Reporting Form

CuNo 3588

Proficiency Test: Determination of Anthropogenic γ-emitting Radionuclides in a Mineral Matrix

Sample requested by:

Customer No.: 3588
PROF.DR. EVANGELOS MARAZIOTIS
LAB. OF NUCLEAR TECHNOLOGY
UNIVERSITY OF PATRAS
GR-26500 PATRAS
GREECE

Tel.: + 30 61 997 241
Fax.: +30 61 997 241
E-mail: maraziot@mech.upatras.gr

Name of Analyst: Christos Ath. Maramathas
Name of Supervisor: Evangelos A. Maraziotis
Laboratory / Division: Nuclear Technology Lab
Organisation / Institute: University of Patras
Street / Number: Dept: Mechanical Engineering
City / Postal Code: Univ.Campus/Patras-Rion 26500
Country: Greece
Tel.: +30610997241
Fax.: +30610997241
E-mail: maraziot@mech.upatras.gr

Signature:
Date: 15-03-2002
Collaborators:

For IAEA use only!

Customer Number

Customer Number # 1
\# 2
\# 3
\# 4
\# 5
\# 6
\# 7
\# 9

Please send back to:
Mr. Zbigniew Radecki
Analytical Quality Control Services,
International Atomic Energy Agency,
P.O. Box 100, A-1400, Vienna, Austria.
Tel.: + 43 1 2600 28226
Fax.: + 43 1 2600 28222
E-mail: AQCS@IAEA.ORG

Reporting Form

CuNo 3588

Proficiency Test: Determination of Anthropogenic γ-emitting Radionuclides in a Mineral Matrix

	Spiked coal fly ash sample (Code 017A)							
	Reference date: 2002-01-01, 00:00 GMT		Combined standard uncertainty [±1σ]*	Limit of Detection	Background		Counting time	Date and time of beginning of measurement YYYY-MM-DD/HH:MM
Radionuclide	Activity	Unit	[Bq/kg]	[Bq/kg]	[Bq]	[±1 σ]	[s]	
Mn - 54	40.415	Bq/kg	0.997	0.771	0.22500	0.00949	200000	2002-03-08/00:00
Co - 57	32.84	Bq/kg	2.11	3.76	2.7364	0.0469	200000	2002-03-08/00:00
Co - 60	121.49	Bq/kg	1.21	0.705	0.2158	0.0102	200000	2002-03-08/00:00
Zn - 65	21.494	Bq/kg	0.620	1.68	0.4406	0.0202	200000	2002-03-08/00:00
Y - 88	36.792	Bq/kg	0.933	0.905	0.2402	0.0105	200000	2002-03-08/00:00
Cd - 109	558.8	Bq/kg	25.5	19.5	20.714	0.244	200000	2002-03-08/00:00
Sb - 125	41.04	Bq/kg	3.69	5.19	2.5084	0.0687	200000	2002-03-08/00:00
Cs - 134	70.00	Bq/kg	1.25	0.900	0.28369	0.00894	200000	2002-03-08/00:00
Cs - 137	152.08	Bq/kg	3.70	0.833	0.2764	0.0100	200000	2002-03-08/00:00
Eu - 152	43.80	Bq/kg	1.79	2.38	11.000	0.184	200000	2002-03-08/00:00
Eu - 155	57.29	Bq/kg	2.62	2.14	1.3464	0.0206	200000	2002-03-08/00:00
Am - 241	40.00	Bq/kg	4.66	2.56	2.9720	0.0372	200000	2002-03-08/00:00
Dry/Wet ratio	99.7526±0.0007	%						

* Combined standard uncertainty is expressed as the square root of the sum of variances of all conceivable sources of uncertainty, evaluated using the law of propagation of uncertainty.

Note: ***Please report all values obtained from measurement and/or calculation, even if the net result is negative. Do not use the expressions or acronyms "less than", "below level of detection", " - " or other unquantified symbols.***

Reporting Form

CuNo 3588

Proficiency Test: Determination of Anthropogenic γ-emitting Radionuclides in a Mineral Matrix

	Standard solution (Code 017B) (Ampoule weight: 5.9891g)							
	Reference date: 2002-01-01, 00:00 GMT		Combined standard uncertainty [±1σ]*	Limit of Detection	Background		Counting time	Date and time of beginning of measurement
Radionuclide	Activity	Unit	[Bq/g]	[Bq/g]	[Bq]	[±1 σ]	[s]	YYYY-MM-DD/HH:MM
Mn - 54	18.481	Bq/g	0.176	0.00850	0.15734	0.00664	200000	2002-02-15/00:00
Co - 57	6.1590	Bq/g	0.0820	0.0420	1.9346	0.0331	200000	2002-02-15/00:00
Co - 60	23.925	Bq/g	0.257	0.0208	0.2247	0.0107	200000	2002-02-15/00:00
Zn - 65	4.2453	Bq/g	0.0622	0.0248	0.4154	0.0191	200000	2002-02-15/00:00
Y - 88	10.1882	Bq/g	0.0892	0.0103	0.17273	0.00755	200000	2002-02-15/00:00
Cd - 109	1.567	Bq/g	0.150	0.366	8.1690	0.0961	200000	2002-02-15/00:00
Cs - 134	11.408	Bq/g	0.104	0.0113	0.22727	0.00716	200000	2002-02-15/00:00
Cs - 137	26.817	Bq/g	0.387	0.00978	0.20822	0.00753	200000	2002-02-15/00:00
Eu - 152	14.0081	Bq/g	0.0741	0.0262	1.6609	0.0278	200000	2002-02-15/00:00
Eu - 155	0.1926	Bq/g	0.0214	0.00952	0.53438	0.00819	200000	2002-02-15/00:00
Am - 241	4.600	Bq/g	0.322	0.00938	0.51829	0.00648	200000	2002-02-15/00:00
-----	-----	Bq/g	-----	-----	-----	-----	-----	-----

* Combined standard uncertainty is expressed as the square root of the sum of variances of all conceivable sources of uncertainty, evaluated using the law of propagation of uncertainty.

Note: ***Please report all values obtained from measurement and/or calculation, even if the net result is negative. Do not use the expressions or acronyms "less than", "below level of detection", " - " or other unquantified symbols.***

Name of analyst: Christos Ath. Maramathas

Information on analytical operations

(If space is insufficient, please make additional copies of these pages).

DILUTION PROCEDURE (for standard solution)

Please provide details of the handling and dilution medium used to prepare of the final source.

Our laboratory uses a standard procedure for liquid solution's γ – radioactivity measurements. The containers which are used for the handling of the samples have a maximum volume capacity of 15.5ml and their structural material consists of acid resistant plastic, that is (γ – ray) transparent. The inner diameter of the containers is about 21.5mm. Due to their airtight closing after the filling, they have the limitation of a single use. Their advantage is that they have a zero radiation background, so they do not increase the measurement's uncertainty. The volume of the sample's solution which is used for our standard measurement procedure is ≅10ml. According to this, in order to maintain this volume, it is necessary the dilution of the main sample into a dilution medium up to the volume of 10ml. The dilution medium that has been used in this particular case was triple distilled water.

Initially it was determined that from the main sample there will be produced four subsamples of volume about 0,5ml. According to this, four blank containers were weighted each one for 20 times. Afterwards, the subsamples were added to the containers, and once again they were weighted each one for 20 times in order to quantify the gross weight. It should be noticed that in both occasions the average mass and the standard deviation were determined (see page 6 of 6 for the evaluation of each subsample's mass uncertainty). The net mass of each subsample derived from the subtraction of the average mass of the container from the average gross mass. The weighting done using an electronic laboratory microbalance (Sartorius/accuracy 1E-04gr). Finally, the dilution medium was added up to the volume of 10ml and then the container was firmly sealed.

The final geometry of the subsamples is cylindrical, with diameter 21.5mm, height 27.5mm and the discoid base of the liquid cylinder, during the measurement, is coaxial to detector's active window at a distance ≅5mm above the detector's active volume. The standard with which accomplished the system's efficiency calibration, had the same cylindrical geometry as the subsamples, contained known activity (with its given uncertainty) of Eu-152 and its measurement, for the calibration procedure, done at the same standard conditions with those used for the measurement of the subsamples. The activity of the calibration standard was comparable with these of the subsamples.

COUNTING METHOD

Please provide details of the counting system and counting geometry used in this exercise.

The γ-radiation that produced by the samples' nuclides was detected with a coaxial HPGe detector, and the signal of γ-spectrum was primarily processed by nuclear electronics (CANBERRA). The final stage of the process was a multichannel analyser (MCA CANBERRA SERIES 35, 4096 channels) interfaced with a 586 PC. The SPECTRAN - AT V4.0 γ – Spectroscopy software (CANBERRA) was used to determine the quality and quantity of the nuclides in the subsamples through pulse-height spectrum process. For the avoidance of high environmental background counting, the active volume of the detector was shielded by 10cm, in width, Pb-made shielding.

Basically, the analysis of a pulse-height spectrum obtained from a γ – ray spectrometer consists of the following steps:

1. Locate peaks of interest in the spectrum
2. Determine the background corrected area and the statistical uncertainty in the area of each peak
3. Identify the nuclides that produced the spectrum
4. Determine the activities of the nuclides of interest, including decay corrections.

Before steps (3) and (4) above can be carried out, the system must be calibrated in order to relate γ – ray energy to pulse height, and nuclide concentrations to measured peak areas. This is accomplished by determining the positions and areas of spectral peaks produced by γ – rays of known energies and intensities, and generating appropriate calibration parameters that may be used in subsequent analyses. For the procedure of calibration are used, for the γ – rays' of known energies and intensities production , suitable calibration standards (containing a known amount of Eu-152). These standards must have the same geometry and matrix' composition with the samples', comparable activities with them and their measurement, through the calibration procedure, must be done at the same standard conditions with those used for the measurement of samples. As well as the liquid solution standard, the coal fly ash standard was in accordance with the above demands.

After the energy calibration, the system is ready for the efficiency calibration. Up to an energy of at least a few MeV, the system's efficiency, E, of HPGe detector as a function of energy may be well represented by simple polynomial functions of *

continued on back page →

*→

$$\text{the form: } \log(E) = \sum_{0}^{n} b_i \cdot [\log(PE)]^i$$

The degree of the polynomial, n, used in the fit depends on the number of calibration points available (for the ten calibration points of Eu-152 used, n=2 for $PE<PE_c$ and n=4 for $PE>PE_c$).

Detection efficiency calibration points are obtained by measuring the areas of well resolved photopeaks produced by γ-rays of known intensities. The absolute system's efficiency at a given energy is determined from:

$$E = \frac{A \cdot e^{[-0.693147 \cdot (T_d/T_{1/2})]}}{T_l \cdot Y \cdot C}$$

where

$C \equiv$ Source's known activity in Bq

See on page 5 of 6 for the definition of the other variables

A weighted least - squares fit is then made to determine the calibration coefficients, b_i, for the two efficiency calibration equations. The values of the b_i coefficients, along with their variances and covariances, are saved in an efficiency calibration file keyed to the detector and geometry numbers for use during analysis.

For the Coal Fly Ash at the measurement's geometry: $\log(E) = -23.4277 + 8.20039 \cdot \log(PE) - 0.827476 \cdot [\log(PE)]^2$

when $0 \leq PE \leq 344.4$keV

and, $\log(E) = -2277.20 + 1368.30 \cdot \log(PE) - 307.529 \cdot [\log(PE)]^2 + 30.6009 \cdot [\log(PE)]^3 - 1.13823 \cdot [\log(PE)]^4$

when $344.4 \leq PE < 2000$keV

For the Standard Solution at the measurement's geometry: $\log(E) = -8.21703 + 2.64976 \cdot \log(PE) - 0.315342 \cdot [\log(PE)]^2$

when $0 \leq PE \leq 344.5$keV

and, $\log(E) = -855.563 + 509.381 \cdot \log(PE) - 113.563 \cdot [\log(PE)]^2 + 11.2018 \cdot [\log(PE)]^3 - 0.413268 \cdot [\log(PE)]^4$

when $344.4 \leq PE < 2000$keV

$PE \equiv$ Photopeak's energy, measured and calculated by the SPECTRAN - AT (from the photopeak's channels at the MCA).

Both in the case of the energy and efficiency calibration, users do not attempt to extrapolate the calibration beyond the energy range of the calibration source used (Eu-152). (To do so will likely result in invalid efficiency values).

As well as the liquid subsamples, the three coal fly ash subsamples was handled in the same containers. The volume of the subsamples which were used for our measurement procedure was ≅15.5ml. Firstly 3 blank containers were weighted each one for 20 times. Afterwards, the subsamples were added to the containers, and the same procedure as the liquid subsamples' weighting procedure was accomplished. The final geometry of the coal fly ash subsamples is cylindrical, with diameter 21.5mm, height 42.8mm and the discoid base of the ashes' cylinder, during the measurement, is coaxial to detector's active window at a distance ≅5mm above the detector's active volume.

All the containers were cleaned intently before their content's γ-spectrum collection, to avoid detector's contamination.

CALCULATIONS

Please provide all formulae used to calculate the activity concentration describing all variables.

All the calculations for the activity concentration, of each nuclide that appeared in each single subsample's measurement, done with the use of SPECTRAN – AT V4.0, γ – Spectroscopy software (for HPGe Detectors), as described below:
After all spectral peaks have been found by the program's routines, their areas determined and nuclides identified, the activities of selected nuclides in the sample as specified in the analysis library are determined. The activity per unit mass, or activity concentration, of a given nuclide, for each single subsample's measurement, is calculated from:

$$I = \frac{C\cdot A\cdot e^{[0.693147\cdot(T_d/T_{1/2})]}}{T_l\cdot Y\cdot E\cdot M}$$

where

$I \equiv$ Decay corrected Activity Concentration in Bq/gr (or Bq/kgr)

$C \equiv$ Correction factor for the decay of short - lived nuclides during data accumulation, given by the equation :

$$C = \lambda\cdot T_c \Big/ [1 - e^{(-\lambda\cdot T_c)}]$$

$\lambda \equiv$ Nuclide's decay constant, $\lambda = \log(2)/T_{1/2}$, ($\lambda$ in sec^{-1})

$T_c \equiv$ Real (or "clock") spectrum collection time, measured by the MCA, $T_c = T_l \big/ (1-F)$, T_c and T_l in sec

$F \equiv$ Fractional ADC's dead time, measured and calculated by the MCA

$T_l \equiv$ Live, spectrum, collection time, preseted by the user in sec (equal to 200000 sec in this particular case)

$T_{1/2} \equiv$ Nuclide's half life, supplied in the analysis library (for every nuclide) by the user in sec

$T_d \equiv$ Decay time (time interval between sample's reference date and measurement's date), supplied by the user as a reference date or time interval in any time unit, and calculated by the program, if it necessary is, in sec

$Y \equiv$ Yield of detected photopeak (different and constant for every nuclide), supplied in the analysis library (for every nuclide) by the user

$M \equiv$ Sample average mass (mass was measured 20 times for every subsample), supplied by the user in gr (or kgr)

$E \equiv$ System's efficiency at the photopeak's energy, calculated through the calibration procedure and supplied by the PC's efficiency file. (Each nuclide's detection efficiency determined as : $\mathrm{Eff}(\%) = 100\cdot E\cdot Y$)

$A \equiv$ Photopeak's net area counts. These areas may be obtained by direct summation of the data under the photopeak and subtraction of the premeasured environmental background as well as the photopeak's underlying background. This is shown at the equation : $A = G - \{[N/(2\cdot n)]\cdot(B_1 + B_2)\} - [(G_{Bkg}\cdot T_l) \big/ T_{l_{Bkg}}]$

$G \equiv$ Gross counts (integral) under the photopeak, calculated by the SPECTRAN - AT

$N \equiv$ Number of channels in the photopeak, calculated by the SPECTRAN - AT

$n \equiv$ Number of bakground channels on each side of the photopeak, preseted by the user equal to 5 channels

$B_1 \equiv$ Sum over n channels below the photopeak, calculated by the SPECTRAN - AT

$B_2 \equiv$ Sum over n channels above the photopeak, calculated by the SPECTRAN - AT

$G_{Bkg} \equiv$ Gross premeasured environmental background counts (sum, at the precollected environmental background spectrum, over N channels above the photopeak's start channel), supplied by the PC's premeasured environmental background file. (Each nuclide's environmental background activity determined as : $I_{Bkg} = \dfrac{G_{Bkg}}{T_{l_{Bkg}}\cdot Y\cdot E}$, the units of I_{Bkg} are Bq)

$T_{l_{Bkg}} \equiv$ Live, environmental background spectrum, collection time; preseted by the user equal to 250000 seconds (in this particular case)

To have better statistics at the final results of our project, multiple "single" measurements of each subsample was undertaken. All the subsamples of a primary sample (017A or 017B), was prepared with the same standard way and measured using the same routine method, under constant settings (conditions) of counting system. Due to previous two propositions, there are *

continued on back page →

* →
multiple measurements of Activity Concentration for every nuclide, for each one of the exercise's samples. (For 017A took place (4 single measurements per subsample) x (3 subsamples) ⇒ 12 measurements of Activity Concentration for every nuclide appeared in the sample. For 017B done (4 single measurements per subsample) x (4 subsamples) ⇒ 16 measurements of Activity Concentration for every nuclide that was found in the sample). From every single measurement and for each nuclide, emerges an Activity Concentration value (I_i), according to previous formulas, that has an uncertainty (U_i) (as show more analytically on page 6 of 6). The final Activity Concentration, of a given nuclide, in the analyzed sample ($I_{\text{nuclide}_{017(\text{A or B})}}$), is calculated manually by the equation below:

$$I_{\text{nuclide}_{017(\text{A or B})}} = \frac{\sum (w_i \cdot I_i)}{\sum w_i}$$

where

$$w_i = \frac{1}{U_i^2}, \begin{cases} i=1,2,3,...,12 \text{ for } 017\text{A} \\ i=1,2,3,...,16 \text{ for } 017\text{B} \end{cases}$$

The quantities w_i called weights of I_i and are reversely proportional to U_i^2. The value of the I_i with the less U_i, contributes more at the determination of the final Activity Concentration value $I_{\text{nuclide}_{017(\text{A or B})}}$.

EVALUATION OF UNCERTAINTY COMPONENTS

When reporting an uncertainty associated with a measurement result, please provide the following information:

1. A list of all components of combined standard uncertainty, identified according to the method used to estimate their numerical values (evaluated by statistical methods or other means).
2. A detailed description of how each component of standard uncertainty was evaluated (including formulae).
3. The formula used for calculation of the combined standard uncertainty.

U_E ≡ System's efficiency uncertainty, calculated through the calibration procedure by Spectran - AT for every energy, and supplied by the PCs efficiency file.

U_A ≡ Uncertainty in the net area A given by the form : $U_A = \sqrt{(\frac{\partial A}{\partial G}\cdot U_G)^2 + (\frac{\partial A}{\partial B_1}\cdot U_{B_1})^2 + (\frac{\partial A}{\partial B_2}\cdot U_{B_2})^2 + (\frac{\partial A}{\partial G_{Bkg}}\cdot U_{G_{Bkg}})^2}$, (1)

It was shown previously that : $A = G - \{[N/(2\cdot n)]\cdot(B_1 + B_2)\} - [(G_{Bkg}\cdot T_1)/T_{1_{Bkg}}] \Rightarrow \left\{\begin{matrix} \frac{\partial A}{\partial G} = 1 \\ \frac{\partial A}{\partial B_1} = -[N/(2\cdot n)] \\ \frac{\partial A}{\partial B_2} = -[N/(2\cdot n)] \\ \frac{\partial A}{\partial G_{Bkg}} = -(T_1/T_{1_{Bkg}}) \end{matrix}\right\}$, (2)

The number of counts observed in any channel of a pulse height spectrum obtained by digitizing the output of a nuclear radiation detector will have an associated statistical uncertainty. Ignoring systematic errors due to temperature drift, etc., the number of counts in a given channel follow a Poisson statistical distribution. The standard deviation in the number of counts in a channel can therefore be estimated on the basis of a single measurement; if N counts are observed, then the estimated standard deviation, σ, is given by : $\sigma = (N)^{1/2}$. Consider now a function, F, that is some combination of the counts in several channels : $F = f(N_1, N_2, ..., N_n)$, where $N_1, N_2, ..., N_n$ are counts in n channels. It is offered without proof that the estimate of the standard deviation of F is given by : $\sigma(F) = \sqrt{[\frac{\partial f}{\partial N_1}\cdot\sigma(N_1)]^2 + [\frac{\partial f}{\partial N_2}\cdot\sigma(N_2)]^2 + ...}$

From this, emanates the following : $\left\{\begin{matrix} U_G = \sqrt{G} \equiv \text{Photopeak's Gross counts uncertainty} \\ U_{B_1} = \sqrt{B_1} \equiv \text{Sum's } B_1 \text{ uncertainty} \\ U_{B_2} = \sqrt{B_2} \equiv \text{Sum's } B_2 \text{ uncertainty} \\ U_{G_{Bkg}} = \sqrt{G_{Bkg}} \equiv G_{Bkg}\text{'s uncertainty} \end{matrix}\right\}$, (3)

$$(1)\overset{(2)}{\underset{(3)}{\Rightarrow}} U_A = \sqrt{G + [(\frac{N}{2\cdot n})^2\cdot B_1] + [(\frac{N}{2\cdot n})^2\cdot B_2] + [(\frac{T_1}{T_{1_{Bkg}}})^2\cdot G_{Bkg}]} \Rightarrow U_A = \sqrt{G + [(\frac{N}{2\cdot n})^2\cdot(B_1 + B_2)] + [(\frac{T_1}{T_{1_{Bkg}}})^2\cdot G_{Bkg}]}$$

continued on back page →

Note:
The term "uncertainty of measurement" is used in these reporting forms as defined by the International Vocabulary of Basic and General Terms in Metrology (VIM), ISO, Geneva, 1993: "Uncertainty of measurement is a parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand" (in this test, the measurand is the activity concentration or activity of the relevant radionuclide).

If participants need more information regarding quantification of uncertainty, please consult the ISO Guide to Expression of Uncertainty in Measurement (ISO, Geneva 1993) and/or EURACHEM/CITAC Guide "Quantifying Uncertainty in Chemical Measurement", 2nd edition 2000. This guide can be accessed via Internet: http://www.eurachem.bam.de/

→

Finally, applies to all subsamples' measurements: $\mathrm{U}_{\mathrm{A}i} = \sqrt{G_i + [(\frac{N_i}{2 \cdot n})^2 \cdot (B_{1i} + B_{2i})] + [(\frac{T_{li}}{T_{l_{Bkg}}})^2 \cdot G_{\mathrm{Bkg}i}]}$, where the symbol (i) is determined by each subsample's measurement code (i.e.: for 017A's subsamples, i = 1, 2, 3, 4, ..., 12).

Uncertainty in the mass measurement

For 017A:

Firstly, 4 subsamples were weighted 20 times each. There is an arithmetic mean of the 20 results (m_{i_n} , i=1, 2, 3, 4 & n=1, 2, 3, ..., 20) for each subsample, that determines its mass (M_{w_i}). The mass' uncertainty is given then by the form:

$$\mathrm{U}_{\mathrm{M}_{\mathrm{w}_i}} = \sqrt{\frac{\sum_{n=1}^{20} (m_{i_n} - M_{w_i})^2}{19}} .$$

These 4 subsamples were dried at 105°C until constant weight and then weighted again 20 times. There is a new arithmetic mean of the 20 results (m_{i_n} , i=1, 2, 3, 4 & n=1, 2, 3, ..., 20) for each subsample, that determines its dry mass (M_{d_i}).

The uncertainty is given now by the form: $\mathrm{U}_{\mathrm{M}_{d_i}} = \sqrt{\frac{\sum_{n=1}^{20} (m_{i_n} - M_{d_i})^2}{19}}$.

The dry/wet ratio r, for the normalization of other mass measurement results to the dry weight, is generated by the:

$\mathrm{r}_{\mathrm{i}} = \frac{M_{d_i}}{M_{w_i}} \cdot 100\%$, i=1, 2, 3, 4 (i.e.: $\mathrm{r}_3 = \frac{M_{d_3}}{M_{w_3}} \cdot 100\% \equiv$ dry/wet ratio for the third subsample), (4)

$$\left.\begin{array}{l} \mathrm{U}_{\mathrm{r}_{\mathrm{i}}} = \sqrt{(\frac{\partial \mathrm{r}_{\mathrm{i}}}{\partial M_{d_i}} \cdot \mathrm{U}_{\mathrm{M}_{d_i}})^2 + (\frac{\partial \mathrm{r}_{\mathrm{i}}}{\partial M_{w_i}} \cdot \mathrm{U}_{\mathrm{M}_{\mathrm{w}_i}})^2} \\ \qquad \frac{\partial \mathrm{r}_{\mathrm{i}}}{\partial M_{d_i}} = \frac{100\%}{M_{w_i}} \\ \qquad \frac{\partial \mathrm{r}_{\mathrm{i}}}{\partial M_{w_i}} = -\frac{M_{d_i}}{M_{w_i}^2} \cdot 100\% \\ \text{form the previous calculations } \mathrm{U}_{\mathrm{M}_{d_i}} = \ldots \\ \qquad \text{and } \mathrm{U}_{\mathrm{M}_{\mathrm{w}_i}} = \ldots \end{array}\right\} \Rightarrow \mathrm{U}_{\mathrm{r}_{\mathrm{i}}} = \ldots \text{ (5)}$$

$$\left.\begin{array}{l} r = \frac{\sum_{i=1}^{4} (w_{r_i} \cdot r_i)}{\sum_{i=1}^{4} w_{r_i}} \\ w_{r_i} = \frac{1}{U_{r_i}^2}, \text{ i=1, 2, 3, 4. } \overset{(5)}{\Rightarrow} w_{r_i} = \ldots \end{array}\right\} \overset{(4)}{\Rightarrow} \text{r} = \ldots \text{ (6)}$$

The dry/wet ratio's uncertainty is given by the form: $\mathrm{U}_{\mathrm{r}} = 1 \Big/ \sqrt{\sum_{i=1}^{4} w_{r_i}}$, (due to uncertainty propagation formulae), (7).

Finally, 3 subsamples were weighted 20 times each to determine their individual (wet) mass. The mass (M_{w_k}) and its uncertainty ($\mathrm{U}_{\mathrm{M}_{\mathrm{w}_k}}$) is produced in the same manner with the previous. These subsamples were measured to determine their anthropogenic γ-emitting Radio-contents. The (normalized) dry mass of each subsample is produced by the following:

continued on next page →

$$\left.\begin{cases} M_{d_k} = \dfrac{\mathrm{r}}{100}\cdot M_{w_k}\ ,\ \mathrm{k}=1,\,2,\,3 \\ M_{w_k} = \ldots \end{cases}\right\} \overset{(6)}{\Rightarrow} M_{d_k} = \ldots\ ,\ \mathrm{k}=1,\,2,\,3 \quad ,\ (8)$$

The respective uncertainty (uncertainty in the mass measurement for 017A) is determined now by the form:

$$\left.\begin{cases} \mathrm{U}_{\mathrm{M}_{d_k}} = \sqrt{\left(\dfrac{\partial M_{d_k}}{\partial r}\cdot U_r\right)^2 + \left(\dfrac{\partial M_{d_k}}{\partial M_{w_k}}\cdot \mathrm{U}_{\mathrm{M}_{w_k}}\right)^2} \\ M_{d_k} = \dfrac{\mathrm{r}}{100}\cdot M_{w_k} \ \Rightarrow \ \begin{Bmatrix} \dfrac{\partial M_{d_k}}{\partial r} = \dfrac{M_{w_k}}{100} \\ \dfrac{\partial M_{d_k}}{\partial M_{w_k}} = \dfrac{\mathrm{r}}{100} \end{Bmatrix} \\ (7) \ \Rightarrow \ U_r = \ldots \\ \mathrm{U}_{\mathrm{M}_{w_k}} = \ldots \\ M_{w_k} = \ldots \\ (6) \ \Rightarrow \ \mathrm{r} = \ldots \end{cases}\right\} \Rightarrow \mathrm{U}_{\mathrm{M}_{d_k}} = \ldots\ ,\ (9)$$

From the previous, it is evident that for the sample 017A and for a specific nuclide, is applied the following for the nuclide's activity concentration and its uncertainty:

$$\mathrm{I}_{\mathrm{i}} = \frac{C\cdot A_i\cdot e^{[0.693147\cdot(T_d/T_{1/2})]}}{T_l\cdot Y\cdot E\cdot M_{d_k}} \ \Rightarrow \ \mathrm{I}_{\mathrm{i}} = \ldots \ ,\ (10)\ ,\ \begin{Bmatrix} \text{for k}=1 \ \Rightarrow \ \text{i}=1,\,2,\,3,\,4 \\ \text{for k}=2 \ \Rightarrow \ \text{i}=5,\,6,\,7,\,8 \\ \text{for k}=3 \ \Rightarrow \ \text{i}=9,\,10,\,11,\,12 \end{Bmatrix}$$

(i.e.: I_7 is the nuclide's activity con/tion value for the 3rd remeasurement of the 2nd subsample). ($\mathrm{I}_1 \simeq \mathrm{I}_2 \simeq \mathrm{I}_3 \simeq \ldots \mathrm{I}_{12}$).

$$\left.\begin{cases} U_i = \sqrt{\left(\dfrac{\partial \mathrm{I}_{\mathrm{i}}}{\partial A_i}\cdot U_{A_i}\right)^2 + \left(\dfrac{\partial \mathrm{I}_{\mathrm{i}}}{\partial E}\cdot U_E\right)^2 + \left(\dfrac{\partial \mathrm{I}_{\mathrm{i}}}{\partial M_{d_k}}\cdot \mathrm{U}_{\mathrm{M}_{d_k}}\right)^2} \\ (10) \ \Rightarrow \ \begin{Bmatrix} \dfrac{\partial \mathrm{I}_{\mathrm{i}}}{\partial A_i} = \dfrac{\mathrm{I}_{\mathrm{i}}}{A_i} \\ \dfrac{\partial \mathrm{I}_{\mathrm{i}}}{\partial E} = -\dfrac{\mathrm{I}_{\mathrm{i}}}{\mathrm{E}} \\ \dfrac{\partial \mathrm{I}_{\mathrm{i}}}{\partial M_{d_k}} = -\dfrac{\mathrm{I}_{\mathrm{i}}}{M_{d_k}} \\ A_i = \ldots \\ E = \ldots \\ (8) \ \Rightarrow \ M_{d_k} = \ldots \end{Bmatrix} \overset{(10)}{\Rightarrow} \begin{Bmatrix} \dfrac{\partial \mathrm{I}_{\mathrm{i}}}{\partial A_i} = \ldots \\ \dfrac{\partial \mathrm{I}_{\mathrm{i}}}{\partial E} = \ldots \\ \dfrac{\partial \mathrm{I}_{\mathrm{i}}}{\partial M_{d_k}} = \ldots \end{Bmatrix} \\ U_{A_i} = \ldots \\ U_E = \ldots \\ (9) \ \Rightarrow \ \mathrm{U}_{\mathrm{M}_{d_k}} = \ldots \end{cases}\right\} \Rightarrow U_i = \ldots\ ,\ (11)\ ,\ \begin{Bmatrix} \text{for k}=1 \ \Rightarrow \ \text{i}=1,\,2,\,3,\,4 \\ \text{for k}=2 \ \Rightarrow \ \text{i}=5,\,6,\,7,\,8 \\ \text{for k}=3 \ \Rightarrow \ \text{i}=9,\,10,\,11,\,12 \end{Bmatrix}$$

(i.e.: U_7 is the nuclide's activity con/tion uncertainty for the 3rd remeasurement of the 2nd subsample).

$$\left.\begin{cases} \mathrm{I}_{\mathrm{nuclide}_{017\mathrm{A}}} = \dfrac{\sum_{i=1}^{12}(w_i\cdot I_i)}{\sum_{i=1}^{12} w_i}\ ,\ \text{where } w_i = \dfrac{1}{U_i^2} \overset{(11)}{\Rightarrow} w_i = \ldots \end{cases}\right\} \overset{(10)}{\Rightarrow} \mathrm{I}_{\mathrm{nuclide}_{017\mathrm{A}}} = \ldots$$

, (nuclide's activity con/tion value for sample 017A). The respective uncertainty is determined now by the form: $\mathrm{U}_{\mathrm{nuclide}_{017\mathrm{A}}} = 1\Big/\sqrt{\sum_{i=1}^{12} w_i} \ \underset{(11)}{\overset{w_i=\frac{1}{U_i^2}}{\Rightarrow}} \ \mathrm{U}_{\mathrm{nuclide}_{017\mathrm{A}}} = \ldots$

continued on back page →

→

For 017B:

Firstly, 4 subsamples were weighted 20 times each. There is an arithmetic mean of the 20 results (m_{k_n} , k=1, 2, 3, 4 & n=1, 2, 3, ..., 20) for each subsample, that determines its mass (M_k). The respective uncertainty (uncertainty in the mass measurement for 017B) is determined now by the form: $U_{M_k} = \sqrt{\dfrac{\sum_{n=1}^{20}(m_{k_n} - M_k)^2}{19}}$.

From the previous, it is evident that for the sample 017B and for a specific nuclide, is applied the following for the nuclide's activity concentration and its uncertainty:

$$I_i = \frac{C\cdot A_i\cdot e^{[0.693147\cdot(T_d/T_{1/2})]}}{T_l\cdot Y\cdot E\cdot M_k} \Rightarrow I_i = \dots \ , \ (12) \ , \left\{\begin{array}{c} \text{for } k=1 \Rightarrow i=1, 2, 3, 4 \\ \text{for } k=2 \Rightarrow i=5, 6, 7, 8 \\ \text{for } k=3 \Rightarrow i=9, 10, 11, 12 \\ \text{for } k=4 \Rightarrow i=13, 14, 15, 16 \end{array}\right\}$$

(i.e.: I_7 is the nuclide's activity con/tion value for the 3rd remeasurement of the 2nd subsample). ($I_1 \simeq I_2 \simeq I_3 \simeq \dots I_{16}$).

$$\left\{\begin{array}{c} U_i = \sqrt{(\frac{\partial I_i}{\partial A_i}\cdot U_{A_i})^2 + (\frac{\partial I_i}{\partial E}\cdot U_E)^2 + (\frac{\partial I_i}{\partial M_k}\cdot U_{M_k})^2} \\ (12) \Rightarrow \left\{\begin{array}{c} \frac{\partial I_i}{\partial A_i} = \frac{I_i}{A_i} \\ \frac{\partial I_i}{\partial E} = -\frac{I_i}{E} \\ \frac{\partial I_i}{\partial M_k} = -\frac{I_i}{M_k} \\ A_i = \dots \\ E = \dots \\ M_k = \dots \end{array}\right\} \overset{(12)}{\Rightarrow} \left\{\begin{array}{c} \frac{\partial I_i}{\partial A_i} = \dots \\ \frac{\partial I_i}{\partial E} = \dots \\ \frac{\partial I_i}{\partial M_k} = \dots \end{array}\right\} \\ U_{A_i} = \dots \\ U_E = \dots \\ U_{M_k} = \dots \end{array}\right\} \Rightarrow U_i = \dots \ , \ (13) \ , \left\{\begin{array}{c} \text{for } k=1 \Rightarrow i=1, 2, 3, 4 \\ \text{for } k=2 \Rightarrow i=5, 6, 7, 8 \\ \text{for } k=3 \Rightarrow i=9, 10, 11, 12 \\ \text{for } k=4 \Rightarrow i=13, 14, 15, 16 \end{array}\right\}$$

(i.e.: U_7 is the nuclide's activity concentration uncertainty for the 3rd remeasurement of the 2nd subsample).

$$\left\{ I_{\text{nuclide}_{017B}} = \frac{\sum_{i=1}^{16}(w_i\cdot I_i)}{\sum_{i=1}^{16} w_i} \text{ , where } w_i = \frac{1}{U_i^2} \overset{(13)}{\Rightarrow} w_i = \dots \right\} \overset{(12)}{\Rightarrow} I_{\text{nuclide}_{017B}} = \dots$$

, (nuclide's activity con/tion value for sample 017B). The respective uncertainty is determined now by the form: $U_{\text{nuclide}_{017B}} = 1\Big/\sqrt{\sum_{i=1}^{16} w_i} \ \underset{(13)}{\overset{w_i=\frac{1}{U_i^2}}{\Rightarrow}} \ U_{\text{nuclide}_{017B}} = \dots$

______________________________***end.***