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Homogeneity of comparison samples for ^{226}Ra, ^{228}Ra, ^{234}U and ^{238}U in mineral waters

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SUMMARY

In anticipation of new European requirements for monitoring radioactivity concentration in drinking water (European Communities, 2011), IRMM organised a comparison on the determination of natural radionuclides in mineral waters among 45 EU laboratories monitoring radioactivity in the environment and foodstuff. This report describes in detail all phases of the homogeneity study performed for the comparison samples. Commercial mineral waters were purchased as their activity concentration of natural radionuclides is higher (and, therefore, more reliably measurable) than in most drinking waters. The homogeneity of the batch of samples to be distributed was demonstrated.

The results are summarised as

- s_{bb} (^{226}Ra) are 3.5 % and 10 % in W1 and W2, respectively;
- s_{bb} (^{228}Ra) are 7.2 % and 5.0 % in W1 and W2, respectively;
- s_{bb} (^{234}U) are 7.0 %, 3.0 % and 2.0 % in W1, W3-50 and W3-51, respectively;
- s_{bb} (^{238}U) are 7.0 %, 4.0 % and 3.0 % in W1, W3-50 and W3-51, respectively.

CONTENTS

1. Introduction

The reference value of a comparison material is assumed to be valid for the whole batch at the level of a subsample with a minimum mass. Therefore, an inhomogeneity in the radionuclide concentration increases the uncertainty of the corresponding reference value, and must be assessed by a dedicated homogeneity study.

2. Homogeneity study

The homogeneity study of the mineral water samples was carried out at IRMM. For this purpose sources were prepared from different sample volumes following the radiochemical separation procedures given in detail in the report EUR 24694 EN, section 3 (Determination of the reference values), paragraph "Sample preparation" (Spasova et al., 2011). In Table 1 the number of samples measured per batch is given.

Table 1: Number of samples measured per batch in the homogeneity study.

Batch	Volume	^{226}Ra	^{234}U + ^{238}U
Water 1 (W1)	0.7 L (Ra meas.) / 3.0 L (U meas.)	20	11
	1.5 L	10	12
Water 2 (W2)	0.7 L (Ra meas.) / 3.0 L (U meas.)	20	10
	1.5 L	14	8
Water 3 (W3)	1.5 L (W3-50 / W3-51)	10	12 / 16
	3.0 L (W3-50 / W3-51)	15	10 / 11

2.1 ^{226}Ra

The procedure given in ISO/FDIS 13528:2005, Annex B (ISO, 2005) was used to check for the homogeneity of the sample batches with respect to ^{226}Ra activity concentration. In order to evaluate the within-samples and between-samples standard deviations, ten bottles of the comparison material selected from the entire batch were taken to prepare two parallel samples of approximately 0.7-0.8 L from each bottle. 0.7 L of sample volume were considered to be a practical minimum sample mass for α-particle spectrometry. Furthermore, sources were prepared using bigger water volume, e.g. 1.5 L and 3.0 L of volume (see Table 1). For the evaluation of the inhomogeneity of W1 the measured activity concentrations of 17 sources were used (instead of 20) as the chemical recovery of three of the sources was too low.

A homogeneity check strictly limited to the principles of the ISO standard requires that the *between-samples standard deviation* $s_s = \sqrt{s_x^2 - (s_w^2 / 2)}$ would contribute less than 10 % to the *standard deviation for proficiency assessment* σ (which is in our evaluation approach replaced by the uncertainty u_c of the reference value) without, however, actually using s_s as contribution to σ or u_c. Here s_x is the standard deviation of sample averages and s_w the within-samples standard deviation. Applying this evaluation renders the result *"homogeneous"* for the ^{226}Ra in batch 2 (W2), but in the case of batch 1 (W1) the result is *"not homogeneous"*. In case the criterion of the ISO standard is not met, the between-bottle standard deviation s_s has to be included in *the standard deviation for the proficiency testing* σ (i.e. the uncertainty u_c of the reference value) which does not include any allowance for the heterogeneity of the samples.

In the case of Water 3 (W3), the ISO procedure could not be followed due to the lower activity concentrations and the need for large sample volumes. The homogeneity of Water 3 with respect to ^{226}Ra was evaluated at a level of 1.5 L and 3.0 L of sample volume.

Beyond the strict application of the ISO standard, the relative quantitative results for s_s can be used as standard uncertainties, describing the (in)homogeneity of the comparison material at the chosen minimum sample intake of 0.7 L of volume and contributing to the combined uncertainty u_c of the reference values (Table 2).

An alternative evaluation uses only the standard deviation s_{bb} of all measured sub-samples, knowing that this results in an overestimation of real physical inhomogeneity, since the reproducibility of the measurements (in particular counting statistics) is not accounted for. The mean value and the standard deviation of the measured activity concentrations are indicated in Figs. 1 and 3 by solid and dashed red lines (Table 3). In relative terms, these standard deviations correspond to s_{bb} *(W1)* = 4.6 % and s_{bb} *(W2)* = 4.0 %, which are consistent with the results given in Table 2 when considering the intrinsic overestimation.

Furthermore, the (in)homogeneity of the radionuclides in the matrix was evaluated by one-way ANOVA statistical tests, using the SoftCRM version 2.0.10 software. The estimate of the between bottle standard deviations (s_{bb}) is given in Table 2. The values of the within bottle standard deviation (s_{wb}) are actually representing the repeatability of the method in case only one sample per bottle was prepared, e.g. for sources prepared from 1.5 L and 3.0 L of sample volume.

The (in)homogeneity values evaluated with the ANOVA test are fully consistent with the results determined following the ISO approach in the cases where two sub-samples per bottle were measured, i.e. for W1 and W2 sources from 0.7 L of volume.

In spite of the good repeatability (s_{wb} = 2.7 %), the results for W2 sources prepared from 1.5 L of water (Fig. 4) show higher variability from one source to another (s_{bb} = 9.7 %). The standard deviation of all measured sources in this case is s_{bb} *(W2)* = 10 %, which is higher than the standard deviation of the 0.7 L samples (s_{bb} = 4.0 %). This variability could be due to a bigger (in)homogeneity) between the two sub-batches indicated as IM-RN-2006-05-001448 and IM-RN-2006-07-001449 (see paragraph "Intercomparison material and sample distribution" in section 1, Introduction, of the report EUR 24694 EN) and the fact that bottles from both sub-batches were used for the preparation of the sources from 1.5 L.

Similar behaviour is observed in batch W3 where also two sub-batches (IM-RN-2006-05-001450 and IM-RN-2006-07-001451) are available (Figs. 5 and 6).

The finally adopted uncertainty contributions u_{bb} due to (in)homogeneity are given in Table 2. The mean activity concentrations and standard deviations for ^{226}Ra in the mineral waters (shown by solid and dashed red lines in the figures) for the different sample volumes are summarised in Table 3.

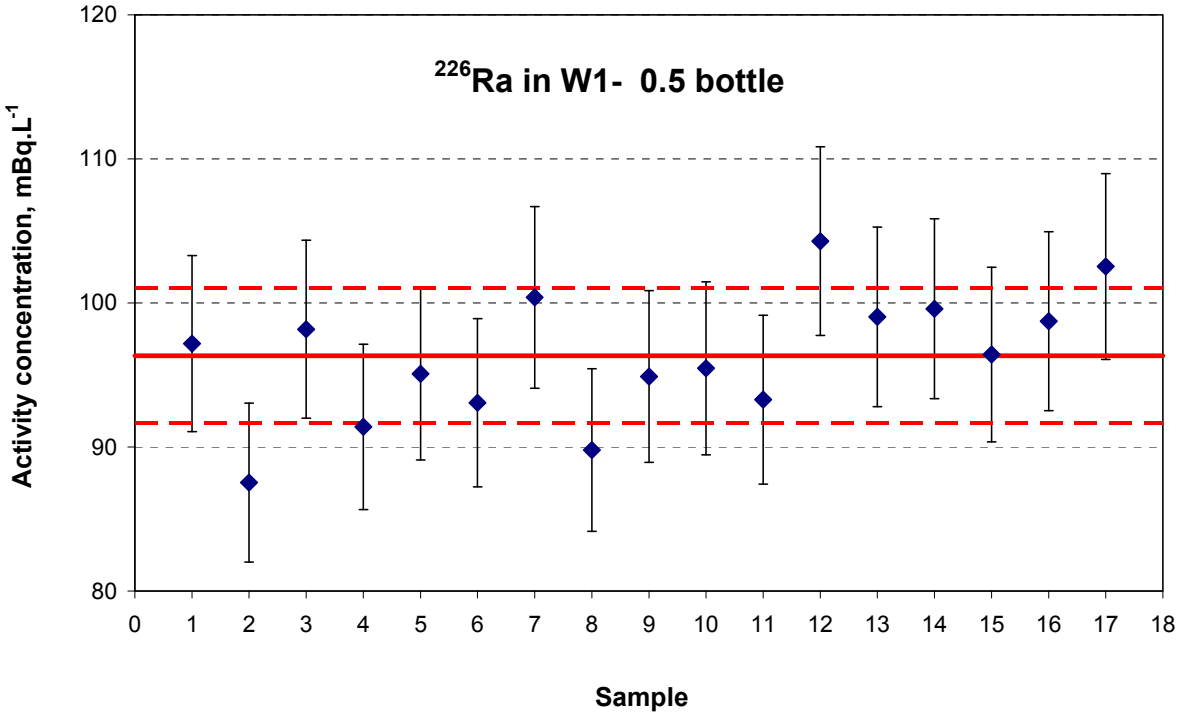

Fig. 1: ^{226}Ra activity concentration in mineral water - Batch 1 (W1 - IM-RN-2006-02-001446). Sources prepared from a volume of 0.7 L to 0.8 L.

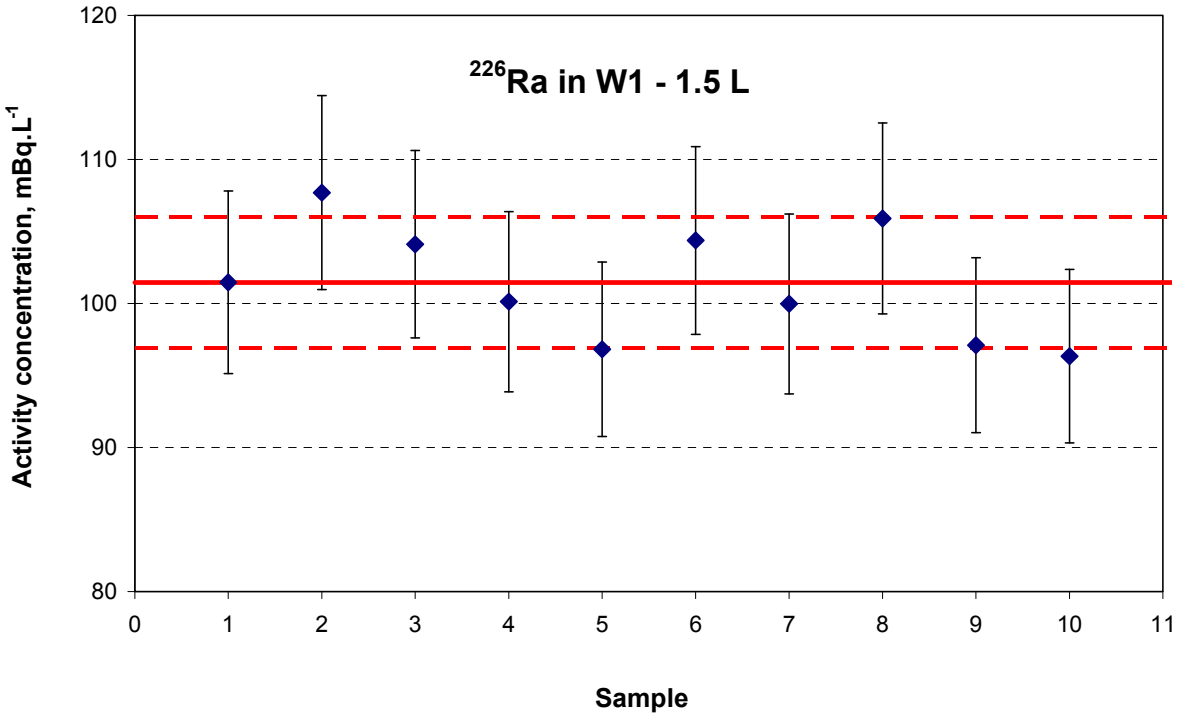

Fig. 2: ^{226}Ra activity concentration in mineral water - Batch 1 (W1 - IM-RN-2006-02-001446). Sources prepared from a volume of 1.5 L.

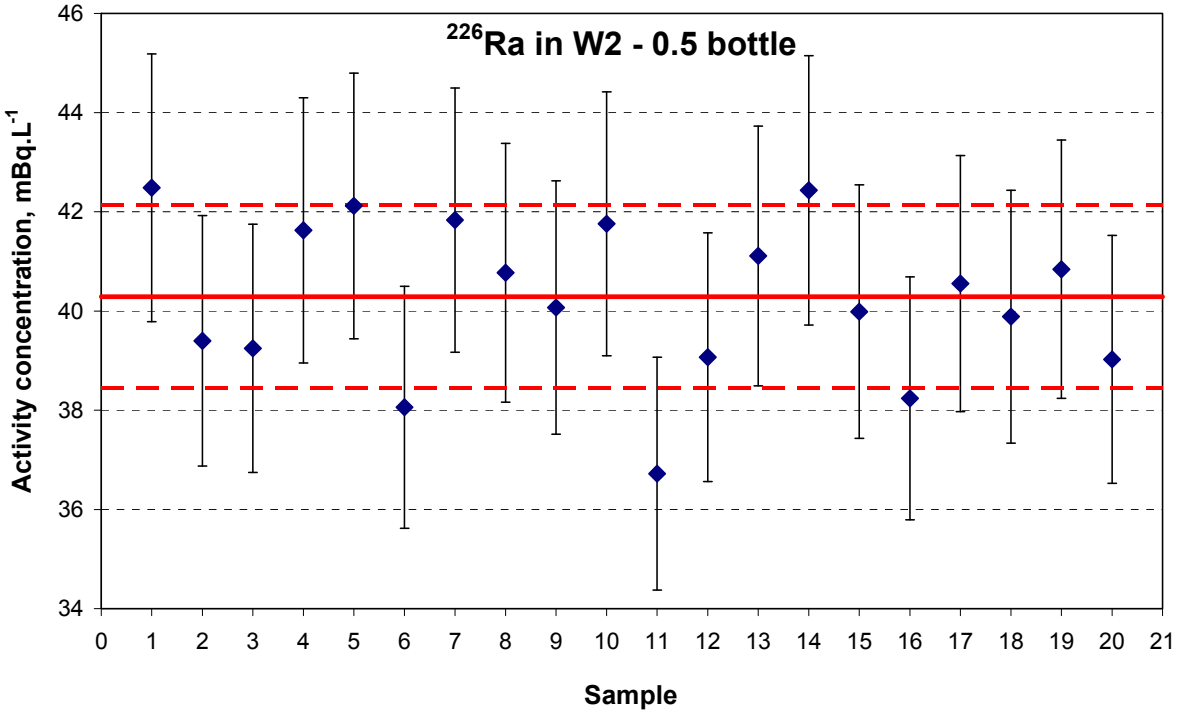

Fig. 3: ^{226}Ra activity concentration in mineral water – Batch 2 (W2 - IM-RN-2006-05-001448/IM-RN-2006-07-001449). Sources prepared from a volume of 0.7 L to 0.8 L.

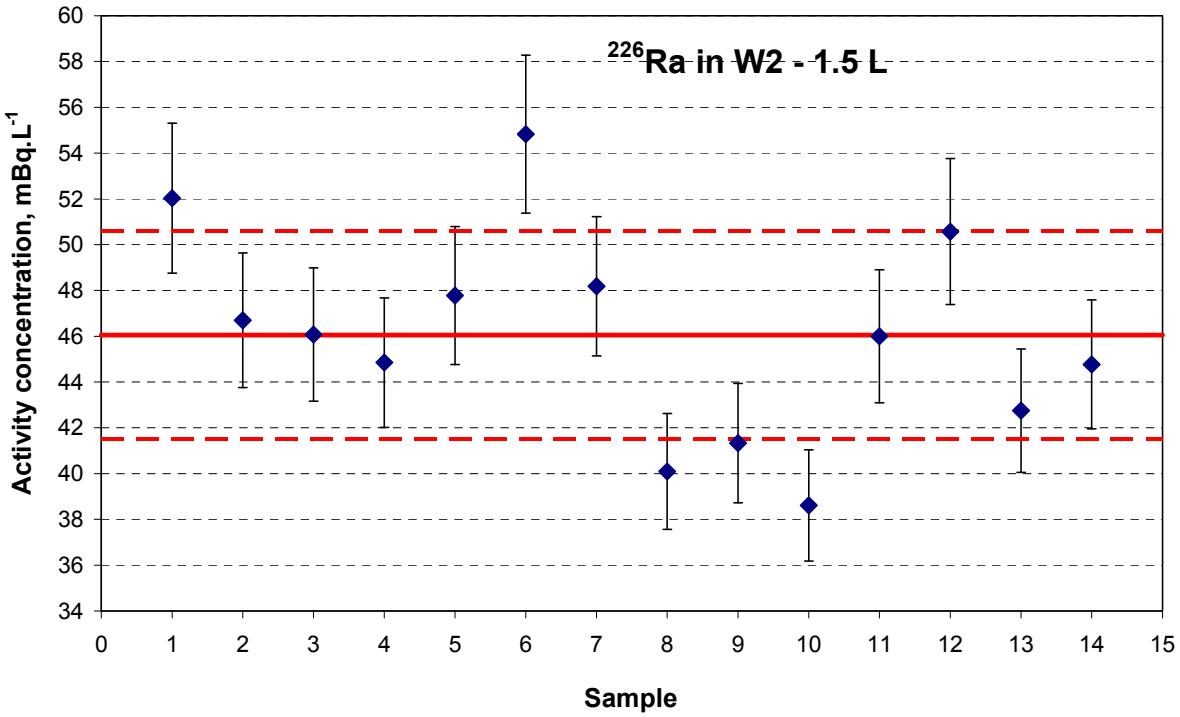

Fig. 4: ^{226}Ra activity concentration in mineral water – Batch 2 (W2 - IM-RN-2006-05-001448 / IM-RN-2006-07-001449). Sources prepared from a volume of 1.5 L.

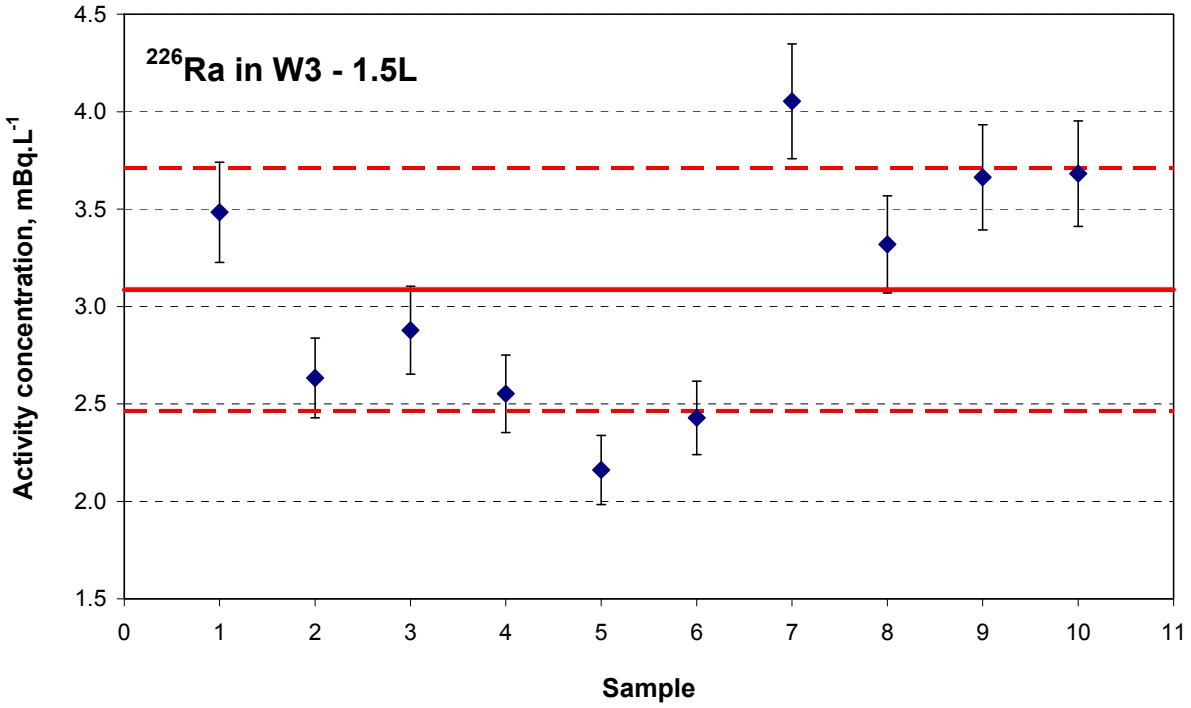

Fig. 5: ^{226}Ra activity concentration in mineral water – Batch 3 (W3 - IM-RN-2006-05-001450 / IM-RN-2006-07-001451). Sources prepared from a volume of 1.5 L.

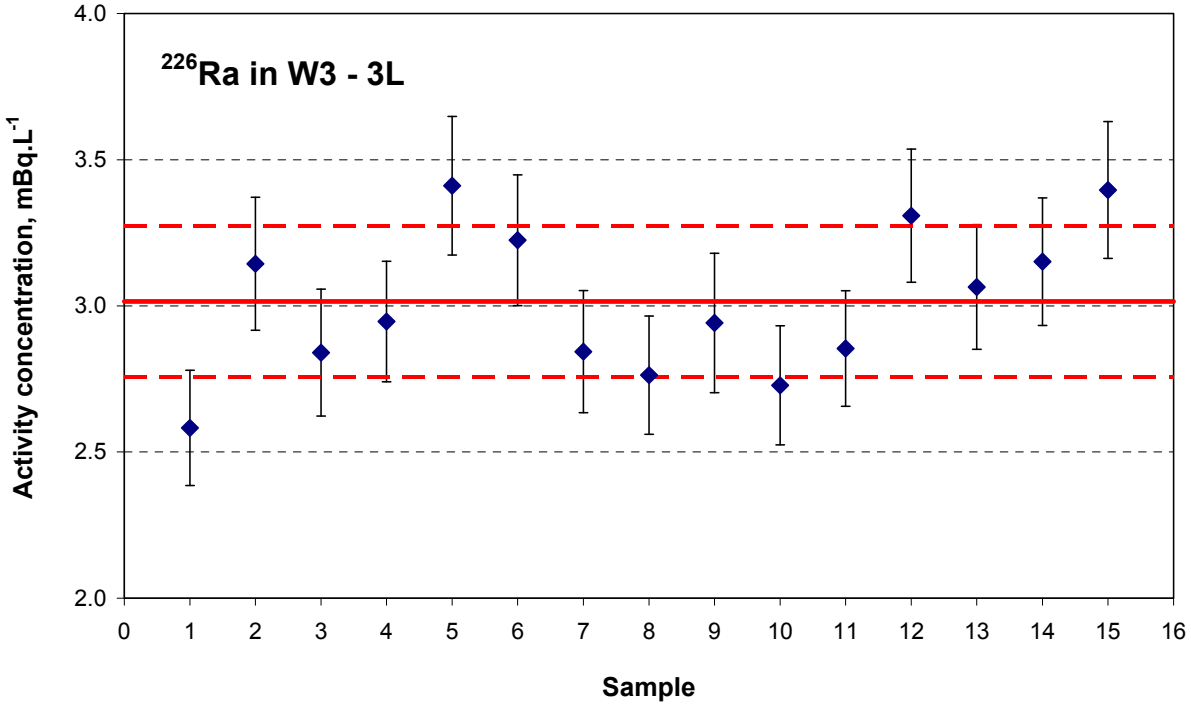

Fig. 6: ^{226}Ra activity concentration in mineral water – Batch 3 (W3 - IM-RN-2006-05-001450 / IM-RN-2006-07-001451). Sources prepared from a volume of 3.0 L.

Table 2: ANOVA test results for ^{226}Ra in mineral waters in %.

Sample batch		W1	W2	W3
ISO/FDIS 13528:2005	s_s	2.3	0.4	-
ANOVA	s_{bb}	2.3	0.4	8.1 (3 L)
	s_{wb}	4.1	3.9	3.3 (3 L)
ANOVA (1.5 L)	s_{bb}	3.3	9.7	20.3
	s_{wb}	3.1	2.7	4.4
u_{bb}, %		**3.5**	**10.0**	**20.0**

Table 3: Mean activity concentrations and standard deviations for ^{226}Ra in mineral waters in mBq·L^{-1} (mean ± 1s).

Sample batch	Volume	W1	W2	W3-50/W3-51*
^{226}Ra	**0.7 L (3 L*)**	97±5	40±2	3.02±0.26
(Mean ± 1s)	**1.5 L**	102±5	46±5	3.09±0.63

2.2 ^{234}U and ^{238}U

For the evaluation of the (in)homogeneity of the mineral water samples with respect to ^{234}U and ^{238}U activity concentration, at least ten samples per batch were prepared from 1.5 L and 3.0 L sample volume, respectively (see Table 1). In this way, the between-bottles standard deviation (s_{bb}) and the repeatability of the method (s_{wb}) were determined by a one-way ANOVA statistical test. The within bottle inhomogeneity of the samples could not be determined due to the lower activity concentrations and the need for large sample volumes.

Results obtained for ^{234}U and ^{238}U activity concentrations in 1.5 L and 3 L mineral waters are plotted in Figs. 7 to 22. The calculated mean activity values and standard deviations (Table 4) are represented by solid and dashed lines, respectively. The error bars indicate combined standard uncertainties of the individual measurements with the major contributions being the counting statistics and the choice of region of interest.

The calculated repeatability (s_{wb}) for each water batch and for both uranium isotopes was in agreement with the random component of the uncertainty budget (see Table 4).

The determination of the uranium isotopes in the mineral water at IRMM was carried out in a period of about 300 days. During this period an increase of the measured activity concentrations with time was observed. An example is given for the measurements done on Batch 3 - W3-50 (Fig. 23). One could speculate that this time-dependency may be due to unknown changes in conditions that influence the radiochemical separation procedure or the solid source deposition. Another possible explanation is inhomogeneity of the material, which might show up as a trend

because the bottles were taken in a particular order from the batch. The observed variation was finally interpreted as inhomogeneity and taken into account in the combined uncertainty of the reference value by including the between bottle standard deviation s_{bb} determined by the ANOVA test (Tables 5 and 6).

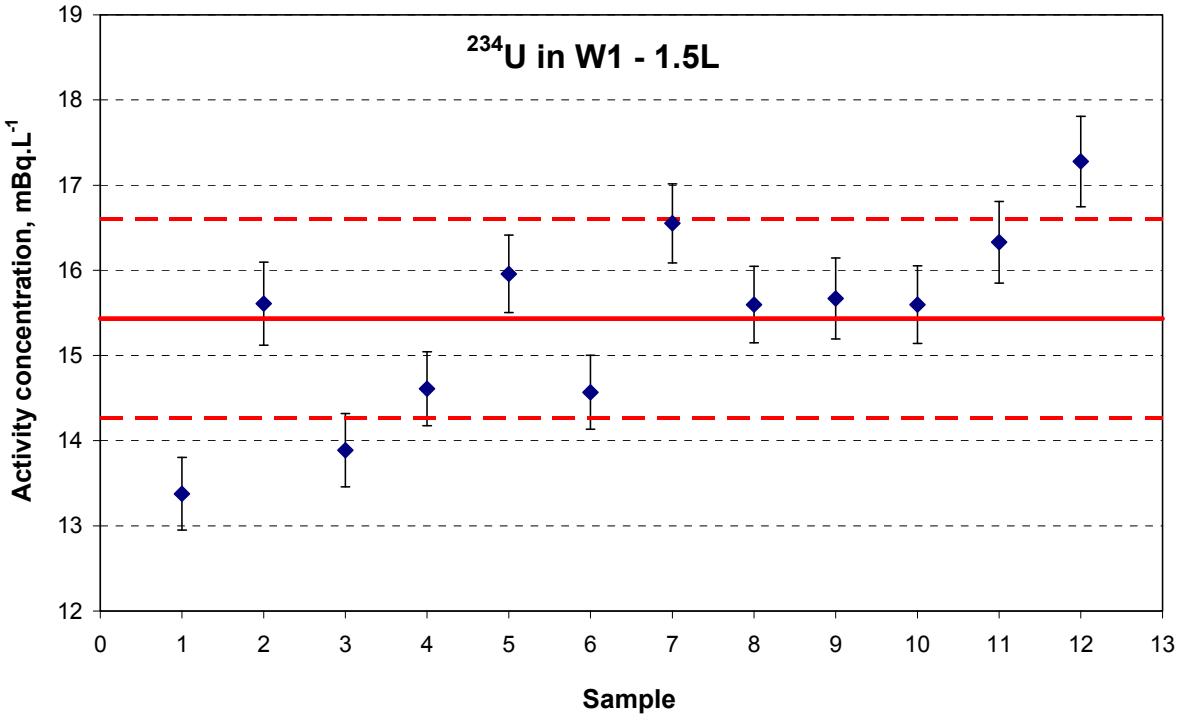

Fig. 7: ^{234}U activity concentration in mineral water - Batch 1 (W1 - IM-RN-2006-02-001446). Sources prepared from a volume of 1.5 L.

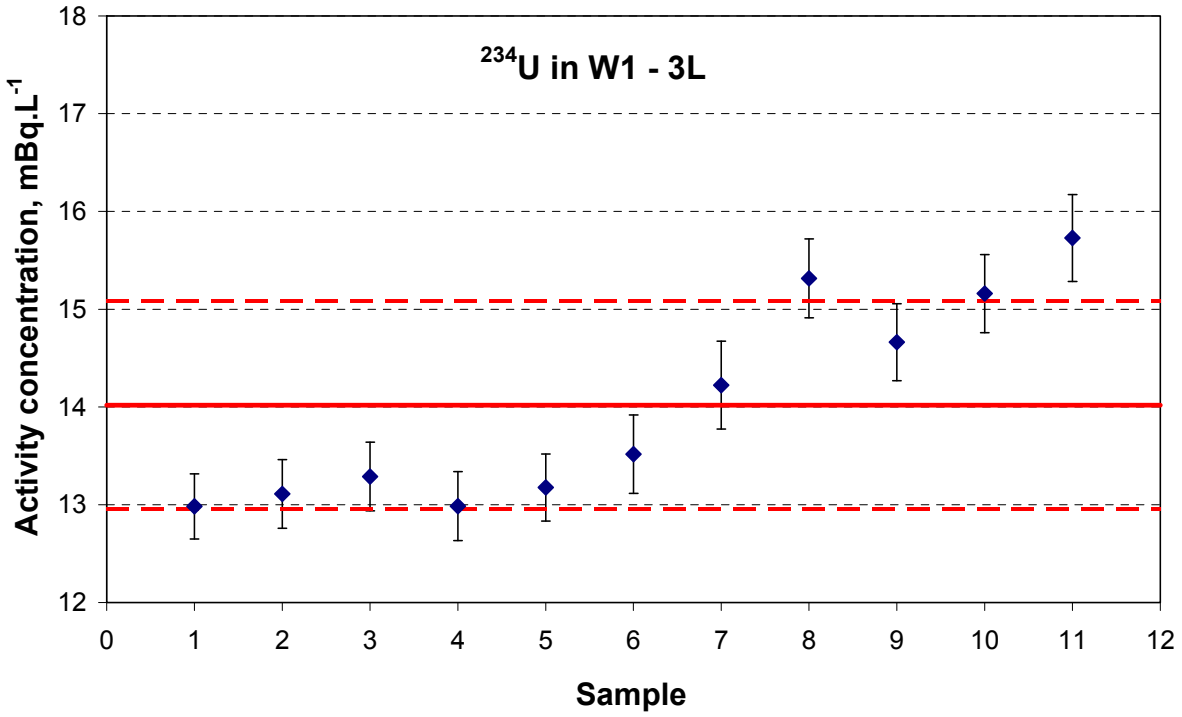

Fig. 8: ^{234}U activity concentration in mineral water - Batch 1 (W1 - IM-RN-2006-02-001446). Sources prepared from a volume of 3.0 L.

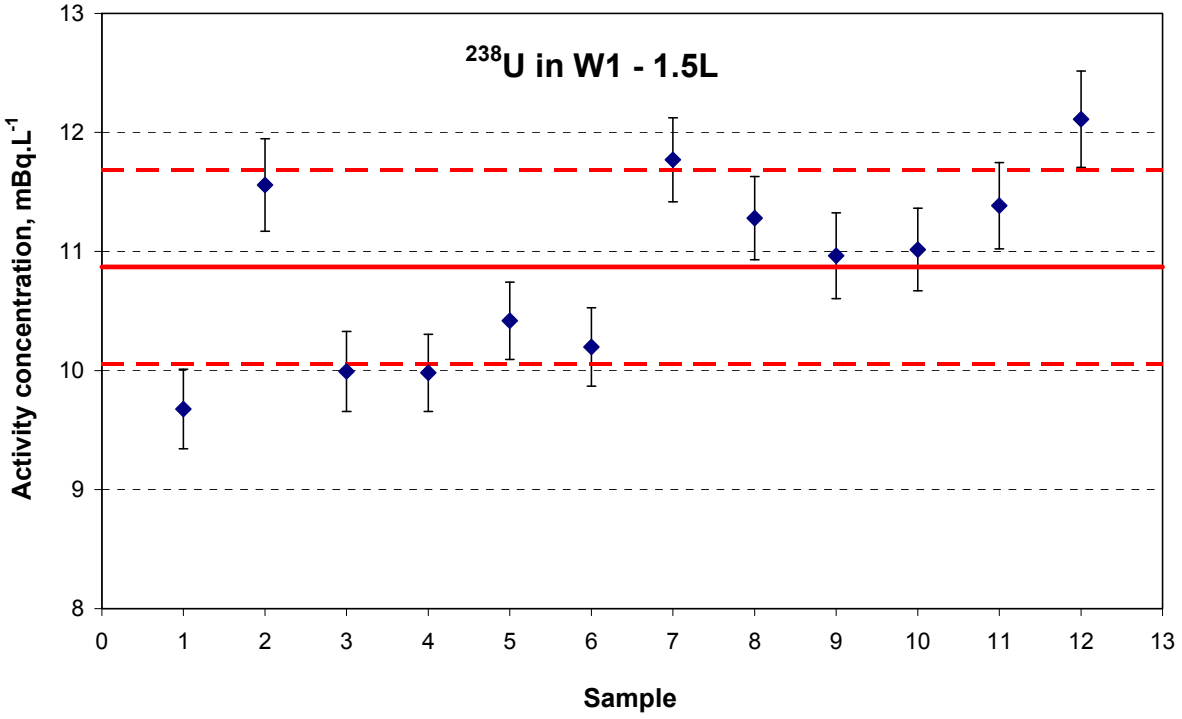

Fig. 9: ^{238}U activity concentration in mineral water - Batch 1 (W1 - IM-RN-2006-02-001446). Sources prepared from a volume of 1.5 L.

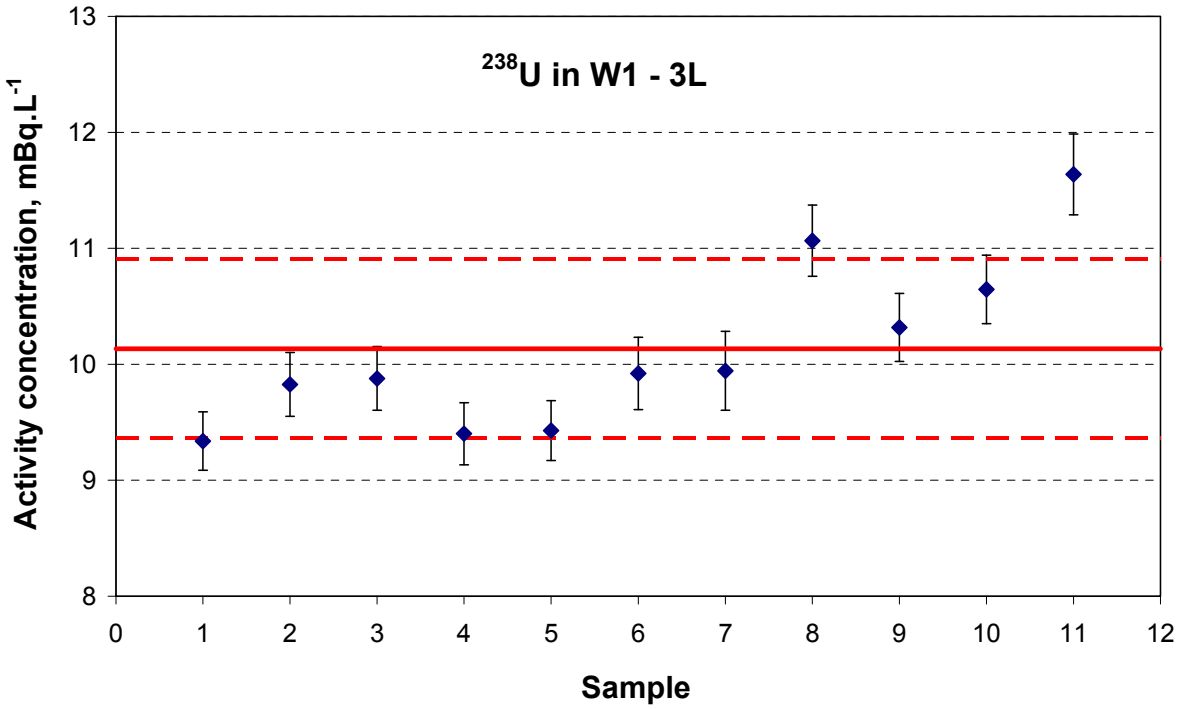

Fig. 10: ^{238}U activity concentration in mineral water - Batch 1 (W1 - IM-RN-2006-02-001446). Sources prepared from a volume of 3.0 L.

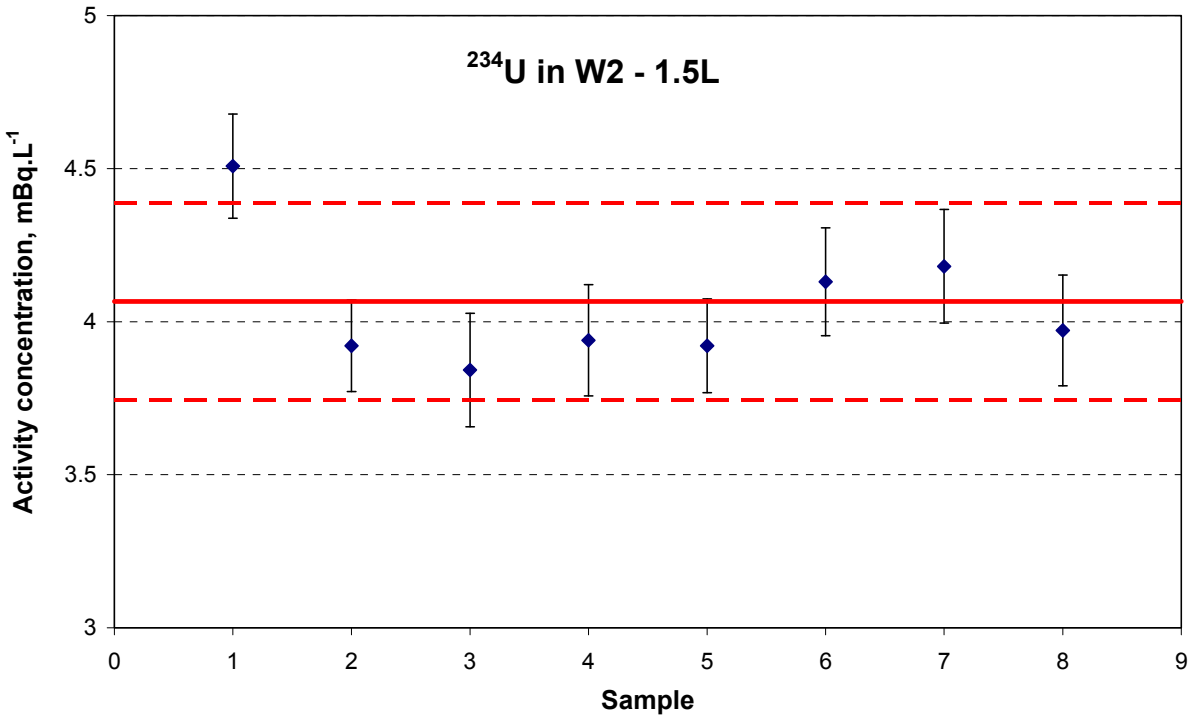

Fig. 11: ^{234}U activity concentration in mineral water - Batch 2 (W2 - IM-RN-2006-05-001448 / IM-RN-2006-07-001449). Sources prepared from a volume of 1.5 L.

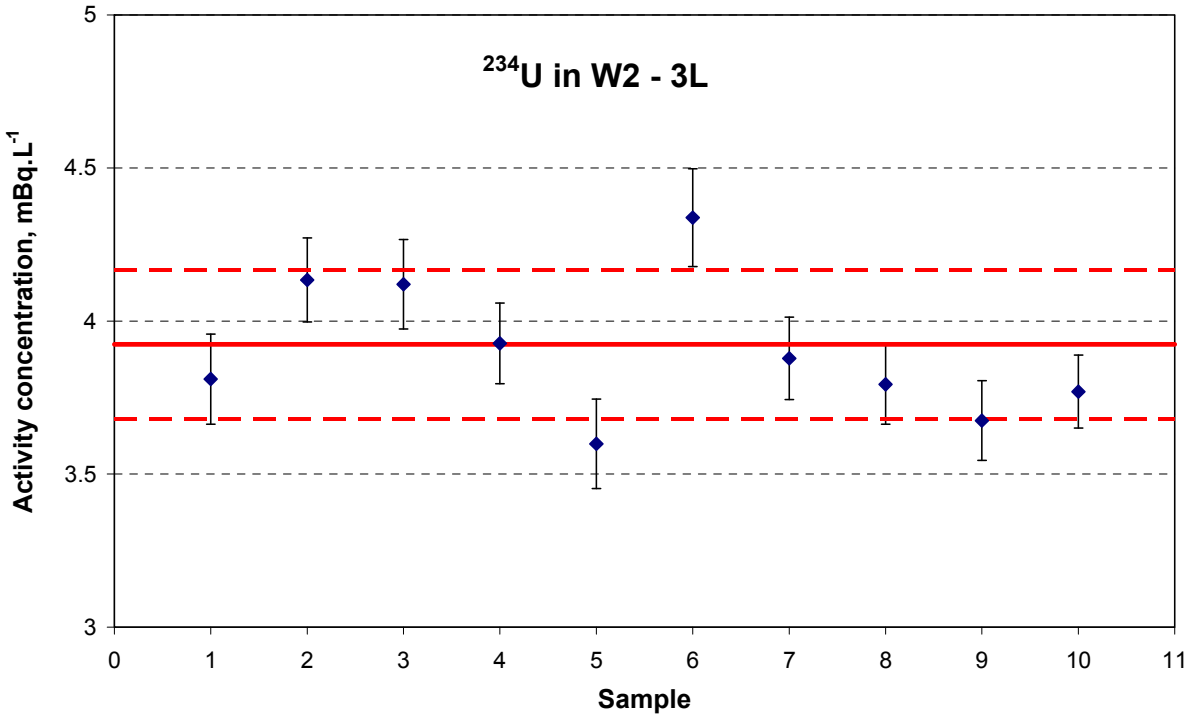

Fig. 12: ^{234}U activity concentration in mineral water - Batch 2 (W2 - IM-RN-2006-05-001448 / IM-RN-2006-07-001449). Sources prepared from a volume of 3.0 L.

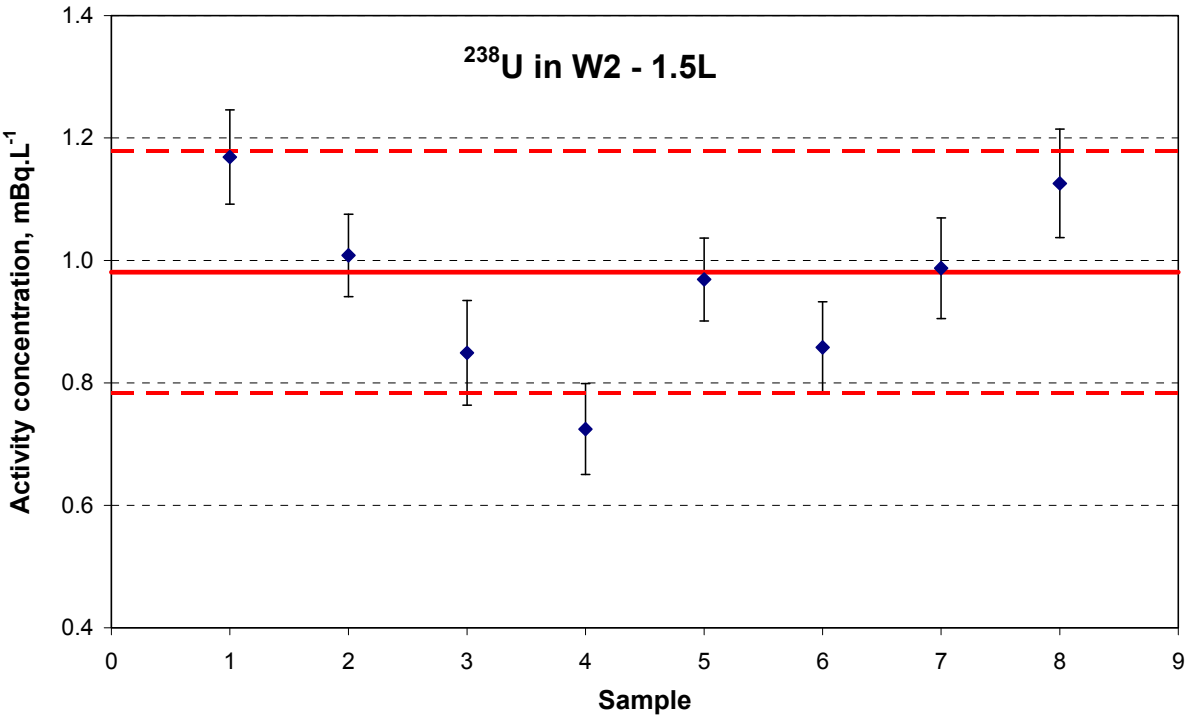

Fig. 13: ^{238}U activity concentration in mineral water - Batch 2 (W2 - IM-RN-2006-05-001448 / IM-RN-2006-07-001449). Sources prepared from a volume of 1.5 L.

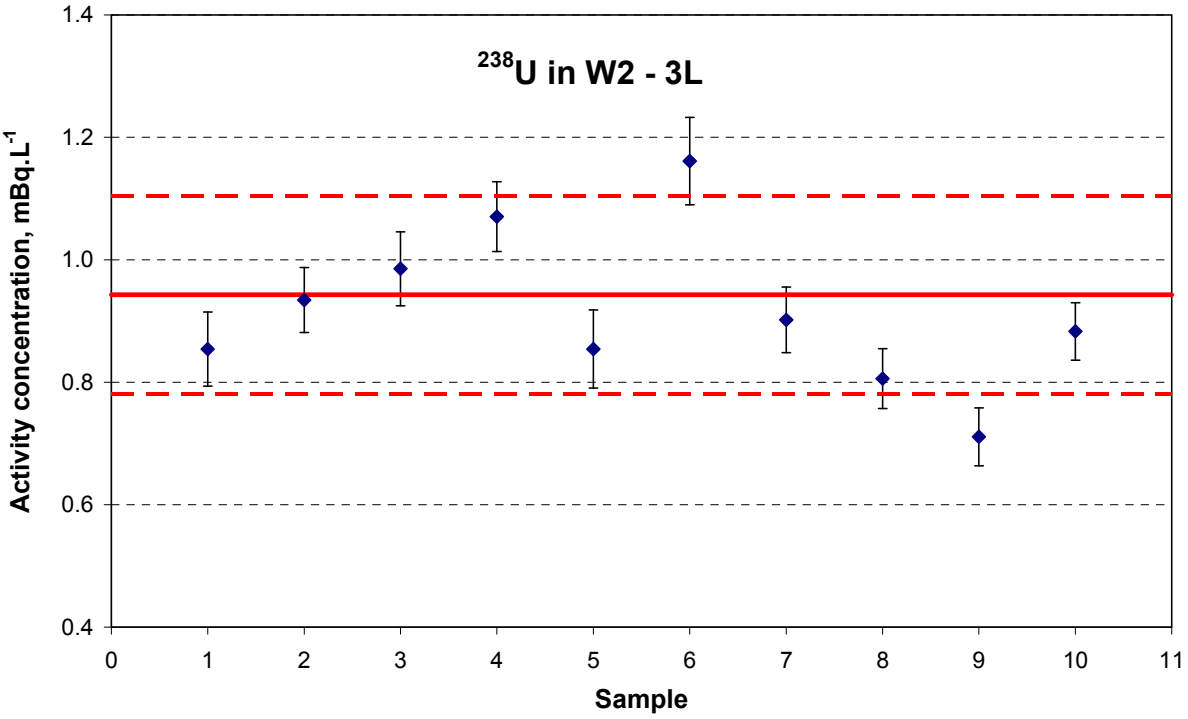

Fig. 14: ^{234}U activity concentration in mineral water - Batch 2 (W2 - IM-RN-2006-05-001448 / IM-RN-2006-07-001449). Sources prepared from a volume of 3.0 L.

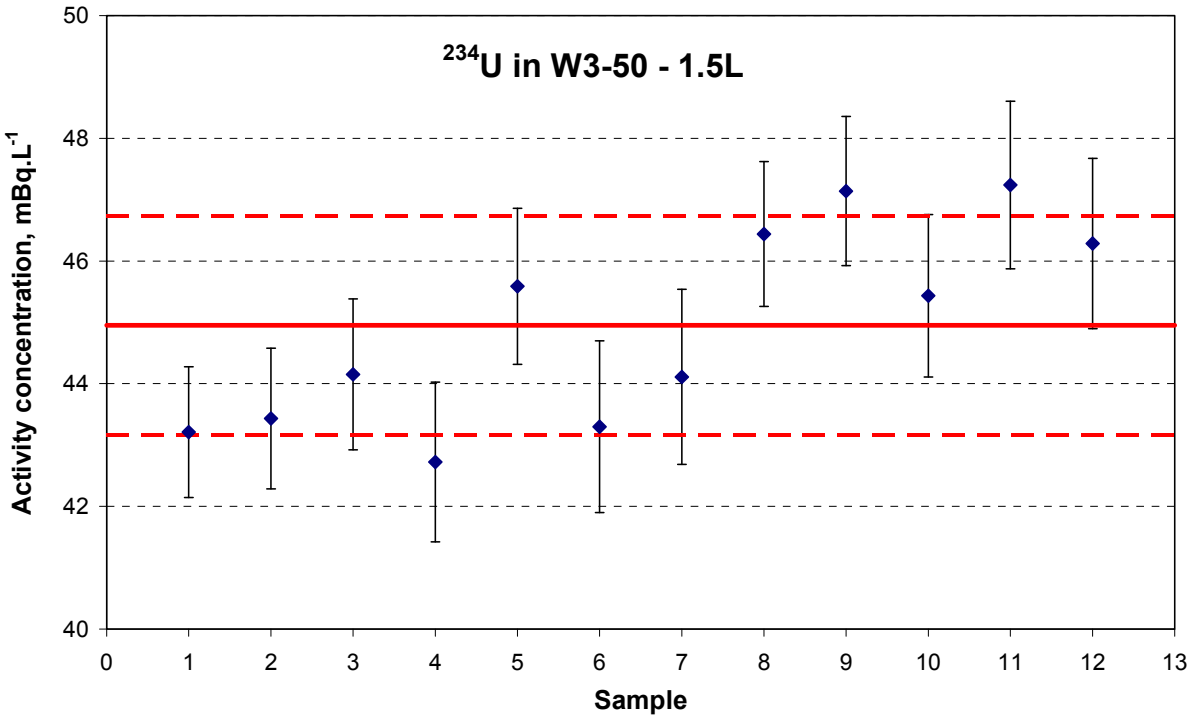

Fig. 15: ^{234}U activity concentration in mineral water - Batch 3-50 (W3 - IM-RN-2006-05-001450). Sources prepared from a volume of 1.5 L.

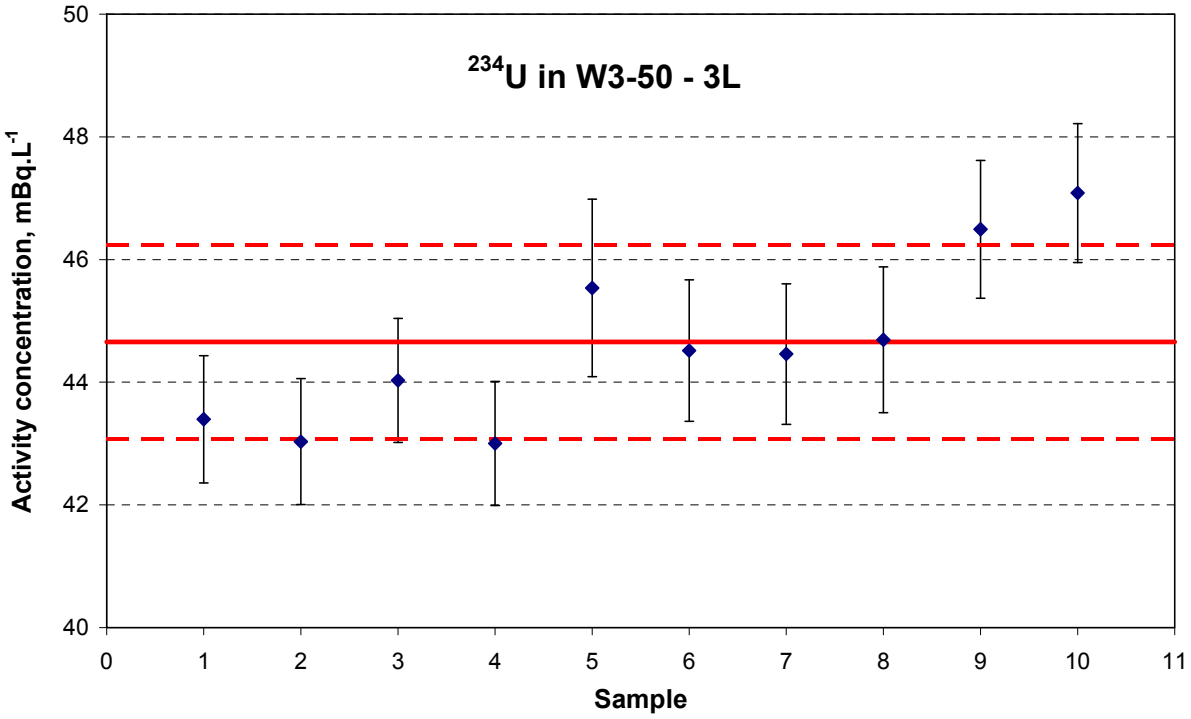

Fig. 16: ^{234}U activity concentration in mineral water - Batch 3-50 (W3 - IM-RN-2006-05-001450). Sources prepared from a volume of 3.0 L.

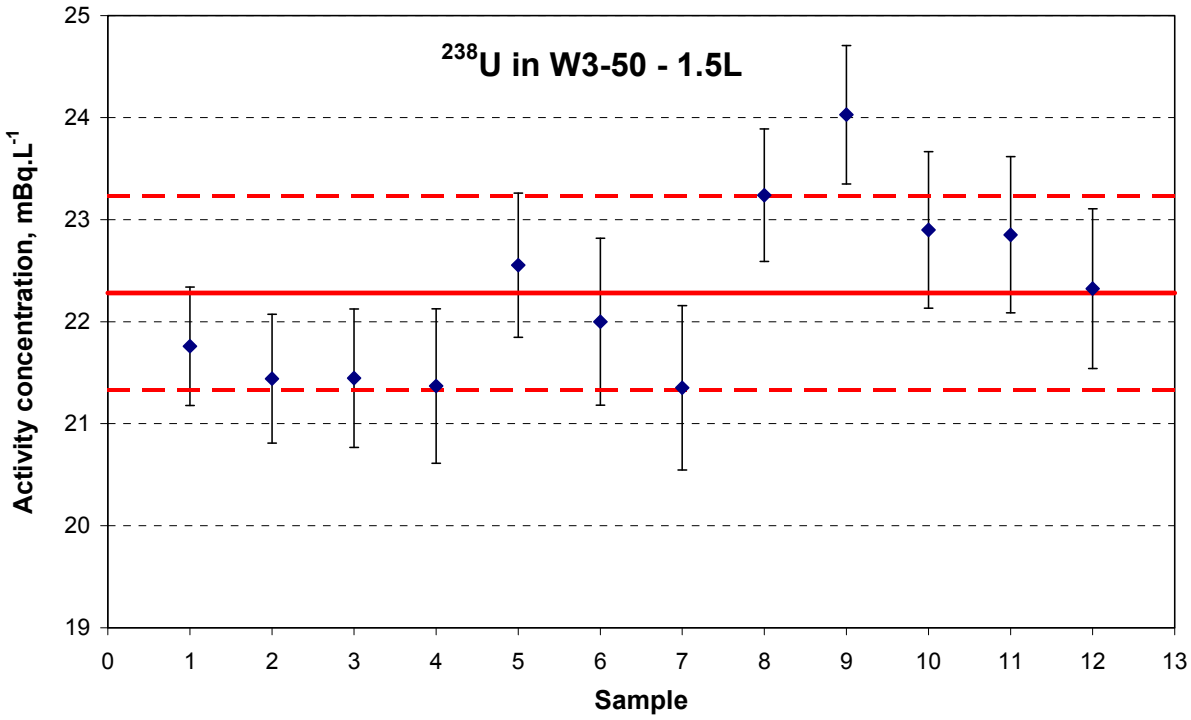

Fig. 17: ^{238}U activity concentration in mineral water - Batch 3-50 (W3 - IM-RN-2006-05-001450). Sources prepared from a volume of 1.5 L.

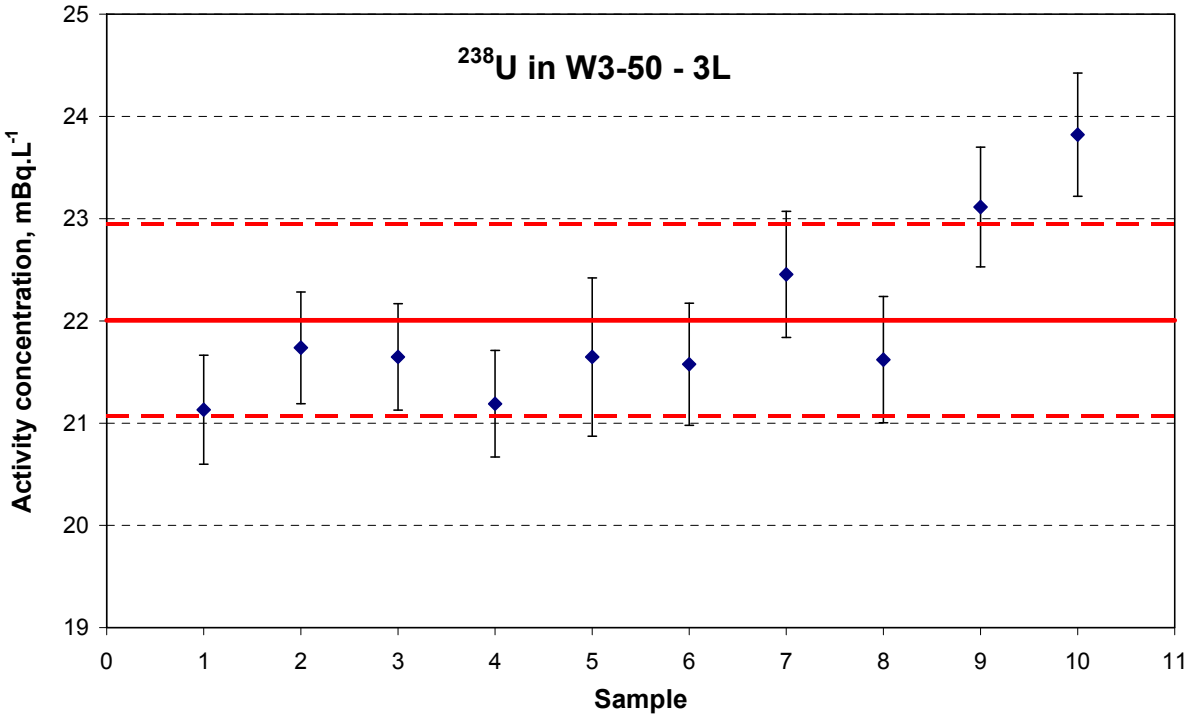

Fig. 18: ^{238}U activity concentration in mineral water - Batch 3-50 (W3 - IM-RN-2006-05-001450). Sources prepared from a volume of 3.0 L.

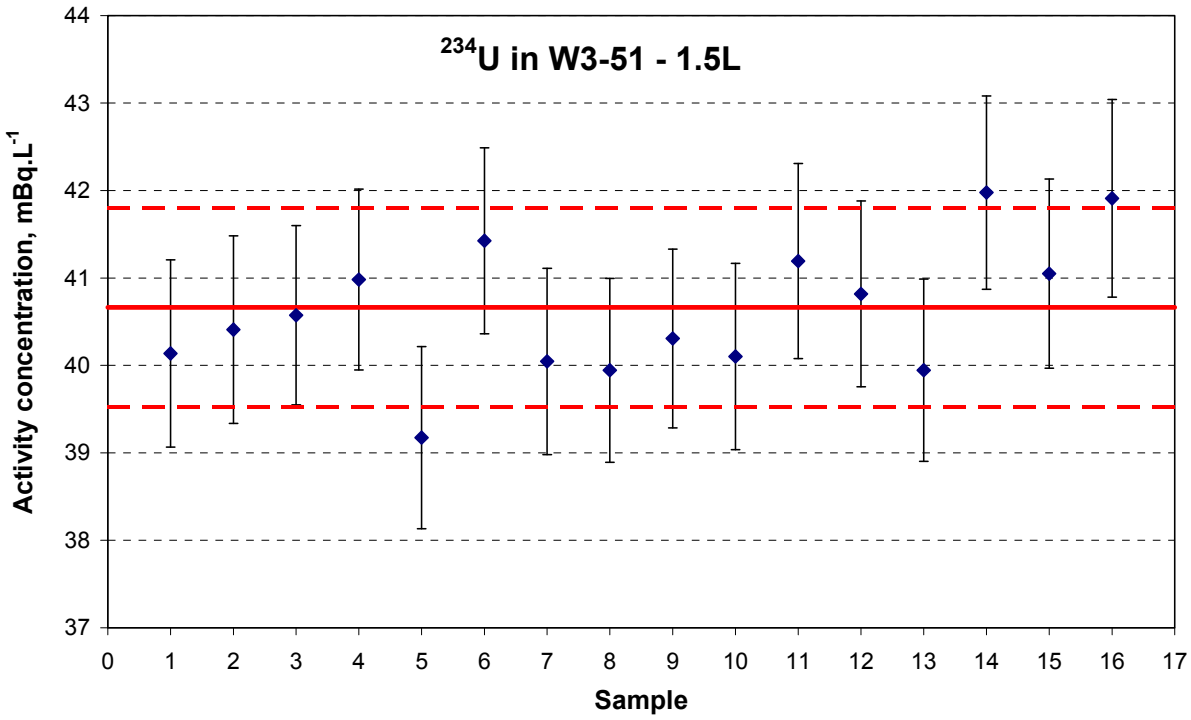

Fig. 19: ^{234}U activity concentration in mineral water - Batch 3-51 (W3 - IM-RN-2006-07-001451). Sources prepared from a volume of 1.5 L.

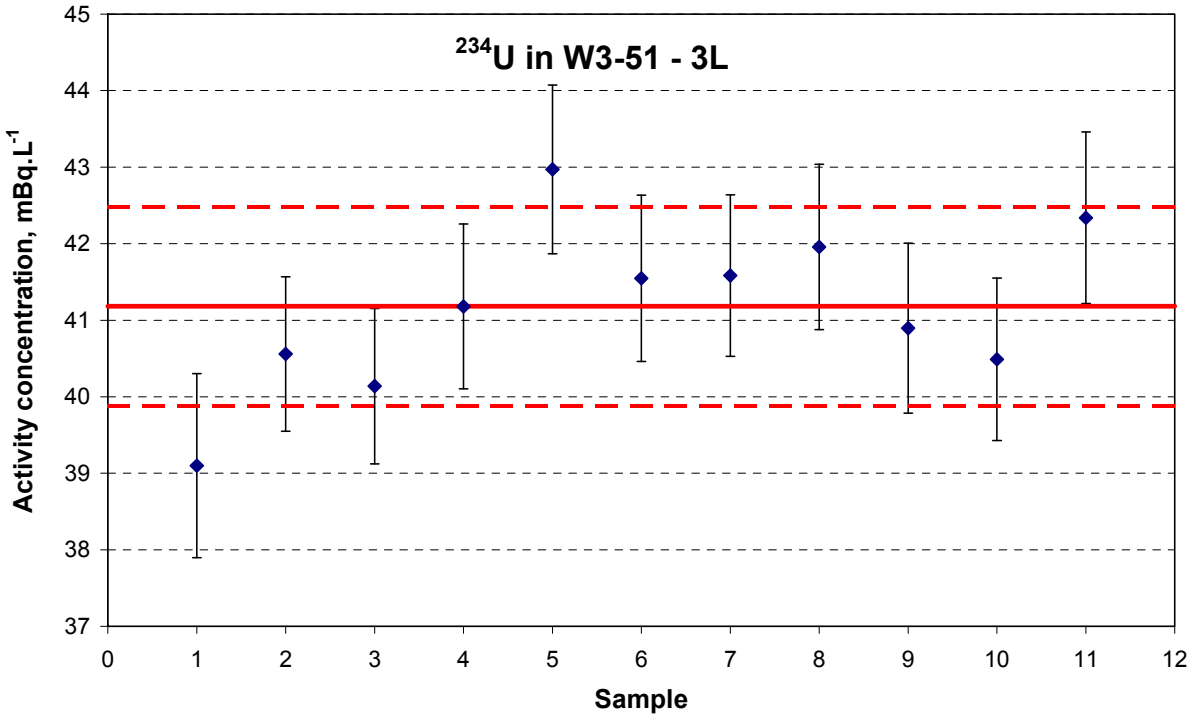

Fig. 20: ^{234}U activity concentration in mineral water - Batch 3-51 (W3 - IM-RN-2006-07-001451). Sources prepared from a volume of 3.0 L.

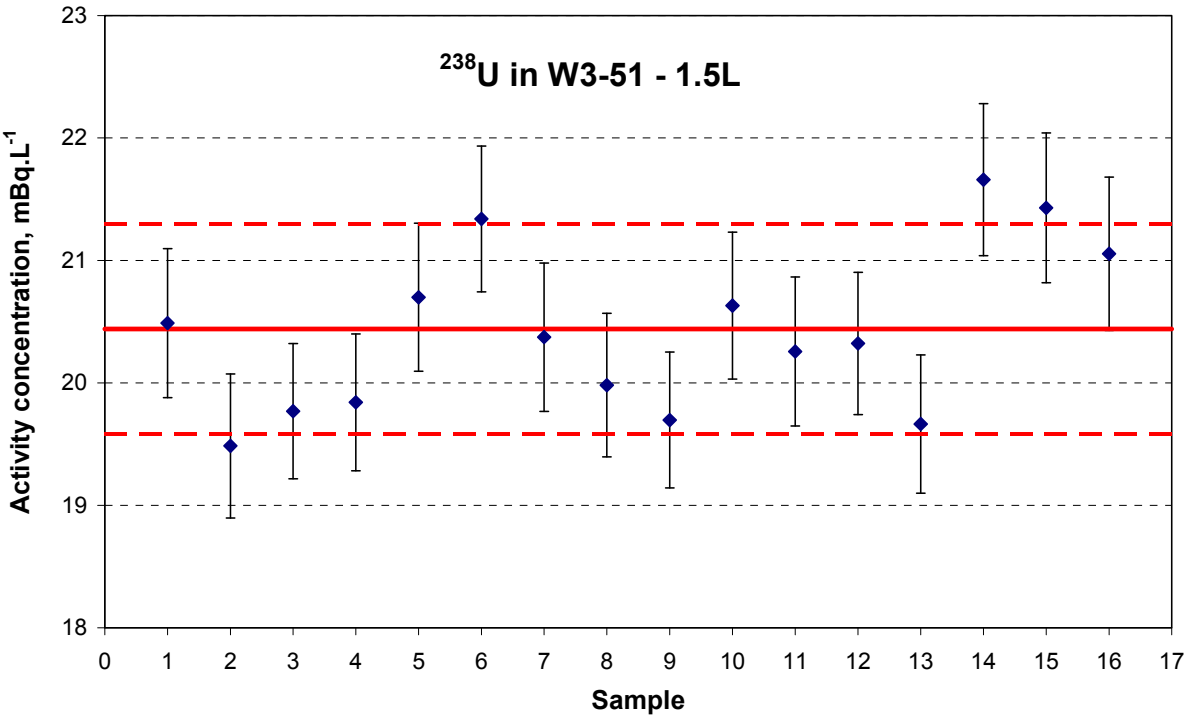

Fig. 21: ^{238}U activity concentration in mineral water - Batch 3-51 (W3 - IM-RN-2006-07-001451). Sources prepared from a volume of 1.5 L.

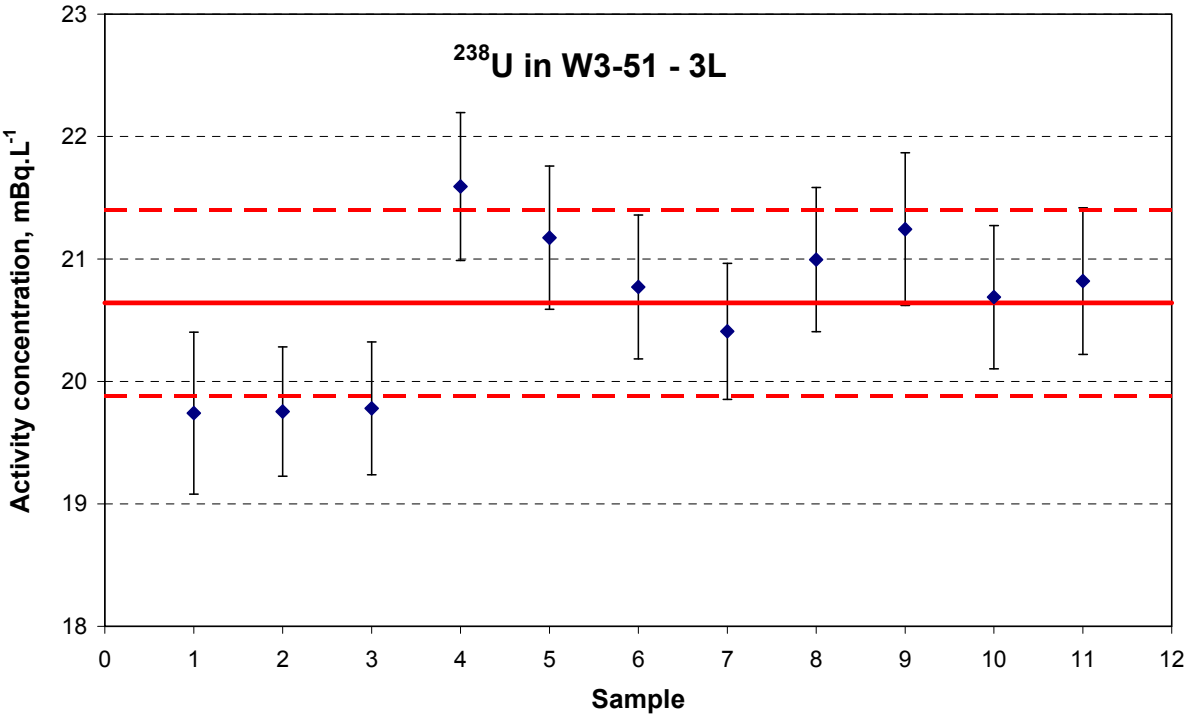

Fig. 22: ^{238}U activity concentration in mineral water - Batch 3-51 (W3 - IM-RN-2006-07-001451). Sources prepared from a volume of 3.0 L.

Table 4: Mean activity concentrations and standard deviations for ^{234}U and ^{238}U in mineral waters in $mBq \cdot L^{-1}$ (mean ± *s*).

Sample batch	Volume	W1	W2	W3-50	W3-51
^{234}U	**1.5 L**	15.4±1.2	4.07±0.32	45.0±1.8	40.7±1.2
(mean ± 1*s*)	**3.0 L**	14.1±1.1	3.92±0.24	44.7±1.6	41.2±1.3
^{238}U	**1.5 L**	10.9±0.8	0.98±0.20	22.3±1.0	20.4±0.9
(mean ± 1*s*)	**3.0 L**	10.1±0.8	0.94±0.16	22.0±1.0	20.7±0.8

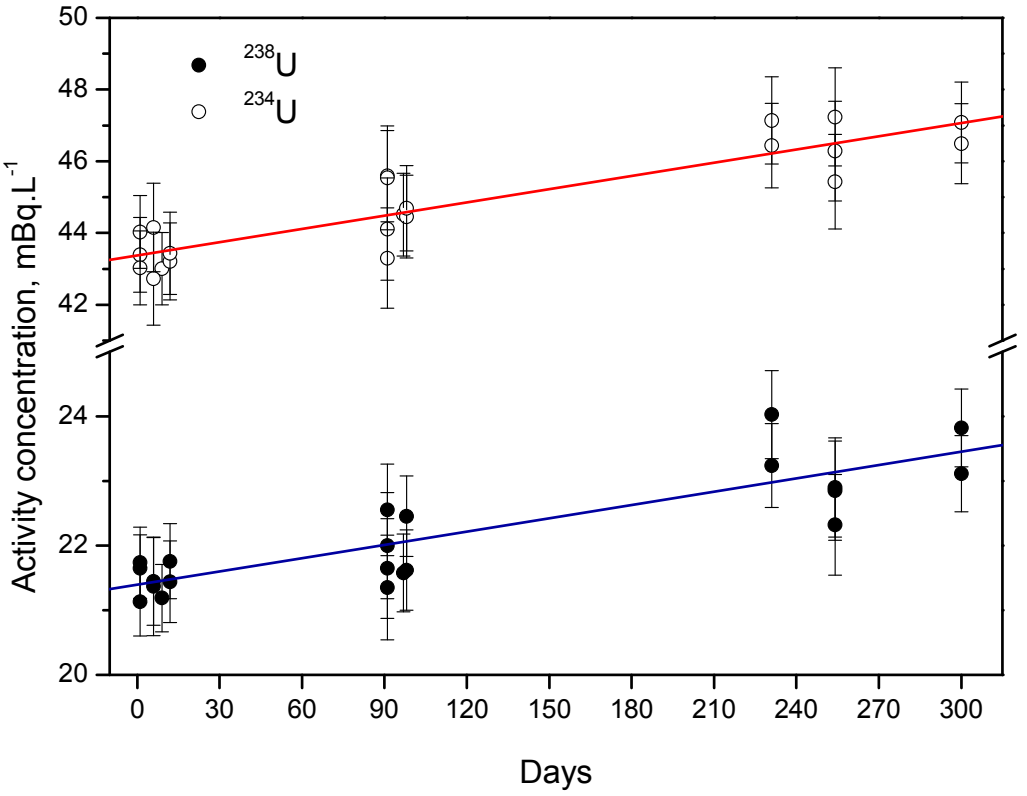

Fig. 23: Time distribution of the measured activity concentrations of ^{234}U and ^{238}U in mineral water - Batch 3-50 (W3 - IM-RN-2006-05-001450).

Table 5: ANOVA test results for ^{234}U in mineral waters (in %).

Sample batch		W1	W2	W3-50	W3-51
ANOVA (1.5 L)	s_{bb}	7.0	2.9	3.2	-
	s_{wb}	3.3	7.4	2.4	3.0
ANOVA (3.0 L)	s_{bb}	7.1	5.0	2.7	2.0
	s_{wb}	3.2	3.9	2.4	2.5
u_{bb}, %		**7.0**	**5.0**	**3.0**	**2.0**

Table 6: ANOVA test results for ^{238}U in mineral waters (in %).

Sample batch		W1	W2	W3-50	W3-51
ANOVA (1.5 L)	s_{bb}	7.0	16.8	3.4	1.9
	s_{wb}	3.1	6.2	2.6	3.8
ANOVA (3.0 L)	s_{bb}	6.6	15.6	3.6	2.5
	s_{wb}	4.2	6.5	2.5	2.8
u_{bb}, %		**7.0**	**16.0**	**4.0**	**3.0**

2.3 ^{228}Ra

For the evaluation of the (in)homogeneity of the mineral water samples with respect to ^{228}Ra activity concentration ten samples per batch were prepared from 1.5 L and 3.0 L sample volume, respectively. The ISO/FDIS 13528:2005 procedure could not be followed due to the low activity concentrations and the need for large sample volumes.

The results obtained for ^{228}Ra activity concentrations in 1.5 L and 3 L mineral water samples are plotted in Figs. 24 to 27. The calculated mean activity values and standard deviations are represented by solid and dashed lines, respectively. The error bars indicate combined standard uncertainties of the individual measurements with major contributions coming from the counting statistics, the efficiency, the sample preparation and the chemical recovery.

One-way ANOVA statistical tests, using the SoftCRM version 2.0.10 software were performed on the activity concentration results. With this test, the between bottles standard deviation (s_{bb}) and the within bottle inhomogeneity (s_{wb}) can be determined. In this case the values of the within bottle standard deviation (s_{wb}) are actually representing the repeatability of the method as only one sample per bottle was prepared. To be able to perform the ANOVA test each set of ten results (in total four sets - two per batch and sample volume) were put in random order and divided into five treatments (groups) of two samples (results). This was necessary as only one measurement per sample was done.

The between bottle standard deviation (s_{bb}) was evaluated with the following formula (ISO, 2006):

$$s_{bb} = \sqrt{\frac{MS_{between} - MS_{within}}{n}} \qquad (1)$$

where $MS_{between}$ is the between bottle variance, MS_{within} is the repeatability variance of the measurements used in the between-bottle homogeneity study, and n is the number of observations per group.

Only in the case of Water 2, samples of 3L sample volume, the between bottle standard deviation (s_{bb}) was evaluated according to the description above. In the rest of the cases, s_{bb} could not be estimated because the calculations render unphysical (imaginary) results (i.e. $MS_{between} < MS_{within}$). The estimated repeatability of the method ($s_{wb} = \sqrt{MS_{within}}$) varied between 4.4 % and 12.8 % for the different samples

and water volumes used (Table 7). These results demonstrated insufficient repeatability of the method used for the homogeneity study.

In order to obtain an uncertainty estimate that accounts for the influence of the repeatability standard deviation on s_{bb}, the following equation was used (ISO, 2006):

$$u_{bb} = \sqrt{\frac{MS_{within}}{n}} \sqrt[4]{\frac{2}{\nu_{MS_{within}}}} \qquad (2)$$

where $\nu_{MSwithin}$ is the degrees of freedom of MS_{within}.

This expression is based on the consideration that a confidence interval can be developed for s_{bb}, and that the half-width of the 95 % confidence interval, converted to a standard uncertainty, can be taken as a measure of the impact of the repeatability of the method on the estimate of s_{bb} (ISO, 2006). The evaluated relative between-unit uncertainties u_{bb}, hidden by the method repeatability, are given in Table 7.

If, as an alternative evaluation, only the standard deviation s_{bb} of all measured samples is used, this will result in an overestimation of real physical inhomogeneity, since the reproducibility of the measurements (in particular sample preparation and counting statistics) is not accounted for. The mean activity concentrations and standard deviations for ^{228}Ra in the mineral waters (shown by solid and dashed red lines in the figures) for the different sample volumes are summarised in Table 8. In relative terms, these standard deviations correspond to s_{bb} (W1) of 12.4 % for 1.5 L and 9.2 % for 3 L of sample volume. In the case of Water 2 (W2), s_{bb} is 6.3 % and 6.4 % for 1.5 L and 3 L, respectively. These results are consistent with the results given in Table 7 when considering the intrinsic overestimation.

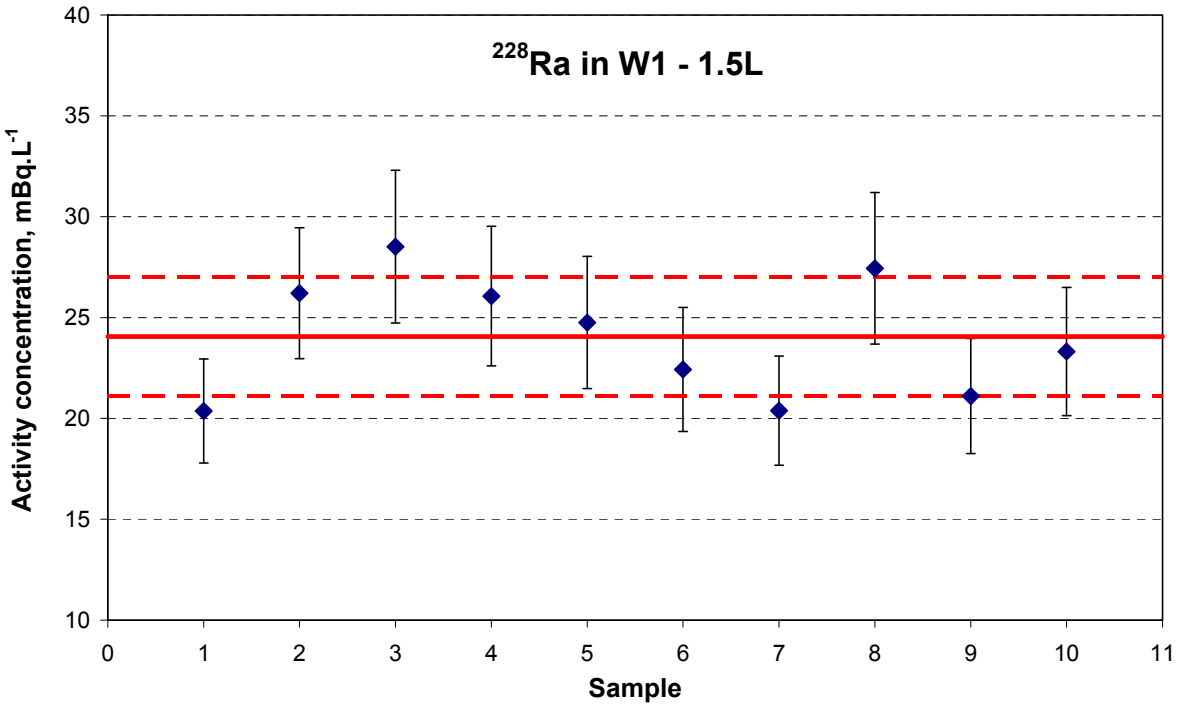

Fig. 24: ^{228}Ra activity concentration in mineral water - Batch 1 (W1 - IM-RN-2006-02-001446). Sources prepared from a volume of 1.5 L.

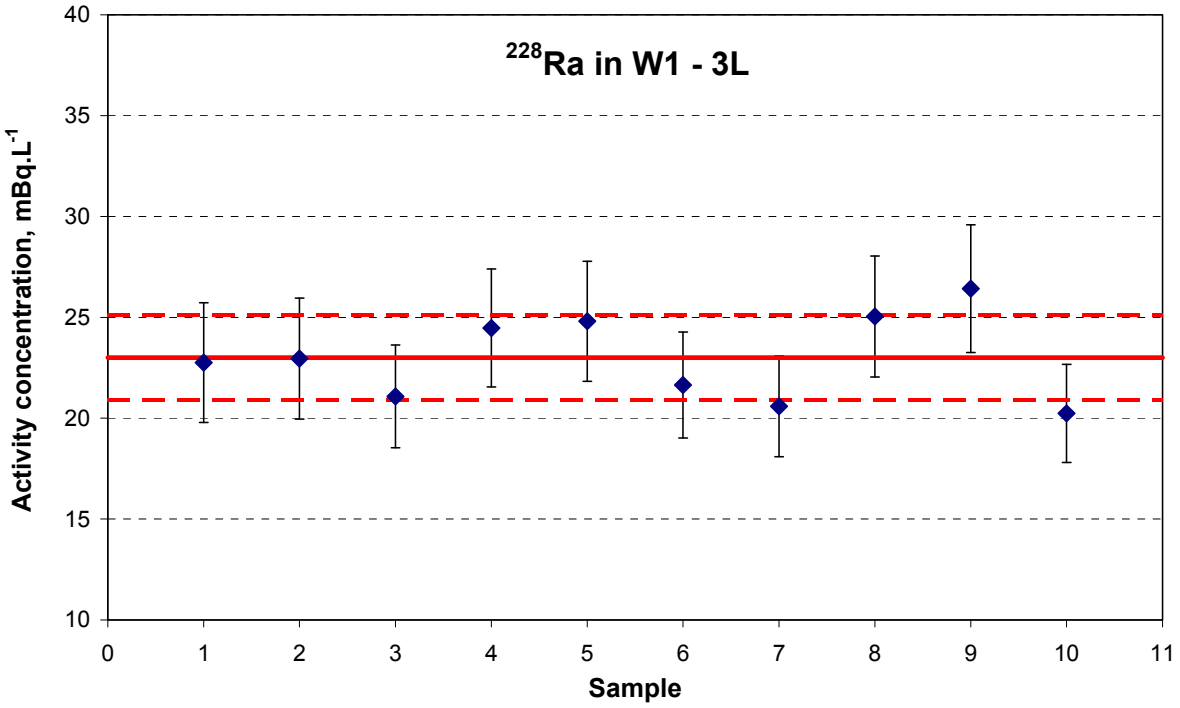

Fig. 25: ^{228}Ra activity concentration in mineral water - Batch 1 (W1 - IM-RN-2006-02-001446). Sources prepared from a volume of 3.0 L.

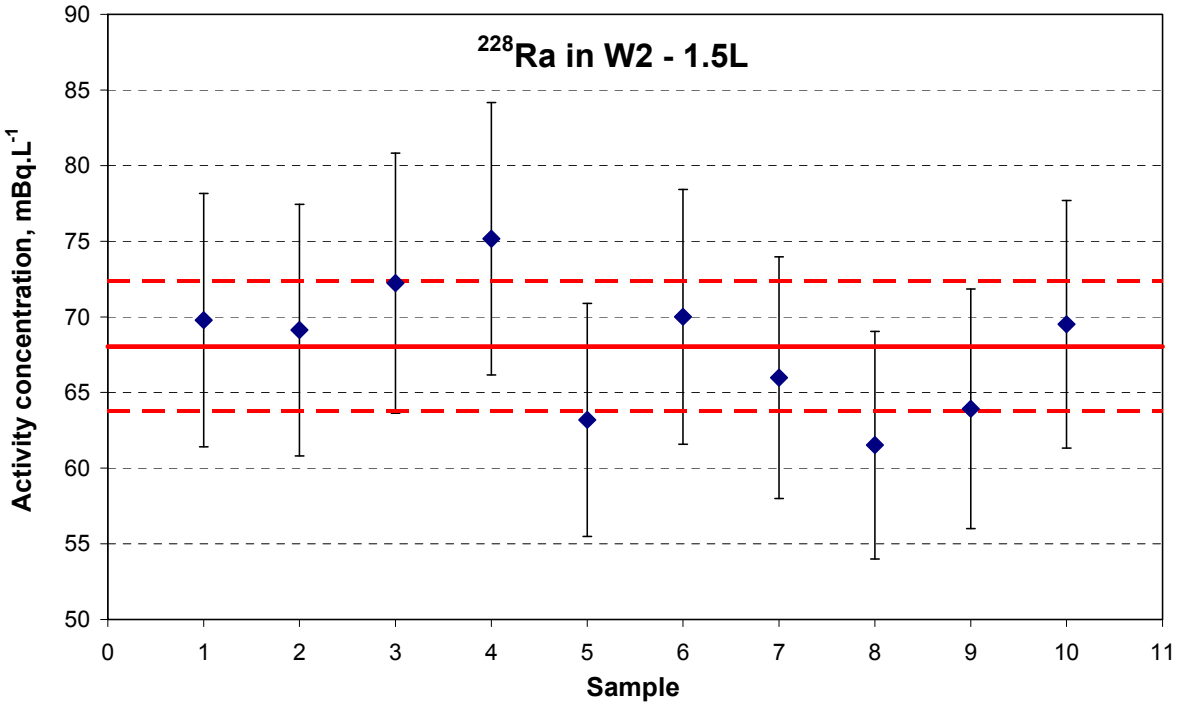

Fig. 26: ^{228}Ra activity concentration in mineral water – Batch 2 (W2 - IM-RN-2006-05-001448/IM-RN-2006-07-001449). Sources prepared from a volume of 1.5 L.

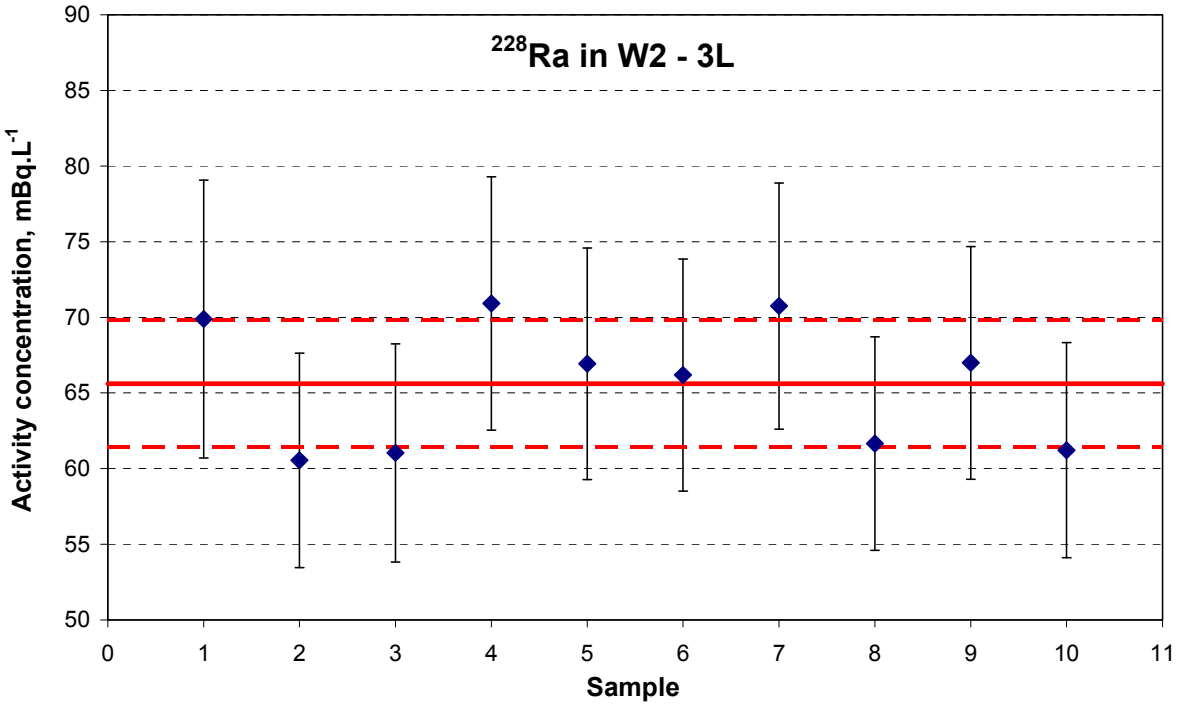

Fig. 27: ^{228}Ra activity concentration in mineral water – Batch 2 (W2 - IM-RN-2006-05-001448 / IM-RN-2006-07-001449). Sources prepared from a volume of 3.0 L.

Table 7: ANOVA test results for ^{228}Ra in mineral waters (in %).

Sample batch		**W1**	**W2**
ANOVA (1.5 L)	s_{wb}	12.8	7.1
	u_{bb}	7.2	4.0
ANOVA (3.0 L)	s_{wb}	9.4	4.4
	u_{bb}	5.3	4.9*
u_{bb}, %		**7.2**	**5.0**

*$u_{bb} = s_{bb}$

Table 8: Mean activity concentrations and standard deviations for ^{228}Ra in mineral waters in mBq·L^{-1} (mean ± 1s).

Sample batch	**Volume**	**W1**	**W2**
^{228}Ra (mean ± 1s)	**1.5 L**	24.1±3.0	68.0±4.3
	3.0 L	23.0±2.1	65.6±4.2

The finally adopted uncertainty contributions u_{bb} due to (in)homogeneity of ^{228}Ra are 7.2 % for sample Water 1 (W1) and 5.0 % for Water 2 (W2) for a minimum sample intake of 1.5 L (Table 7).

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Abstract

This report describes all details of the homogeneity study for the radionuclides ^{226}Ra, ^{228}Ra, ^{234}U and ^{238}U in large batches (more than 700 bottles each) of four different, commercially available mineral waters. These samples are intended to be used in an intercomparison for European laboratories monitoring radioactivity in food and the environment.

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