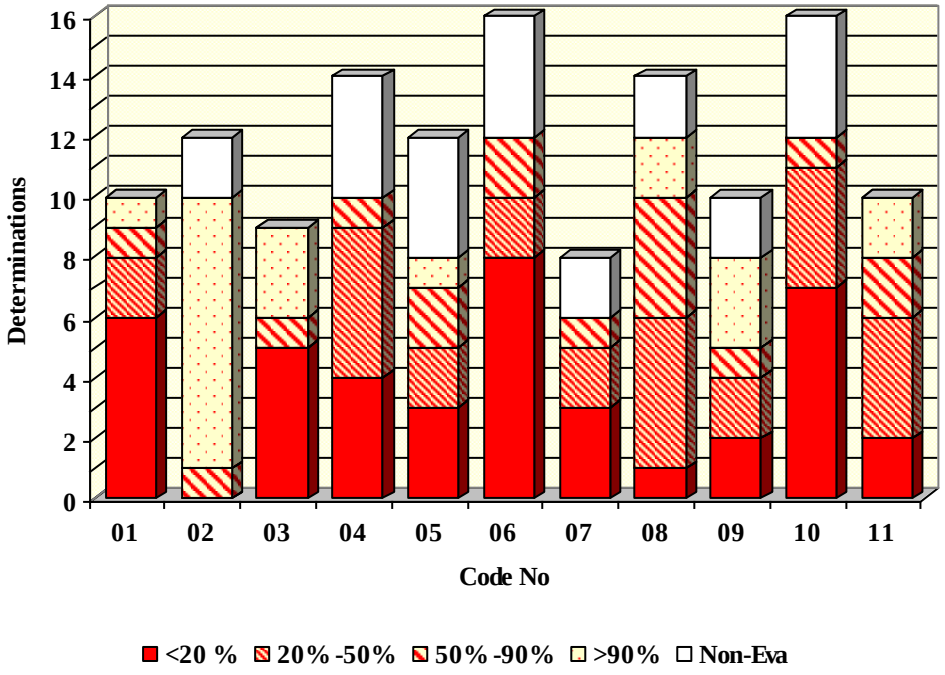


Fig. 9 Beta emitters Q-score evaluation per Lab

Resin sample evaluation shows better results than the concentrate sample with both u-score and Q-score. This behaviour is attributable to the concentrate sample in-homogeneity because several phases can be found in any aliquot and a homogeneous and representative portion is not easy to take.

2.5.2.2. Summary of Alpha emitters evaluation

Calculations of 138 weighted average values were needed for the evaluation of alpha emitter nuclides determinations submitted from 11 labs, two samples (C and R) and seven nuclides.
Reference value of ^{234}U and ^{238}U in the resin sample was not possible to calculate due to their concentration, which did not allow a determination up to detection limits in most of the procedures applied. So 118 results were used for the proficiency test (85%) from which 30 data managed are MDA results treated as up to the detection limit data only for evaluation purposes.

Outliers test dropped from the reference value calculation were 37 weighted averages (31% of valid input data): 13 due to MDA reporting, 14 by Grubbs test and 8 by Cochran test (Figure 10).

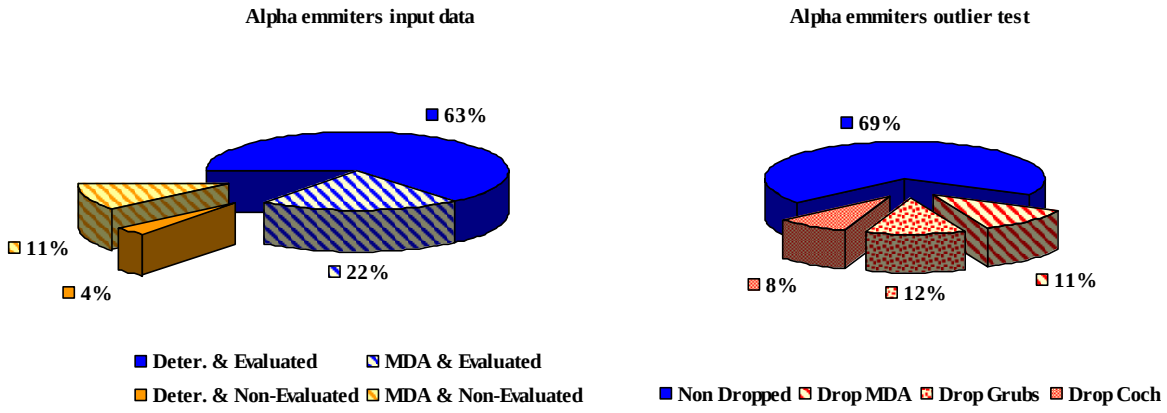


Fig. 10 Input Data and outlier summary for alpha emitters evaluation

Qualification of alpha emitters in the resin sample by u-score gives a 77% total of good results from the expert labs: satisfactory (60%), acceptable at level 1(4%) and acceptable at level 2 (13%) values. A lower percentage (58%) with an accuracy lower than 50% with regards to the reference value (35% lower than 20% deviation) is observed in the Q-score evaluation in the resin sample such as is plotted in figure 11.

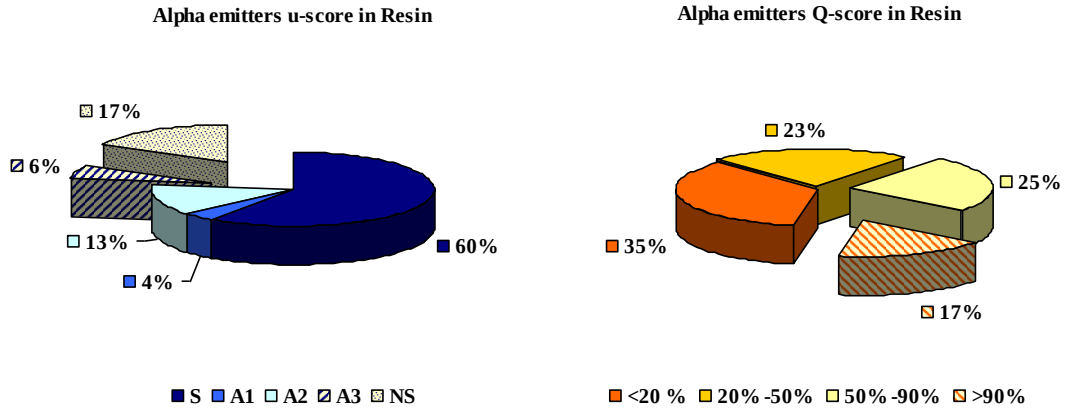


Fig. 11 Alpha emitters evaluation in resin sample

The difference between both tests could be due to the low concentration of alpha-emitting nuclides in the samples. This gives more inaccurate values but a higher uncertainty because the results are closer to the MDA in the different procedures. This fact quoted a good value of u-score with a worse value of activity regarding to the reference value.

Alpha emitters in the concentrate sample by u-score shows a 70% total of good results from the experts labs: satisfactory (54%), acceptable at level 1(8%) and acceptable at level 2 (8%) values. A lower ratio (49%) with an accuracy lower than 50% with regards to the reference value (26% lower than 20% deviation) is observed in the Q-score evaluation in the concentrate sample as is plotted in figure 12.

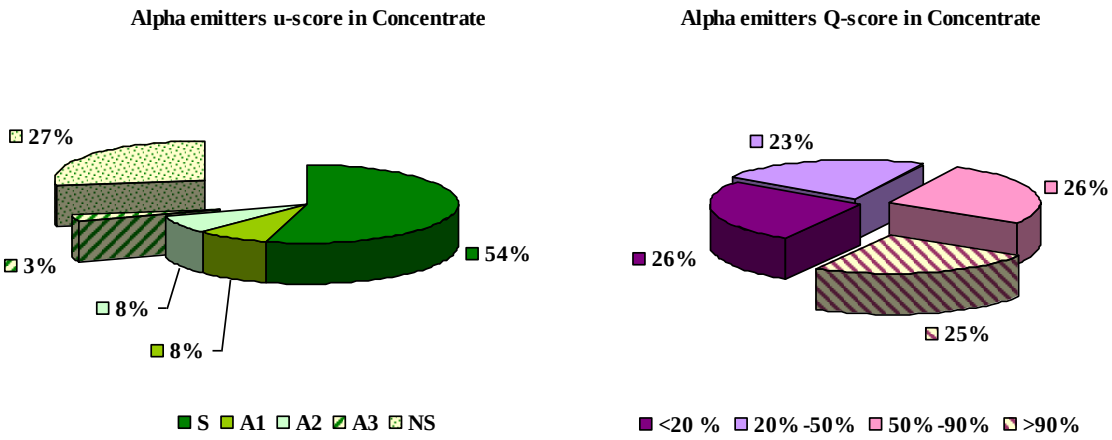


Fig. 12 Alpha emitters evaluation in concentrate sample

The evaluation by lab of u-score test is summarised in figure 13 where we find the frequency pile-up distribution per lab. Excellent results in u-score are observed for CN1, CN3, CN4, CN6, CN10 and CN11 (>80% of submitted results quoted satisfactory or acceptable at level 1). Very good results for CN5, CN7 and CN8 with more than 55% of results quoted acceptable at level 2 or satisfactory and 2 labs CN2 and CN9 whose results are non-satisfactory for all alpha emitting nuclides determination.

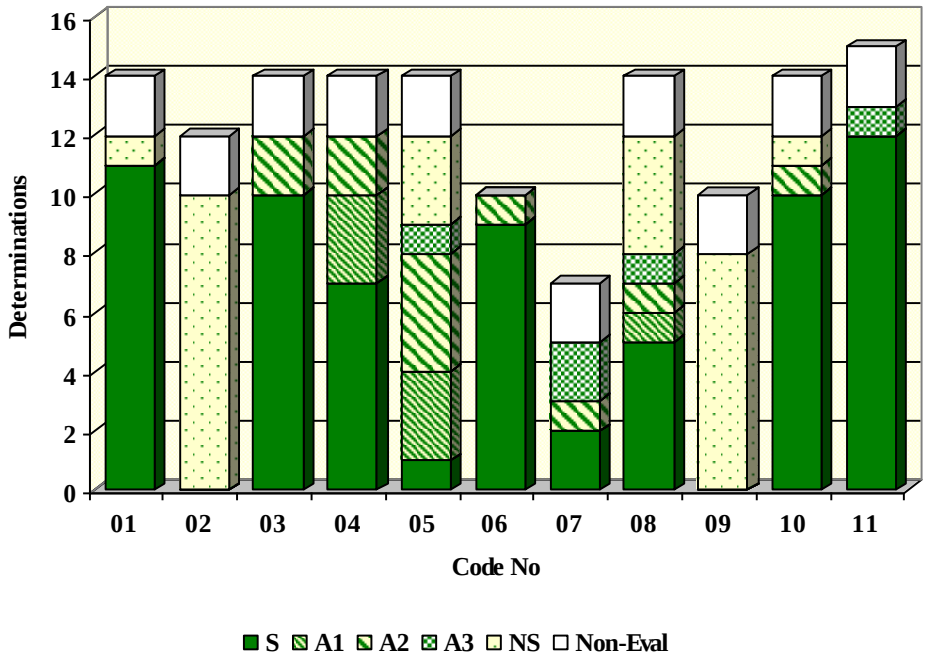


Fig. 13 Alpha emitters u-score evaluation per Lab

Evaluation results per lab in accuracy terms are plotted as Q-score qualification in figure 14. Labs CN3, CN4, CN7, CN8 and CN11 present an accuracy lower than 20% of the reference value in more than 50% of the evaluated nuclides submitted. Lab CN5 gives this accuracy level for more than 30% of results. CN1, CN6 and CN10 present an accuracy lower than 50% for more than 40% of the data (20% for CN10). CN2 and CN9 present an accuracy level higher than 90% in all results submitted.

The apparent inconsistency between results obtained by u-score and Q-score could be due to the activity level of alpha emitting nuclides in both samples which increase the uncertainty of the weighted average and for this reason it is possible to find a good quotation by u-score and, at the same time, a bad quotation by Q-score. As for the beta emitters the resin sample evaluation shows better results than for the concentrate sample with both u-score and Q-score.

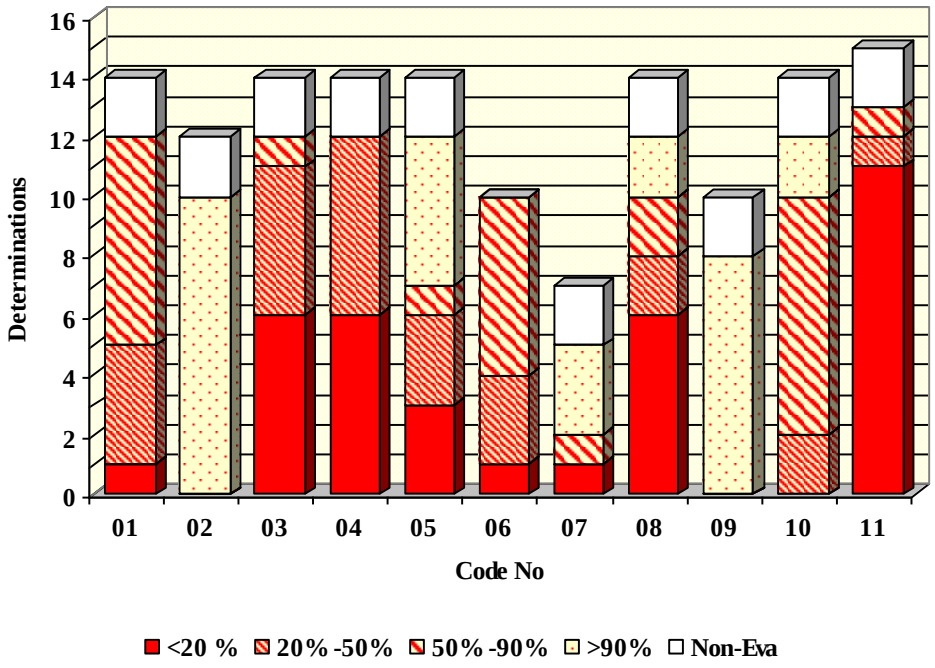


Fig. 14 Alpha emitters Q-score evaluation per Lab

This behaviour may be attributed to the in-homogeneity of the concentrate sample. Different phases can be found in any aliquot and it is not easy to take a homogeneous and representative portion for analyses.

3. WORK PACKAGE 6. CONCLUSIONS

3.1. Individual laboratories' conclusions

In order to preserve anonymity, the order of presentations here is not the same as the previous sections, where laboratory names have been given.

CODE NUMBER 1

Tritium: The use of a simple distillation technique without any pre-treatment for the tritium analysis of the concentrate sample resulted in a satisfactory result according to the statistical evaluation. The applied method should minimise the risk for contamination or losses.

For the resin sample, a higher value is reported than for the majority of the partners. The reason for this may be a difference in the interstitial liquid in the resin at the time of analyses. In the past, experiments have shown that all tritium in the resin is found in the liquid phase. The storage conditions of the sample and/or opening of the sample bottle at different time intervals may lead to evaporation of the liquid and thus loss of tritium in the water vapour. Reporting of the percentage of liquid with regard to the dry resin weight at the time of the analyses was not required. Recalculation of the tritium concentration to Bq per g interstitial liquid might be more convenient for the comparison of the results reported by the laboratories.

Carbon-14: The technique applied for collecting carbon-14 as the CO_2-gas in NaOH traps has the disadvantage that losses can occur. Especially in the case of the concentrate sample, where vigorous acidic conditions were needed for the destruction of the sample, significant amounts of acidic vapours were liberated during the dissolution process. This resulted in an acidification of the 4M NaOH collection traps and loss of carbon-14 during the first dissolution experiments. The concentration of NaOH in the collection traps was increased and the dissolution experiments were repeated. Even so only detection limits could be reported for the concentrate. For the resin samples, this problem did not occur.

Iron-55: The applied separation of iron using ion exchange chromatography is a well-known method. Separation yields were determined with ICP/MS by measuring the iron already present in the sample before and after separation. The measurement method using low energy gamma-spectrometry gives reliable results.

Nickel-63: In accordance with the ^{55}Fe analysis method, the radiochemical measurement of ^{63}Ni is a well-established procedure. The separation yield is monitored by adding a Ni-carrier to the dissolved sample and quantifying the Ni-content before and after separation using ICP/MS. For the concentrate the results are close to the calculated weighted average. For the resin sample, where the same method was applied, a higher ^{63}Ni concentration was found compared to other labs.

Strontium-90: The use of a Sr-spec® extraction resin for the separation of ^{90}Sr has been proven to be a reliable and robust method for the preparation of a measurement source for beta counting. The separation yield could be determined with low uncertainty by relative measurement of the gamma-emitter ^{85}Sr added as a tracer.

Alpha emitters: As the samples were analysed for the presence of actinides in a laboratory dedicated to the analyses of environmental samples, the amount of dissolved sample that could be taken through the analysis procedure was limited and therefore for some of the actinides only low counting statistics could be achieved. As a result the uncertainty on the reported values may be high.

Despite this fact the majority of the results for U, Pu, Am and Cm were accepted as satisfactory. Only exception is ^{238}Pu for the resin where a higher value than most laboratories was reported. No explanation can be offered for this discrepancy. For ^{242}Cm only detection limits were reported. This short-lived actinide is best detected in fresh nuclear waste. The averaged value for $^{243/244}Cm$ in the resin was rated as significant though the two separate dissolutions that each were analysed in threefold gave different results. This may be due to an inhomogeneous distribution of the curium in the resin or an incomplete recovery of Cm-fraction during the elution from the ion exchange column. For the resin only detection limits for ^{234}U and ^{238}U could be reported.

CODE NUMBER 2

From the analysis of the results that are consistently many orders of magnitude higher than the values reported by the other partners, the following suggestion can be indicated:

The methods used, with some variations, are the same as used by the other partners; as well as the instrumentation, used for counting, represents the qualitative standard, present in chemical and radiochemical European laboratories.

Therefore, we may consider: the cross-contamination in the places of work, “the glove boxes”.

It is considered urgent that we perform decontamination operations of the glove boxes and to repeat some tests made in the INTERLAB project.

CODE NUMBER 3

All radionuclides chosen to be analysed from both resin and evaporate concentrate were mainly successfully analysed. Overall the alpha results were better than the beta results.

Tritium: ^{3}H results of the concentrate were slightly lower than the evaluated average. This is possibly due to the error in pipetting small amounts of the original solution of high viscosity. Also the concentrate had solid material from which tritium perhaps was not totally leached.

Iron-55: ^{55}Fe results of the concentrate were satisfactory. But the results from the resin were clearly different from the evaluated average. The discrepancy may be due to in an incomplete

leaching at the beginning of the procedure or incomplete dissolution in the final step of the procedure. A longer contact time and larger acid volume may improve the procedure. Also, human error cannot be excluded.

Nickel-63: ^{63}Ni results of the resin were satisfactory. But the results from the concentrate were different. The concentrate may have contained nickel compounds that by this method were not dissolved. The use of other destruction methods for this kind of sample could be better. Also the yield determination of nickel and iron from the original sample can be affected by interfering elements.

Stontium-89/90: $^{89/90}$Sr results both from concentrate and resin were good.

Plutonium-241: ^{241}Pu results from the resin were satisfactory. They showed small variation although they were close to the detection limit. In the concentrate sample there was more variation, but the results were the same magnitude as the evaluated average. It is possible that some interfering substance or element is present in small amounts in the samples although the spectra were fine. Longer measuring time or increasing the sample amount could improve the results. Also, due to collapse of the alpha measurement equipment, the older alpha system was used with detectors of high background. In addition the procedure has several steps where accumulation of errors may occur.

Alpha emitters: ^{234}U, ^{238}U, $^{243/244}$Cm, ^{238}Pu and $^{239/240}$Pu results both from the concentrate and the resin were satisfactory. ^{241}Am and ^{242}Cm results from the resin were satisfactory. The results from the concentrate were affected with the lower quality of the measurement equipment. The higher background leads to a higher detection limit. With the new alpha system and longer counting times the results could have been better.

This kind of comparison test gave an opportunity to validate our present day procedures and improve their quality, especially regarding the analysis of beta nuclides. The evaporator concentrate of a multiphase matrix was a challenging experiment since the samples from nuclear industry can be very complex. The used procedures give mainly results sufficiently accurate and precise for the purpose of nuclear industry.

CODE NUMBER 4

Tritium: The results of Tritium show good values that are close to the reference values for both samples.

Carbon-14: We found an MDA for Carbon-14 in the evaporator concentrate. We performed a combustion and it was not possible to incinerate the evaporator concentrate completely. Therefore, it is assumed that the Carbon-14 is still in our residue. A full dissolution of the concentrate was achieved with microwave decomposition. But with our microwave equipment gaseous phases cannot be captured. So we can draw the conclusion that we need for Carbon-14 in evaporator concentrate a new and better method. The "procedure report" offers to us various methods to try and adapt.

Our result for the ion exchange resin lies higher than the reference value. There are two other labs lying in the same order of magnitude. We noticed that these labs performed combustion of the resin, which guarantee in this case a full disintegration. Despite this, the reference value is less than the value of these three laboratories. Due to the statistical evaluation, which takes several factors (e.g. uncertainties) into account, the lower values with the better uncertainties are weighted more.

Iron-55: Our lab was the only one who performed an x-ray measurement with a low energy Ge-detector. The others measured it by LSC. Furthermore, we only dissolved the samples completely by microwave decomposition and measured it without any further separation. All other labs used various kinds of separation methods for Iron-55 that can explain the great discrepancies of the results. Especially in this case it would be interesting to know a “true” value, which is not possible from real waste samples. Nevertheless, our Iron-55 value of the ion exchange resin is in good agreement with the other values using a totally different separation and measurement method. It is difficult for us to find out and explain what happened with the evaporator concentrate sample that delivered a value twice as much as the reference value. A possible explanation is that we calculated a wrong chemical yield, which was about 40 %. For the ion exchange resin it was 80 % and we did perform exactly the same method in both cases. To check this we would have to recapitulate our analysis and therefore, at this moment, it is an assumption.

Nickel-63: The results for the ion exchange resin show very good agreements with the reference value. In contrary, the results of the evaporator concentrate feature a bigger deviation from the reference value. It is possible that this indicates problems with a complete dissolution or problems with drawing a homogenous sample. In the case of the ion exchange resin we can draw the conclusion that the dimethylglyoxime method is an excellent method for the determination of Nickel-63.

Strontium-89 and Strontium-90: The determination of Strontium-89/90 led to good results close to the reference value.

Technetium-99: All laboratories found a minimum detectable activity for ^{99}Tc. So there is no “real” reference value, only one calculated out of the MDAs, and therefore it is counterproductive to draw any conclusions.

Iodine-129: All laboratories found a minimum detectable activity for Iodine-129. So there is no “real” reference value, only one calculated out of the MDAs, and therefore, again it is counterproductive to draw any conclusions.

Actinide isotopes: In general all results for the actinides are very good results although the actinides were only present in small amounts (mBq/g) in the two samples.

CODE NUMBER 5

The matrices of interest that routinely are sent to our installations have not included evaporator concentrates or ion-exchange resins. These were new matrices of interest for us and as such have not been routinely analysed. This may account for any abnormalities in our individual analytical results.

Tritium: Satisfactory results were obtained for both matrices. Lower result obtained for the concentrate relative to the other labs possibly due to the particulate nature of the sample. It was difficult to homogenise to take a representative sample. Some of the ^{3}H could have been bound up in the solids. It was found during the distillation analysis that low boiling point amines are first distilled with the tritiated water as indicated by measuring the pH of the initial distillate. If the first 10ml of the distillate are not discarded then the collected amines will interfere with the tritiated water analysis by liquid scintillation counting (LSC). Some labs may collect all the distillate for measurement and will therefore have impurities present due to the amine fraction.

Carbon-14: Satisfactory results were obtained for the concentrate. Higher result obtained for the resin relative to the other labs possibly due to the destruction technique of the sample. We ensure a complete destruction of the matrix with chromic acid to trap all organic and inorganic carbon as CO_2. Other labs may not have completely converted all the carbon to CO_2 for analysis.

Iron-55: Satisfactory results were obtained for the concentrate. Higher result obtained for the resin relative to the other labs. There is no internal iron yield monitor in the analysis only method efficiency correction by reference standard, so any differences may be due to variable recoveries between replicate analyses.

Technetium-99: Only MDA reported not significantly different from the other labs.

Iodine-129: Mostly MDA values measured. The ^{129}I is measured on a low energy gamma/x-ray HPGe spectrometer. This has low counting efficiencies at the energies measured for ^{129}I which can lead to variable results when compared to analysis by other techniques such as LSC.

Plutonium-241: Satisfactory results were obtained for the concentrate. Higher result obtained for the resin relative to the other labs. The internal ^{242}Pu reference standard used in the analysis contains ^{241}Pu as a natural impurity content but this is corrected for in the analytical calculations. No obvious reason for why the resin results should be higher than the others.

Pu isotopes: ^{238}Pu results OK for both matrices. $^{239/240}Pu$ results OK, slightly higher than the average for the resin but not significantly different. Differences may be due to the low weights of resin initially taken for the leaching and subsequent dilution to 250ml prior to analysis with regard to the low activity levels.

Americium-241: Much higher than the average for the concentrate sample and lower for the resin. There is no obvious reason why the concentrate result should be so much higher. The ^{243}Am tracer used for the method efficiency has a natural ^{241}Am component present as an impurity but this should be accounted for in the background subtraction used with the reagent blank sample analysed at the same time. This would not explain why the resin result was OK. It may be due to an interfering radionuclide with a similar energy to ^{241}Am that follows Am in the method and that is present in the concentrate sample but not in the resin.

Curium-242: MDA reported for the resin. Very high result for the concentrate. This could imply there is an interfering radionuclide present in the concentrate sample but not in the resin. This radionuclide is again following the Am/Cm through the analytical method and is not being separated. ^{242}Cm is not normally an isotope that we look for so we do not know what is interfering at its energy - possibly a ^{212}Bi daughter product from a Thorium radioisotope.

Curium-243/244: Results acceptable for the low activity levels present in the leach solution. ^{243}Am is used as the recovery tracer for both Am and Cm radioisotopes. Experiments have shown with our usual matrices that recoveries are comparable for Am and Cm with both following the same chemistry. This may be slightly different for these two matrices as there may be some slight difference in the recoveries for Am and Cm which would only need to be a few % points different to bias the results.

Uranium-234: MDA for resin. Higher for the concentrate than the average. Again probably due to the very low activity levels being measured and especially with our dilution factors. A larger sample size taken of resin and concentrate initially for the prepared leach would have been useful for the alpha analysis.

Uranium-238: MDA reported.

CODE NUMBER 6

All results, both resin and concentrate, were accepted as significant although in some cases a high uncertainty was reported.

CODE NUMBER 7

The results are good in general, even though some difficulties have been encountered in terms of reproducibility and accuracy.

Tritium: The data could not be exploited since all the samples were dried.

Carbon-14: It has to be noted that we got in fact two sets of results for the two sample aliquots, and that the second one is very close to the reference value.

Technetium-99 and Iodine-129: It should be interesting to emphasise that the use of ICP-MS for the determination of these nuclides allowed us to reach very low detection limits.

Alpha emitters: It appears that our results for Am and Pu isotopes are systematically higher than the other ones. It is considered that it is very likely that this difference comes from a contamination during the dissolution stage.

Uranium isotopes: The dissolution has been carried out on specific aliquots and very low activity levels could be measured using ICP-MS.

CODE NUMBER 8

It must be pointed out how important it is to take aliquots of the homogenised sample materials for quantitative digestion. Volatile radionuclides and radionuclide compounds like ^{3}H (as H_2O) should be prepared at first, immediately after opening the sample material containment the first time. In case of adding tracer nuclides as internal standards for determination of the chemical yield, care must be taken to get radiochemical equilibrium. In the same manner, attention must be paid when working with carrier compounds and their use for internal chemical yield standards.

CODE NUMBER 9

Very specific analyses are carried out by external labs. Up to now we do not have the knowledge for performing some extraction procedures, which are available for the analysis of individual nuclides, as there is also only a rather limited need to make such measurements.

Beta emitters: The pure beta-emitters have been measured exclusively by beta spectrometry. This means that, also measured were the activity of all other beta-emitters, which are situated in the same region of the beta-spectrum, and that the result of the analysis must in fact be considered as a maximum for the isotopic activity that had to be determined.

The results for ^{3}H, ^{55}Fe and ^{63}Ni, where we were able to give measured values for the activities, are quite good, especially taking into account the limitations of our lab.

Alpha emitters: As we are not able to measure such low level of alpha-activities for specific actinides, we have taken the measured value of the total alpha-activity as a detection limit for the isotopic activity of the different alpha-emitters. It is evident that this total activity is a maximum for the activity of each alpha-emitter, which can be much higher than the real isotopic activity of that nuclide.

CODE NUMBER 10

According to the weighted average calculated, the separation procedures and measurement methods both for alpha and beta emitting radionuclides have given reliable results. For alpha emitters however, although satisfactory results are obtained, these values present a high uncertainty due to the low activity concentration present in the samples.

On the other hand, with respect to the values obtained for ^{234}U and ^{238}U, it must be indicated that once the evaluation was performed and after observing the big difference between the weighted average and our results, the procedure was checked. Finally, we realised that the tracer (^{232}U) used for determining the chemical yield was contaminated with ^{234}U and ^{238}U.

CODE NUMBER 11

All results from both resin and concentrate were accepted as significant although in some cases a high uncertainty was reported.

3.2. General conclusions from the analytical exercise

In this point the general conclusions corresponding to each radionuclide are mentioned.

Tritium: Two different sample pre-treatment methods can be distinguished between the laboratories. A first method using distillation and a second method using combustion at elevated temperatures.

In the concentrate, sample values for tritium were reported ranging from 1.64 to 27.7 Bq/mL.

In the resin sample, this range for all results is much smaller with a minimum of 18.8 and maximum of 35.7 Bq/g dry resin. This indicates that the analysis of the complex matrix of the concentrate for the presence of tritium is less straightforward than for the resin.

No important difference in the results between both procedures can be demonstrated.

Carbon-14: Partly due to the wide range of reported results (414 to 3200 Bq/g resin) and partly due to the limited number of participating laboratories from a statistical viewpoint, care should be taken in drawing conclusions from the statistical evaluation.

The wide range of reported results may be due to the pH stability of carbon-14 in the sample conditions or not all the carbon (organic and inorganic) has been converted to CO_2 for analysis.

Iron-55: The results reported by all partners for the ^{55}Fe analysis in the concentrate fall within a range of 226 to 735 Bq/g. Seven of the ten laboratories that participated in this test, scored satisfactory to acceptable in a range of 226 to 425. The laboratories that were defined as outliers all reported higher amounts of ^{55}Fe.

For the resin again the width of the range of reported results was comparable: 3390 to 9340 Bq/g.

Nickel-63: All laboratories worked with a precipitation with dimethylglyoxime. The results for the ion exchange resin show very good agreement for nearly all measured values with the reference value.

For the evaporator concentrate, the considerable difference between the measured activities by the laboratories can be the result of problems with a complete dissolution of the sample or problems withdrawing a homogeneous sample.

Strontium-90: For both the concentrate and the resin 78% of all laboratories reported results in a narrow range. And this despite the many different analyses procedures that are applied by the laboratories: precipitation, liquid-liquid extraction and extraction chromatography.

Technetium-99: The concentration of technetium was much higher in the resin sample then in the concentrate but most of the laboratories found detection limits. Not enough results were obtained to calculate useful statistics.

Iodine-129: Only a few partners detected iodine-129 in the samples. Mostly detection limits were reported. Not enough data were reported for useful statistics.

Plutonium-241: In general the results for the resin are very good results. Regarding the concentrate it is difficult to draw any conclusion.

Actinides isotopes: In general all results for the actinides are very good. The laboratories could prove that all different kind of separation method like precipitation, using ion exchange resins, extraction chromatography and liquid-liquid extraction led to the good values although the actinides were only present in small amounts (mBq/g or mBq/mL) in the two samples.

U-234 and Uranium-238: For the resin sample, all the labs have reported detection limits. In the concentrate very low activity level have been detected. A larger sample size taken of resin and concentrate initially for the prepared leach would have been useful for the alpha analysis.

3.3. Final conclusions

The destructive measurement of the different alpha, beta and gamma emitting-radionuclides present in the radioactive wastes arise from Nuclear Power Plants, implies a complex process starting with the sampling up to obtaining the final result. It includes several steps such as mineralisation 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. Each of these steps introduces an additional uncertainty to the analysis process and therefore a thorough understanding and control of each step is imperative.

The high degree of difficulty in obtaining an accurate chemical measurement of the critical nuclides in a radioactive concentrate and resin waste form originating from the primary waste of a nuclear plant has been proven once more by the interlaboratory exercise. Although the participating laboratories have routine methods at their disposal, the composition of the wastes can vary from one reactor to another and even one batch to another. As a result in some cases small modifications have to be made to dissolution and separation procedures to meet the requirements of the measurement technique. As a consequence any alteration to a method will add an additional uncertainty to the final analysis result.

According to the results presented in this paper, laboratories that score well for the concentrate do not necessarily do so for the resin. Besides, in general the results of the evaporator concentrate are worse than the results of the ion exchange resin. Of course both matrices are very different. Dissolution of a concentrate is not always easy to do. The composition can be very different from one batch to another. It often contains high concentrations of salt and metallic constituents that can interfere with the separation. It may be heterogeneous and have viscous characteristics, making it difficult to take representative subsamples. Despite the correct approach that has been taken towards the sampling to prepare a test sample for each partner, it still may well be that small hotspots are present in the sample. In the case where small quantities of sample are dissolved for an analysis, this may become more important. Therefore for this type of samples, one should not go beneath a recommended sample size.
Finally, as a summary, it is thought that the procedures used give results sufficiently accurate and precise for the purpose of the nuclear industry.

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