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A COMPARISON OF PROCEDURES USED AT UK NUCLEAR SITES FOR GAMMA ASSAYS OF POTENTIALLY CONTAMINATED OR ACTIVATED MATERIALS

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A Comparison of Procedures Used at UK Nuclear Sites for Gamma Assays of Potentially Contaminated or Activated Materials

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ABSTRACT

The National Physical Laboratory (NPL) has run a comparison exercise in which a single 200 L drum (containing a 'soft-waste' simulant spiked with a low-activity mixture of ^{241}Am, ^{137}Cs and ^{60}Co, all traceable to national standards of radioactivity) was circulated to 18 groups on 16 UK nuclear sites for non-destructive assay. The exercise was followed by a workshop for discussion of the results, after which some participants submitted supplementary or replacement data and other information. This report summarises the background to the exercise, how the drum was prepared and standardised, the conduct of the exercise, the data analysis methods used at NPL, the outcomes of the workshop and the final results obtained. All submitted data (including any original data later revised by the participants) are tabulated, and the reasons for any changes are given. Of the final 88 results submitted, 51 agreed with the NPL values. Twenty-four of the remaining 37 results were either explained by the participants concerned or had been revised by the participants to provide supplementary values, but there were still 13 results which were either clearly discrepant or questionable. The exercise highlighted differences between laboratories who had used 'ISOCS' to model their sample detection efficiencies and facilitated an exchange of models between these laboratories. The exercise underlined the importance of a good knowledge of a sample in the modelling of detection efficiencies. A wide range of uncertainties was quoted, suggesting a need for guidance in the compilation of budgets. Some participants quoted MDA values for one or more radionuclides and some of these were below the activity concentration actually present. A second comparison, based on a sample with a heterogeneous activity distribution, is planned.

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1. INTRODUCTION

The UK nuclear industry is now heavily involved in site decommissioning and remediation and will be for many decades to come. A major aspect of this work is the need to measure radioactivity accurately in a wide range of potentially contaminated (or potentially activated) materials such as concrete, steel and soft waste in order that those materials can be sentenced with confidence to the correct waste streams in accordance with national legislation.

The lack of suitable reference materials and calibration services to support these measurements led to a call for the National Physical Laboratory (NPL) to establish a national measurement infrastructure in this field. In response, NPL commissioned a survey[1] of the industry to establish the exact needs of the UK user base. This survey, although informative, demonstrated a wide range of requirements in the UK for samples matrices, with no particular material being dominant. It was therefore decided to convene a workshop at NPL, involving as wide a range of stakeholders as possible, to discuss the industry's needs further and identify the priorities in terms of:

- Sample matrices and substrates
- Radionuclides
- Activity concentrations
- Sample containers
- Other services (e.g. instrument type-testing and training)

The workshop was held in June 2005. Its highest priority finding (in terms of needs for reference materials) was as follows:

- Concrete and 'soft waste'
- ^{241}Am, ^{60}Co and ^{137}Cs
- < 0.4 Bq g^{-1} in total
- 205 L drum

with a preference for the provision of certificated standards as opposed to test samples. NPL therefore decided to proceed with the development of a soft waste standard meeting the above requirements. This raised two further questions:

(i) Which material best represents soft waste?
(ii) How many sources should be prepared?

Several industry experts were consulted regarding the first question and, again, a range of suggestions was made, the main finding being that a material with a density of approximately 300 kg m^{-3} was needed. Regarding the number of sources to be made, it was decided in retrospect to initially prepare just one drum as a 'prototype' standard and to circulate it to any interested laboratories, at the same time using it as a comparison sample to gauge standards of measurement within the industry. A second workshop would then be held at NPL to discuss the results of the measurements, to identify any further work needed to resolve any observed problems, and to obtain feedback on the prototype standard (for example, does the format need to change, how many sources are needed initially, and should they be provided for sale or for loan?).

This report describes:

- The preparation and certification of the standard drum
- The results of the comparison
- Discussion of the results, conclusions and recommendations for future work, taking into account discussions from the second workshop.

2. PRIMARY AND SECONDARY STANDARDISATION

NPL, as the UK's national standards laboratory, provides measurement standards, reference materials, calibration services and support to users (e.g. via guidance documents, training, comparison exercises and workshops) across some 20 generic areas of science and engineering. At the international level, NPL forms part of the international measurement system, being one of many National Measurement Institutes (NMIs) worldwide who work together under the auspices of organisations such as the BIPM (Bureau International des Poids et Mesures) to share resources and to harmonise standards.

NPL's Radioactivity Metrology Group (RMG) holds the laboratory's expertise in radioassay, and has provided support to UK measurements in this field for many years. The group has adapted to changes in user requirements when required (for example, by responding to the needs of the environmental radioactivity monitoring community since the mid-1980s). As part of its role, RMG develops and maintains primary and secondary systems for the measurement of radioactivity. Several of these systems were used in the development of the standard source for this exercise and they are briefly described below. Fuller details can be found in the appropriate references. By using these systems, NPL was able to produce a source directly traceable to national standards of radioactivity.

For β/γ-emitting radionuclides, the normal method for primary standardisation is the 4π β/γ-coincidence counting technique[2]. Solutions standardised by this method are often used to calibrate a secondary standard instrument such as a re-entrant ionisation chamber (for example, for 2ml and 5ml British Standard glass ampoule geometries). This chamber is the instrument of choice for most applications, its only disadvantage being the larger overall measurement uncertainty than is obtained using the primary method. The secondary standard ionisation chamber has been calibrated for some 60 radionuclides, including those of interest in this exercise (^{241}Am, ^{60}Co and ^{137}Cs).

In developing low-level standards of radioactivity for the environmental monitoring community, a key problem with validating such standards is that the required activity concentrations are of the order of 1 – 10 Bq g^{-1}, being some four orders of magnitude below the measurement range of the ionisation chamber. Such standards are therefore dependent on the accurate and verifiable dilution of a higher-level standard. At NPL, double-weighing (i.e. weighing of both the dispensing and receiving containers before and after dispensing) is used, but is complemented with radiometric dilution checking using a 'well'-type NaI(Tl) γ-ray detector. This involves preparing and counting samples of both the diluted and undiluted solutions (ensuring that the activity per ampoule is constant to minimise dead-time effects). For example, for a 10-fold

dilution, several ampoules, each containing 10 g of diluted solution, would be compared with other ampoules each containing 1 g of undiluted solution topped up to 10 g with inactive carrier. This procedure provides the user with a 'radiometric' dilution factor to compare with the 'gravimetric' factor. This methodology is also applicable to achieving the low-levels of activity which may be required for standards in the decommissioning area.

High-resolution γ-ray spectrometry is frequently used at NPL for:

(i) Impurity checking
(ii) Comparitive measurements
(iii) Assay (when a suitable calibration has been derived)

(ii) and (iii) being applicable to dilution checking of low-activity standards.

3. PREPARATION OF STANDARD SOURCE

Some users were canvassed for their views as to what would be the most suitable material to use as a soft-waste simulant. A number of materials were suggested (e.g. ion-exchange resin, paper, plastic and vermiculite), but there was concern that these materials may degrade with time following addition of the acidic radionuclide 'spike' and/or would not absorb and retain the active species in a stable manner. The only material fulfilling these criteria was the ion-exchange resin. However, such materials have densities typically in the region of 700 kg m^{-3}, which is significantly higher than the preferred value given above. Therefore, it was suggested that the overall density of the contents of the drum could be lowered by packing the resin into a series of identical plastic bottles and then loading the bottles into the drum, choosing a resin mass per bottle which would yield an overall density for the drum's contents of 300 kg m^{-3}. It was found that 240 x 500 ml bottles fitted very well into a standard 205 L drum (in 5 layers of 48 bottles), so this methodology could produce a standard drum consisting of a highly homogeneous array of 240 'diffuse' sources, provided that (i) each bottle was spiked with identical (or almost identical) activities of the same combination of radionuclides mixed in the same proportions, and (ii) the activity was homogeneously distributed throughout the resin in each bottle.

Dowex 'Marathon C' Cation Exchange Resin (The Dow Chemical Company, Michigan, USA) was chosen* on the basis of its being a typical resin of this type. It has a bulk density of 800 kg m^{-3}. The required overall density of 300 kg m^{-3} could be achieved by loading each bottle with approximately 190 g of resin. However, there was a further problem with the resin in that it is supplied as damp material. This would make homogenisation of the resin (after addition of the active material) difficult. It was decided, therefore, that the resin should be dried prior to bottling. The preferred method was freeze-drying so as to completely avoid any thermal degradation of the resin, but low-temperature oven-drying could also be used.

Regarding spiking of the resin, the options were:

* Use of this particular resin is not meant to imply that NPL recommends it over other similar products.

a) to add the weighed, active solution to a small batch of resin before freeze-drying it, then adding a weighed aliquot of this active resin to each bottle of (dried) inactive resin;
b) to add the active solution directly to the dry inactive resin, and 're-dry'.

(b) was considered simpler provided the liquid volume was kept low (say, around 0.1 ml) – this would leave a small damp area on the resin surface that would dry in air in a few hours.

Homogenisation of the resin within each bottle could be achieved by rotation in a mechanical mixer.

The following materials were therefore procured:

- Single radionuclide solutions of ^{241}Am, ^{60}Co and ^{137}Cs
- Dowex 'Marathon C' Cation Exchange Resin (approx. 80 kg)
- 240 x 500 ml HDPE bottles
- 1 x 205 L drum
- 1 x freeze-drier and accesssories

The next step was to prepare a mixed radionuclide standard solution for spiking the resin. The single radionuclide solutions of ^{241}Am, ^{60}Co and ^{137}Cs were weighed out into ampoules before being assayed on the NPL secondary standard ionisation chamber (and also on a γ-ray spectrometer to check for any γ-emitting impurities). The ^{241}Am and ^{137}Cs sources were then diluted gravimetrically (with radiometric checking as described above). Ampoules of the diluted ^{241}Am and ^{137}Cs were then used, along with undiluted ^{60}Co, to prepare a mixed nuclide solution. The activity concentrations of the three radionuclides were confirmed by high-resolution γ-spectrometric assay in a 10ml ampoule format and were approximately 600 Bq g^{-1} for ^{241}Am and 60 Bq g^{-1} each for ^{60}Co and ^{137}Cs.

The inactive resin was dried initially using just the freeze-drying technique. However, this resulted in a rather slow resin throughput, so low-temperature oven drying (at around 70^{0}C) was also used. The dried material was dispensed into 500 ml HDPE bottles (approximately 190 g per bottle) with weighing until 240 bottles had been filled.

The bottles were then spiked with approximately 0.1 g of standardised solution each. The dispensing bottle was weighed both initially and also after every 12th bottle, so the total activity in each set of 12 bottles, and therefore the total activity overall, was known. The bottles were left overnight with the lids off and were then sealed before being loaded (in batches of 16) into a mechanical mixer and then being mixed for 6 hours. This mixing time had been determined previously by spiking a single bottle with ^{241}Am and measuring its homogeneity on a NaI(Tl) detector after several mixing times (see Figure 1). The bottles were then loaded into the 205 L drum with double weighing (i.e. the drum was weighed empty and full and the resin bottles were weighed separately, in batches, on another balance before being loaded into the drum). The drum was then certificated (see Table 1).

Finally, the drum was checked for homogeneity (externally) using a collimated 2" x 2" NaI(Tl) crystal linked to an Electra ratemeter set up in the 'gross count' mode. This was a fairly crude check and was done to confirm that gross errors had not been made during the manufacture of the source.

4. CIRCULATION OF DRUM AND REPORTING OF DATA

Around 440 contacts in the nuclear industry were sent an initial mailshot regarding the exercise (see Appendix A). A total of 19 contacts expressed an interest in participating. Three later withdrew and it was possible to accommodate all the remaining laboratories in the actual exercise. All the participating contacts are listed in Appendix B. Some of these contacts are 'secondary', having learnt of the comparison from the initial contact in their organisation. In total, 18 participants from 16 sites took part.

In the event, the timescales given in the mailshot were changed to the following:

- Participants to measure drum within agreed dates between March and July 2007
- Participants to return results to NPL by 10th August
- NPL to issue draft report by mid-September
- NPL to hold workshop on 21st September
- NPL to issue final report in late September or early October

The drum was dispatched, as an Exempt package, to the first participant; thereafter, it was moved directly from one participant to the next according to a pre-determined timetable with NPL organising the courier service each time. Each site was given approximately five working days (excluding the delivery and pick-up days) in which to carry out their measurements.

A spreadsheet (see Appendix C) was sent to the participants for reporting of their data. The participants were also sent details of the drum's dimensions (as provided by the manufacturer) and details of the drum's contents, such as the resin used and the mass and approximate overall density of the contents. The mass of the empty drum was also provided. These details were provided at the request of the participants.

Once all the data had been submitted, the true activity concentrations were sent to the participants to allow any participants whose data clearly differed from NPL to check for any transcription errors or to send NPL any explanatory information and/or further data. All submitted data (including any initial values later corrected by the participants) were included in the final overall data set.

To preserve anonymity in the final report, each participant was assigned a code number between 1 and 17, and their results were coded accordingly.

5. RESULTS AND DATA ANALYSIS

On receipt of the results, NPL carried out data analyses as described below.

Firstly, the deviation from the assigned (NPL) value of each laboratory value was calculated, given by:

$$D = 100\frac{L-N}{N} = 100\left(\frac{L}{N} - 1\right) \quad [1]$$

where:

D = deviation from the NPL value (%)
L = the participant's value (Bq g^{-1})
N = the NPL value (Bq g^{-1})

The deviations are given in Tables 2 – 7 and are plotted in Figures 2, 6 and 10. The error bars in the graphs represent the standard uncertainty (k=1) of the deviation:

$$u_{\mathrm{D}} = 100\frac{L}{N}\sqrt{\left(\frac{u_{\mathrm{L}}}{L}\right)^2 + \left(\frac{u_{\mathrm{N}}}{N}\right)^2} \quad [2]$$

where:

u_{D} = standard uncertainty of the deviation (%)
u_{L} = standard uncertainty of the participant's value (Bq g^{-1})
u_{N} = standard uncertainty of the assigned value (Bq g^{-1})

The results were evaluated using three tests:

$$\zeta = \frac{L-N}{\sqrt{u_{\mathrm{L}}^2 + u_{\mathrm{N}}^2}} \quad [3]$$

$$R_{\mathrm{L}} = \frac{u_{\mathrm{L}}}{L} \quad [4]$$

$$z = \frac{L-N}{R_{\mathrm{med}}N} \quad [5]$$

where:

ζ = zeta score
R_{L} = relative uncertainty of the participant's value
z = z-score
R_{med} = median of the values of R_{L}

The zeta and *z*-scores were used to determine whether the difference between the participant's value and the NPL value was significantly different from zero. One-sided Dixon's Q outlier tests[3] were used to determine whether a particular R_L value was significantly larger than the other values in the data set. A limiting value of R_L, 'R_{lim}', was calculated for each radionuclide. The zeta scores, z-scores and outlier results are given in Tables 2-7. The zeta scores are plotted in Figures 3, 7 and 11 and the R_L values are plotted in Figures 4, 8 and 12.

Results for which the absolute values of the zeta score and the z-score were both ≤ 2.58 (corresponding to a significance levels of $\alpha = 0.01$) and for which the relative uncertainty R_L was not significantly larger than the other values in the data set are regarded as being 'in agreement' with NPL. These are marked in dark blue in Figures 2, 6 and 10. If either (i) the relative uncertainty R_L was significantly larger than the other values in the data set, (ii) the result passes the zeta test but not the z-test (i.e. large deviation from the NPL value combined with a large uncertainty), or (iii) the result passes the z-test but not the zeta test (small deviation from the NPL value combined with a small uncertainty), the participant's value is classified as 'questionable' (these are given in yellow in Figures 2, 6 and 10). If the absolute values of both the zeta score and the z-score are > 2.58, then the participant's value is classified as 'discrepant' from the NPL value (red points), regardless of the value of the relative uncertainty R_L. The findings for all the data are given in Tables 2-7.

Now, the zeta score and the *z*-score are related by:

$$\zeta = \frac{\sigma_p}{\sqrt{u_L^2 + u_N^2}} z \qquad [6]$$

(where $\sigma_p = R_{med}N$, the standard uncertainty for proficiency assessment (Bq g^{-1})).

This can be rewritten as:

$$\frac{z^2}{\zeta^2} - \frac{u_N^2}{\sigma_p^2} = \frac{u_L^2}{\sigma_p^2} \qquad [7]$$

The relative uncertainty of the laboratory R_L and the z-score are related by:

$$\frac{u_L}{R_L} = z\sigma_p + N \qquad [8]$$

This can be rewritten as:

$$R_L^2 \left\{ z + \frac{N}{\sigma_p} \right\}^2 = \frac{u_L^2}{\sigma_p^2} \qquad [9]$$

Consequently, comparison data can be neatly summarised by plotting the square of the ratio of u_L to σ_p against the z-score, and superimposing one parabola to represent a zeta score of 2.58, a second parabola representing the outlier limit R_{lim} of the relative

laboratory uncertainty R_L, and vertical lines representing a z-score of 2.58. These are known as 'Kiri' plots, and are given in Figures 5, 9 and 13. Data points that are inside the zeta parabola (i.e., for which zeta ≤ 2.58), within the *z*-score lines and outside the R_{lim} parabola (i.e., for which $R_L \leq R_{lim}$) are 'in agreement' with NPL. Data points which fail either the *z*-test, the zeta test or the relative uncertainty outlier test (but not both the *z*-test and zeta test), are classified as 'questionable' and are either:

(i) inside the zeta parabola with a *z*-score < –2.58 or > 2.58, or
(ii) outside the zeta parabola with a z-score > –2.58 or < 2.58; or
(iii) inside zeta parabola with a *z*-score > –2.58 or < 2.58, but inside the R_{lim} parabola.

All other data points are classified as 'discrepant'.

n.b. Since the draft report was issued, NPL amended this data analysis method slightly to reduce the effect of correlated uncertainties. The procedure above was followed, but only one value of R_L per participant was used, and this has resulted in changes to the classification of some data. These changes are pointed out in the text. The revised method identified no outlier uncertainties and this was checked by applying an IQR method which also identified no outliers.

At the post-comparison workshop, it was suggested that plots of deviation by participant would be useful. These are given in Figures 14 to 29.

6. DISCUSSION

This discussion should be read in conjunction with the minutes of the post-comparison workshop (see Appendix D).

The reported results are presented in Tables 2 to 9, and the corresponding data plots are given in Figures 2 to 29.

n.b. Tables 2 to 9 include <u>all</u> submitted data for the radionuclides concerned (even original data which had later been revised) but only the final values were used in preparing Figures 2 to 29. The values given in Tables 8 and 9 have not been plotted.

Of the 18 participants who received the drum, 17 performed measurements, the other participant being unable to do so due to equipment failure at the time the drum was available. Sixteen participants reported at least one result for each of the three radionuclides in the drum. In some cases, Minimum Detectable Activities were reported for one or more radionuclides. Some participants reported results for more than 1 detector, or reported more than one result for one detector (e.g. by using different efficiency models). One participant reported a value for the total activity present.

Of the 17 participants who measured the drum, 13 performed γ-spectrometry using hyperpure Ge crystals, with one of the participants using a three-crystal detector system.

Of the 13 participants who performed γ-spectrometry:

- Ten rotated the drum during (or between) measurements, either manually or using a turntable;
- One participant rotated the drum for some measurements but not others;
- Six participants carried out 'segmented' scans of, typically, eight horizontal layers of drum;
- Nine participants used shielded and/or collimated detectors for some or all measurements;
- Seven participants reported carrying out background measurements.

For γ-spectrometry, source-to-detector distances varied from 10 cm to 100 cm but were typically 30 – 50 cm. Counting times varied widely - from 15 minutes to 2.7 days.

A variety of detector efficiency models and calibration standards was used. Three participants used ISOCS software, one saying that the detector had been characterised by Canberra using NIST-traceable sources and MCNP. Four participants used NDA2000 (some with Genie 2000) software, two of them saying the software had been validated by using 'mock' waste drums (one traceable to national standards), and a third saying Canberra had validated the software. Another participant used 'SNAP' software, validated by MCNP and simulated waste containing NPL standard sources, and a detector calibrated by Eberline and traceable to NIST. Three participants used MCNP, one in conjunction with a ^{152}Eu source. One of these had validated MCNP 5.1.4 using 'standard drums' and had found a ± 20 % variation over the 60 – 1836 keV range. Their detector had been characterised using an AI mixed radionuclide source and a ^{137}Cs point source. Two participants used Ortec's ISOTOPIC software with calibrated γ-emitting sources. This software had been validated by Ortec.

Three participants used transmission sources for density corrections and with detector calibrations having been done using traceable sources, using 'traceable software', or by the detector manufacturer.

Turning to the four participants who had not used high-resolution γ-spectrometry, two each used NaI(Tl) scintillator-based systems based on three vertically aligned crystals. Of these two, one rotated the drum, and used a shielded and collimated detector and a background measurement. The count time was 300 s. The second reported a count time of 2 hours. One carried out matrix correction using predetermined factors and the other weighed the source and assumed a 50/50 mix of paper and plastic. Two other participants measured the drum by placing it in a six-sided detection cell incorporating solid plastic scintillation detectors.

One of the latter two participants (Participant 16) was only able to report an estimate of the total activity concentration within the drum (see Table 9). This was because the analyst was not aware of either the radionuclidic composition of the drum's contents or the nature of the matrix. They used a calibration based on a ^{137}Cs point source. In normal operations, this participant would have more sample information available and could apply a suitable calibration.

6.1 Americium-241

Measurement of ^{241}Am is difficult because the attenuation within the drum wall is much greater than for the other radionuclides present. Small differences between the actual composition of the drum and the composition assumed in efficiency models will also be much more important. In the event, 21 of the 27 (final) results submitted for ^{241}Am were in agreement with the NPL value.

Some of the data submitted by Participants 4, 7, 11 and 17 were either questionable or discrepant. Participant 4 reported two results, one obtained using a single HPGe detector and the other using a triple-HPGe instrument. One of these results were in agreement with NPL but the other (for the triple detector) was discrepant; however, the latter result was higher than the true value because the detector software had selected the wrong attenuation factor for the NPL drum; this problem was compounded by the fact that the instrument's transmission sources were positioned at unrepresentative locations with respect to the 'layers' of resin in the drum. The participant had made it clear at the outset that they expected the attenuation problem to result in an incorrect value for ^{241}Am. They also pointed out that the detector was being evaluated and was not yet in use.

Participant 7's discrepant result was attributed by the participant to their use of a Monte Carlo model based on materials typically found in LLW drums, including soft materials, plastics and metals. Crucially, the assumed drum wall thickness was 1.2 mm compared with the actual value of 0.8 mm. This participant submitted a supplementary Monte Carlo-based value using a model based on the NPL drum and obtained a value which, although found 'questionable' by NPL data analyses, was much closer to the NPL value.

Before covering the results from Participants 11 and 17, it is useful here to bring in the data from Participant 1, who had based their results on an ISOCS model. Their results 1A to 1D (from four different detectors) originally had only the random components of the uncertainties quoted, resulting in them all being discrepant. This participant subsequently submitted the revised uncertainties seen on the final plot. They were quoted as 'minimum uncertainties' owing to the fact that the particular version of the ISOCS software they had used had limited capacity for assessing uncertainties, but the true values of the uncertainties would be at least the value quoted. Another point about their first submission was that they had misunderstood the degree of 'layering' of resin within the drum. They subsequently ran their original data through a revised model (which took account of the true layering) and obtained results 1E to 1H, which were much closer to the true values. They also ran their data through the ISOCS model which had been used by Participant 8 (who had used a later version of ISOCS), which changed the values but not enough to bring all their data into line with the true value. It is not clear why.

Participant 11's original value (11A) was also based on ISOCS (n.b. originally it had been classified by NPL as discrepant, but this was later revised to questionable for the reason given on page 8 above). They also ran their data through Participant 8's model and arrived at value 11B, requesting that it also be included here. Although closer to the true value than 11A, it was still questionable.

Participant 8 themselves submitted a revised uncertainty (see 8B) because their initial uncertainty (on 8A), although resulting in agreement with NPL, had been compiled in such a way as to allow for the presence of high-density materials (e.g. Lead and Iron). It had not been possible, at the time of measurement, for them to re-evaluate the uncertainty to remove these components. Note that the actual reported activity was unchanged.

Turning to Participant 17, their results were based on Monte Carlo modelling of the response of a single HPGe detector. Three of these results were based on the assumption that the drum consisted of ion-exchange resin, polyethylene or PVC (17A, 17B and 17C respectively). The other three (17D to 17F) assumed that the same materials were in the drum, but in layers (the laboratory had radiographed the drum and had detected the layering of the bottles inside). Originally, their data were discrepant, but this was due to the fact that the wrong drum wall thickness had been used in their original model, the reason being that they had not been aware of the true thickness at the time of measurement. One of their final results (17B) was questionable, attributed by the participant to the fact that the polyethylene model represented an 'extreme matrix option' for soft waste. Their other results were in agreement with NPL.

Participants 9 and 12 submitted MDA values; however, they were well below the activity present. In the case of Participant 12, this was because their value was derived from a site fingerprint and was not actually a measure of what was in the NPL drum.

6.2 Caesium-137

Turning to the ^{137}Cs results, here 17 out of the 29 final submitted results agreed with NPL. Again, Participant 1 initially submitted results 1A to 1D, and with random uncertainties only. The revised uncertainties on the final plot were very similar to the original values and did not change the classification of their data (result 1A changed from 'questionable' to 'in agreement', but this was for the reason given on page 8 above – incidentally, results 4B and 8A changed to 'in agreement' for the same reason). Again, Participant 1 used their second model to produce results 1E to 1H, which were closer to the true value. Participant 11's initial result (11A) was discrepant and low, and again they submitted a second value (11B) which agreed with NPL. Again, Participant 8 submitted a revised uncertainty (on value 8B). Participant 7 was again discrepant using their initial model but in agreement when using their NPL drum model.

The results for Participants 2 and 5 were low and discrepant this time. Participant 2 suspected their result may be due to the low activity of the source and/or the fact that a segmented count was carried out and that the ^{137}Cs was found in fewer than half of the segments (n.b. The value submitted by participant 2 was a revised value, the original value having been based on an assumed, but incorrect, tare for the weight of the drum in their SGS program.). Participant 5 reported that their result (as for the other two radionuclides) was based on the sum of the positive measurements in 8 segments and did not include MDA calculations for radionuclides not being measured; however, had they done so, the results would have actually been much

higher than the NPL value. They also pointed out that their monitor was set up for counting drums with activities typically > 10 Bq g^{-1} and that the equipment in its current configuration and location was not suitable for clearance monitoring and is not used for this purpose. They regarded the results of this exercise as merely providing confirmation that the monitor was capable of detecting the radionuclides in the NPL drum.

Participant 3 submitted a questionable (high) result, curiously as they had been accurate with the ^{241}Am measurement. Participant 6 reported a questionable value. Participant 10 submitted two results using a plastic-scintillator based system. They were both discrepant (high), but this was because the system measured gross γ-emissions and in routine use attributes all the observed γ-emissions to the most prevalent γ-emitter within a known fingerprint.

Participants 9, 12 and 14 submitted MDA values for ^{137}Cs.

6.3 Cobalt-60

The data for ^{60}Co appeared to follow a similar pattern to ^{137}Cs. Here, 13 out of 32 values agreed with NPL. Participant 1's final results 1A to 1D had slightly revised uncertainties, and they submitted a second set (1E to 1H) using their second model. All their final data were questionable. Again, Participant 11's initial result was discrepant and a second value (11B) was submitted, and although it was closer to the true activity it was still discrepant. Participant 8 submitted results for both the principal lines (1173 keV and 1333 keV) and again submitted a second data set with revised uncertainties. Participants 3's result was again questionable, and participant 7's first result was discrepant and their second in agreement. Participant 6 this time submitted a discrepant (low) result which they attributed to the low activity of the source which had resulted in the software sometimes not seeing both principal peaks and consequently rejecting some of the counts. Participant 4 submitted a questionable value (4B) for their triple-detector instrument. Participants 13 and 15 submitted discrepant (high) results. In the case of Participant 15 it was very high, and the reasons for this are not clear. They were using a 180L drum calibration and were measuring in a varying background field, which may be partly the reason. Participant 5's result was again discrepant and low. Participant 10's plastic scintillator measurement yielded values which, although questionable, were much closer to the true value.

Three data points were affected by NPL's revised data analysis method – 4B, 10A and 10B (all going from 'discrepant' to 'questionable').

Participant 2, 9, 12 and 14 submitted MDA values, participant 2's value being lower than the true value.

7. CONCLUSIONS & RECOMMENDATIONS

In the final data set (i.e. excluding MDA submissions and excluding the one value submitted for the total activity in the drum), 51 of the 88 results were found to be in

agreement with the NPL value. Twenty-four of the remaining 37 results (all of which were discrepant or questionable) were either explained by the participants concerned or had been revised by the participants to provide supplementary values. This still left 13 results either discrepant or questionable for no obvious reason. Most of these problems arose with ^{137}Cs and ^{60}Co. Contributory factors seemed to be the low activities present of these radionuclides and (in the case of measurements involving Segmented Gamma Scanners) the presence of what were, in effect, horizontal layers of sample within the drum.

At the post-comparison workshop, the delegates were asked if the observed discrepancies at that time represented a problem with measuring real waste. None of the delegates said that they did. However, NPL is happy to advise any laboratories with remaining discrepancies on how to resolve them.

The exercise highlighted differences between laboratories who had used ISOCS and facilitated the exchange of models between these laboratories. It was felt at the workshop that it may be useful for NPL to set up a modelling forum to continue this and help the wider measurement community. The exercise has also emphasised the importance of a good knowledge of a sample in modelling γ detection efficiencies.

A wide range of uncertainties was quoted in this exercise (even within sub-groups using the same technique), suggesting a need in some cases for guidance in the compilation of budgets. Measurement Good Practice Guide GPG34 (‘Radiometric Non-Destructive Assay’) provides some advice on uncertainties for samples of this type, but if more detail is required it would be timely for NPL to revise the guide.

It is of concern that some of the quoted MDA values were below the activity concentration actually present. Again, NPL would be happy to advise users on this subject.

A second comparison, based on a more challenging sample (e.g. with a heterogeneous activity distribution), was requested by the participants.

It is suggested that:

- Participants quoting discrepant or questionable data, or quoting MDA values lower than the activity present should investigate the causes, taking advice from NPL if needed;
- NPL should run a second such comparison based on a drum containing a heterogeneous distribution of activity;
- NPL should consider setting up a forum for discussion of mathematical modelling techniques in waste assay;
- NPL should revise Measurement Good Practice Guide GPG34 (‘Radiometric Non-Destructive Assay’) so that it better assists users in compiling uncertainty budgets for measurements of sources like the NPL drum.

8. ACKNOWLEDGEMENTS

The author wishes to thank:

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Miss J Wong for organising the transport of the drum;

Mr P H Burgess for reviewing this report and for his advice throughout the project.

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9. REFERENCES

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[3] RORABACHER, D.B. 'Statistical Treatment for Rejection of Deviant Values: Critical Values of Dixon's "Q" Parameter and related Subrange Ratios at the 95% Confidence Level', Anal. Chem., 1991, 63, 139-146.

10. TABLES

Table 1 - Principal radionuclides in NPL standard source

Radionuclide	Decay mode	Activity concentration (averaged across contents of drum) @ 1200 GMT 1/12/07 (Bq g^{-1})	Standard uncertainty (k=1) (Bq g^{-1})	Standard uncertainty (k=1) (%)
^{241}Am	α/γ	0.2594	0.0015	0.57
^{137}Cs	β^-, β^-/γ	0.0295	0.0003	0.87
^{60}Co	β^-/γ	0.03731	0.00023	0.62

Table 2 – Reported results for ^{241}Am for Participants 1 to 7 and results of NPL data analyses

NPL activity concentration = (0.2594 ± 0.0015) Bq g^{-1} (k=1) Reference time = 1200 GMT 1 December 2006

Participant code	Reported ^{241}Am activity concentration (Bq g^{-1})	Reported uncertainty (k=1) (Bq g^{-1}, unless indicated)	Deviation from NPL value (%)	Z score	Zeta score	Result of outlier test	Conclusion
1A	0.190	20 % (0.0380)[1]	-26.66	-1.18	-1.82	Not outlier	In agreement
1B	0.188	20 % (0.0376)[2]	-27.65	-1.23	-1.91	Not outlier	In agreement
1C	0.189	20 % (0.0378)[3]	-27.33	-1.21	-1.88	Not outlier	In agreement
1D	0.186	20 % (0.0372)[4]	-28.27	-1.26	-1.97	Not outlier	In agreement
1E	0.278	0.058	7.17	0.32	0.32	Not outlier	In agreement
1F	0.252	0.051	-2.85	-0.13	-0.15	Not outlier	In agreement
1G	0.261	0.053	0.62	0.03	0.03	Not outlier	In agreement
1H	0.249	0.050	-4.01	-0.18	-0.21	Not outlier	In agreement
2	0.2103[5]	0.0601	-18.93	-0.84	-0.82	Not outlier	In agreement
3	0.271	25 % (0.0678)	4.47	0.20	0.17	Not outlier	In agreement
4A	0.21	50 % (0.11)	-19.04	-0.85	-0.47	Not outlier	In agreement
4B	2.051	24 % (0.4922)	690.7	30.70	3.64	Not outlier	Discrepant
5	0.31	62 % (0.19)	19.51	0.87	0.26	Not outlier	In agreement
6	0.257	0.021	-0.93	-0.04	-0.11	Not outlier	In agreement
7A	0.766	7.30 % (0.0559)	195.3	8.68	9.06	Not outlier	Discrepant
7B	0.2196	5.3 % (0.01164)	-15.34	-0.68	-3.39	Not outlier	Questionable

[1] Replaces original submitted value of 0.003 Bq g^{-1}
[2] Replaces original submitted value of 0.002 Bq g^{-1}
[3] Replaces original submitted value of 0.005 Bq g^{-1}
[4] Replaces original submitted value of 0.004 Bq g^{-1}
[5] Replaces original submitted value of 0.2321 Bq g^{-1}

Table 3 – Reported results for ^{241}Am for Participants 8 to 17 and results of NPL data analyses

NPL activity concentration = (0.2594 ± 0.0015) Bq g^{-1} (k=1) Reference time = 1200 GMT 1 December 2006

Participant code	Reported ^{241}Am activity concentration (Bq g^{-1})	Reported uncertainty (k=1) (Bq g^{-1}, unless indicated)	Deviation from NPL value (%)	Z score	Zeta score	Result of outlier test	Conclusion
8A	0.244	0.165	-5.94	-0.26	-0.09	Not outlier	In agreement
8B	0.244	0.056	-5.94	-0.26	-0.27	Not outlier	In agreement
11A	0.138	0.014	-46.80	-2.08	-8.62	Not outlier	Questionable
11B	0.176	0.019	-32.15	-1.43	-4.38	Not outlier	Questionable
17A	0.28[1]	0.025	7.94	0.35	0.82	Not outlier	In agreement
17B	0.18[2]	0.019	-30.61	-1.36	-4.17	Not outlier	Questionable
17C	0.27[3]	0.026	4.09	0.18	0.41	Not outlier	In agreement
17D	0.31[4]	0.027	19.51	0.87	1.87	Not outlier	In agreement
17E	0.22[5]	0.024	-15.19	-0.68	-1.64	Not outlier	In agreement
17F	0.31[6]	0.027	19.51	0.87	1.87	Not outlier	In agreement
17G	0.26[7]	0.027	0.23	0.01	0.02	Not outlier	In agreement

[1] Replaces original submitted value of (0.362 ± 0.032) Bq g^{-1}
[2] Replaces original submitted value of (0.238 ± 0.025) Bq g^{-1}
[3] Replaces original submitted value of (0.347 ± 0.034) Bq g^{-1}
[4] Replaces original submitted value of (0.401 ± 0.036) Bq g^{-1}
[5] Replaces original submitted value of (0.283 ± 0.031) Bq g^{-1}
[6] Replaces original submitted value of (0.397 ± 0.035) Bq g^{-1}
[7] Replaces original submitted value of (0.307 ± 0.032) Bq g^{-1}

Table 4 – Reported results for ^{137}Cs for Participants 1 to 7 and results of NPL data analyses

NPL activity concentration = (0.0295 ± 0.0003) Bq g^{-1} (k=1) Reference time = 1200 GMT 1 December 2006

Participant code	Reported ^{137}Cs activity concentration (Bq g^{-1})	Reported uncertainty (k=1) (Bq g^{-1}, unless indicated)	Deviation from NPL value (%)	Z score	Zeta score	Result of outlier test	Conclusion
1A	0.025	8 % (0.0020)[1]	-16.10	-1.93	-2.37	Not outlier	In agreement
1B	0.024	8 % (0.0019)[2]	-17.51	-2.10	-2.62	Not outlier	Questionable
1C	0.024	8 % (0.0019)[3]	-19.49	-2.34	-2.99	Not outlier	Questionable
1D	0.023	8 % (0.0018)[4]	-22.88	-2.75	-3.66	Not outlier	Discrepant
1E	0.027	0.002	-8.47	-1.02	-1.24	Not outlier	In agreement
1F	0.026	0.002	-11.86	-1.42	-1.73	Not outlier	In agreement
1G	0.025	0.002	-15.25	-1.83	-2.23	Not outlier	In agreement
1H	0.023	0.002	-22.03	-2.64	-3.21	Not outlier	Discrepant
2	0.0118[5]	0.0031	-60.00	-7.20	-5.68	Not outlier	Discrepant
3	0.043	25 % (0.011)	45.76	5.49	1.26	Not outlier	Questionable
4A	0.0282	15 % (0.00423)	-4.41	-0.53	-0.31	Not outlier	In agreement
4B	0.0282	7 % (0.00197)	-4.41	-0.53	-0.65	Not outlier	In agreement
5	0.0053	59.5 % (0.0032)	-82.03	-9.84	-7.64	Not outlier	Discrepant
6	0.024	0.002	-18.64	-2.24	-2.72	Not outlier	Questionable
7A	0.0413	6.8 % (0.00281)	40.00	4.80	4.18	Not outlier	Discrepant
7B	0.0297	5.5 % (0.00163)	0.68	0.08	0.12	Not outlier	In agreement

[1] Replaces original submitted value of 0.001 Bq g^{-1}
[2] Replaces original submitted value of 0.000 Bq g^{-1}
[3] Replaces original submitted value of 0.002 Bq g^{-1}
[4] Replaces original submitted value of 0.001 Bq g^{-1}
[5] Replaces original submitted value of 0.01312 Bq g^{-1}

Table 5 – Reported results for ^{137}Cs for Participants 8 to 17 and results of NPL data analyses

NPL activity concentration = (0.0295 ± 0.0003) Bq g^{-1} (k=1) Reference time = 1200 GMT 1 December 2006

Participant code	Reported ^{137}Cs activity concentration (Bq g^{-1})	Reported uncertainty (k=1) (Bq g^{-1}, unless indicated)	Deviation from NPL value (%)	Z score	Zeta score	Result of outlier test	Conclusion
8A	0.0276	0.0127	-6.44	-0.77	-0.15	Not outlier	In agreement
8B	0.0276	0.005	-6.44	-0.77	-0.38	Not outlier	In agreement
10A	0.1056	0.002189	258.0	30.96	34.44	Not outlier	Discrepant
10B	0.0959	0.003061	225.1	27.01	21.59	Not outlier	Discrepant
11A	0.021	0.001	-28.81	-3.46	-8.14	Not outlier	Discrepant
11B	0.025	0.002	-15.25	-1.83	-2.23	Not outlier	In agreement
17A	0.0257	0.0020	-12.91	-1.55	-1.89	Not outlier	In agreement
17B	0.0278	0.0022	-5.85	-0.70	-0.77	Not outlier	In agreement
17C	0.0259	0.0020	-12.22	-1.47	-1.76	Not outlier	In agreement
17D	0.0284	0.0022	-3.59	-0.43	-0.48	Not outlier	In agreement
17E	0.0296	0.0024	0.29	0.03	0.04	Not outlier	In agreement
17F	0.0283	0.0022	-4.10	-0.49	-0.55	Not outlier	In agreement
17G	0.0280	0.0016	-5.22	-0.63	-0.95	Not outlier	In agreement

Table 6 – Reported results for ^{60}Co for Participants 1 to 7 and results of data analyses

NPL activity concentration = (0.03731 ± 0.00023) Bq g^{-1} (k=1) Reference time = 1200 GMT 1 December 2006

Participant code	Reported ^{60}Co activity concentration (Bq g^{-1})	Reported uncertainty (k=1) (Bq g^{-1}, unless indicated)	Deviation from NPL value (%)	Z score	Zeta score	Result of outlier test	Conclusion
1A	0.031	6 % (0.0019)[1]	-16.91	-1.84	-3.37	Not outlier	Questionable
1B	0.031	6 % (0.0019)[2]	-16.91	-1.84	-3.37	Not outlier	Questionable
1C	0.031	6 % (0.0019)[3]	-16.91	-1.84	-3.37	Not outlier	Questionable
1D	0.029	6 % (0.0017)[4]	-22.27	-2.42	-4.73	Not outlier	Questionable
1E	0.032	0.002	-14.23	-1.55	-2.64	Not outlier	Questionable
1F	0.029	0.002	-22.27	-2.42	-4.13	Not outlier	Questionable
1G	0.030	0.002	-19.59	-2.13	-3.63	Not outlier	Questionable
1H	0.029	0.002	-22.27	-2.42	-4.13	Not outlier	Questionable
3	0.0564	25 % (0.0141)	51.17	5.56	1.35	Not outlier	Questionable
4A	0.03621	15 % (0.0053)	-2.95	-0.32	-0.20	Not outlier	In agreement
4B	0.029	7 % (0.0020)	-22.27	-2.42	-4.07	Not outlier	Questionable
5	0.022	16.7 % (0.0037)	-41.03	-4.46	-4.16	Not outlier	Discrepant
6	0.009	0.001	-75.88	-8.25	-27.59	Not outlier	Discrepant
7A	0.0551	6.6 % (0.00364)	47.68	5.18	4.88	Not outlier	Discrepant
7B	0.0377	3.8 % (0.00143)	1.05	0.11	0.27	Not outlier	In agreement

[1] Replaces original submitted value of 0.001 Bq g^{-1}
[2] Replaces original submitted value of 0.001 Bq g^{-1}
[3] Replaces original submitted value of 0.002 Bq g^{-1}
[4] Replaces original submitted value of 0.001 Bq g^{-1}

Table 7 – Reported results for ^{60}Co for Participants 8 to 17 and results of data analyses

NPL activity concentration = (0.03731 ± 0.00023) Bq g^{-1} (k=1) Reference time = 1200 GMT 1 December 2006

Participant code	Reported ^{60}Co activity concentration (Bq g^{-1})	Reported uncertainty (k=1) (Bq g^{-1}, unless indicated)	Deviation from NPL value (%)	Z score	Zeta score	Result of outlier test	Conclusion
8A	0.0335	0.0133	-10.21	-1.11	-0.29	Not outlier	In agreement
8B	0.0347	0.0139	-7.00	-0.76	-0.19	Not outlier	In agreement
8C	0.0335	0.0060	-10.21	-1.11	-0.63	Not outlier	In agreement
8D	0.0347	0.0063	-7.00	-0.76	-0.41	Not outlier	In agreement
10A	0.0454	0.001188	21.68	2.36	6.69	Not outlier	Questionable
10B	0.0457	0.001508	22.49	2.44	5.50	Not outlier	Questionable
11A	0.023	0.001	-38.35	-4.17	-13.95	Not outlier	Discrepant
11B	0.027	0.002	-27.63	-3.00	-5.12	Not outlier	Discrepant
13	0.89	0.30	2285	248.42	2.84	Not outlier	Discrepant
15	7.1	2.3 % (0.16)	18930	2057.58	43.25	Not outlier	Discrepant
17A	0.0368	0.0027	-1.23	-0.13	-0.17	Not outlier	In agreement
17B	0.0384	0.0029	2.79	0.30	0.35	Not outlier	In agreement
17C	0.0371	0.0028	-0.66	-0.07	-0.09	Not outlier	In agreement
17D	0.0399	0.0030	6.96	0.76	0.87	Not outlier	In agreement
17E	0.0417	0.0032	11.82	1.28	1.38	Not outlier	In agreement
17F	0.0398	0.0030	6.73	0.73	0.84	Not outlier	In agreement
17G	0.0399	0.0021	6.83	0.74	1.21	Not outlier	In agreement

Table 8 – Reported Minimum Detectable Activities for ^{241}Am, ^{137}Cs and ^{60}Co

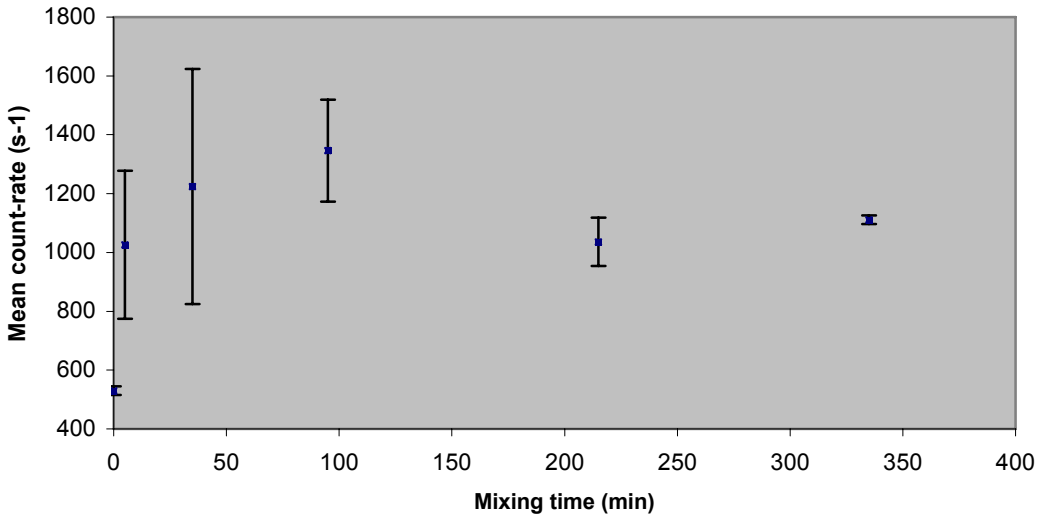
Participant code	Reported ^{241}Am MDA (Bq g^{-1})	Reported ^{137}Cs MDA (Bq g^{-1})	Reported ^{60}Co MDA (Bq g^{-1})
2	-	-	<0.01674
9	<0.004	<0.07	<0.06
12	<0.002997	<0.07118	<0.05529
14	-	<0.102	<0.227

Table 9 – Reported total activity concentrations

Participant code	Reported total activity concentration (Bq g^{-1})	Reported uncertainty (k=1) (Bq g^{-1})
16	0.081	0.003

11. FIGURES

Figure 1 – Variation of mean count-rate with mixing time for an ^{241}Am source on a NaI(Tl) gamma-counter



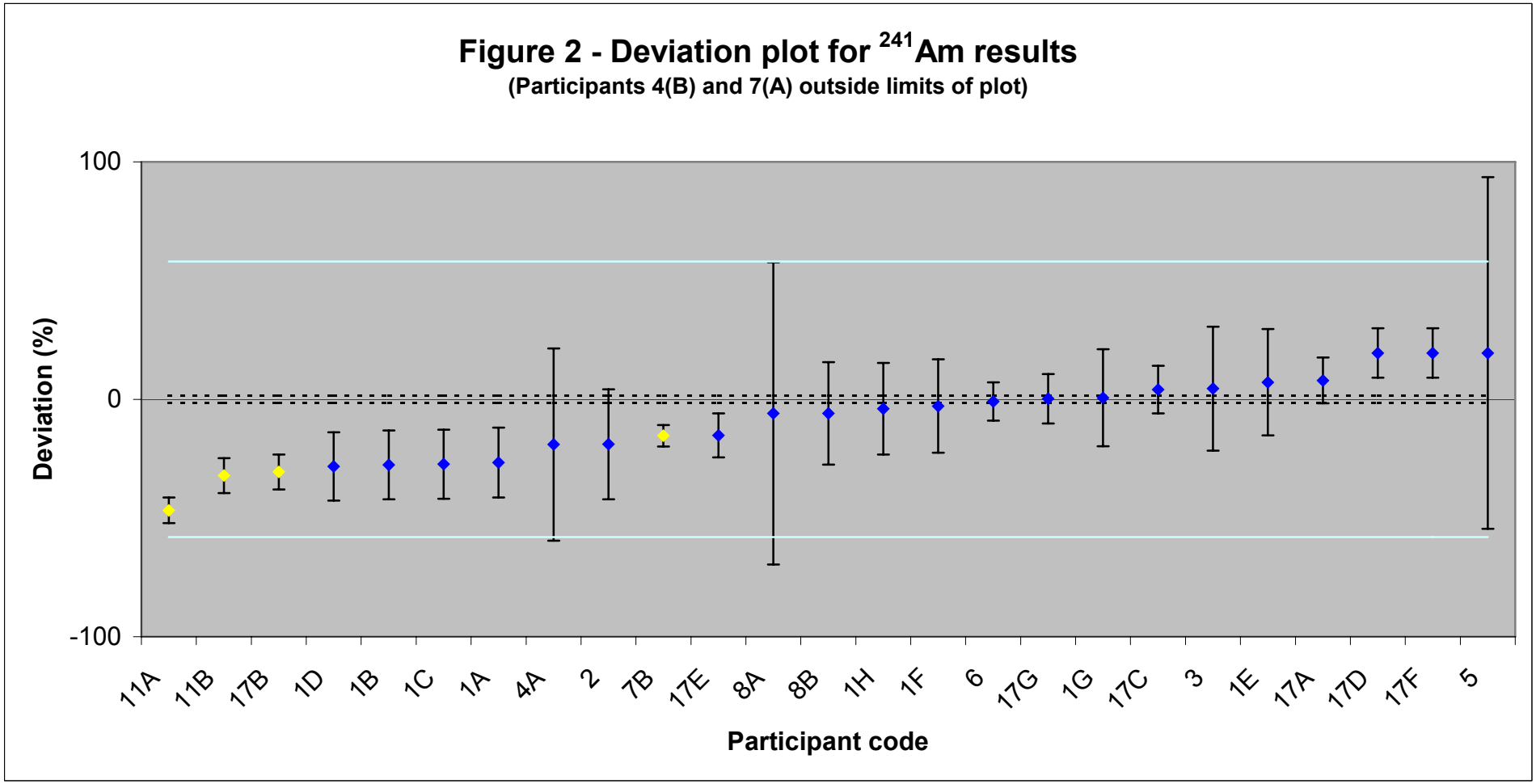


Figure 2 - Deviation plot for 241Am results
(Participants 4(B) and 7(A) outside limits of plot)
100
0
-100
Deviation (%)
11A
11B
17B
1D
1B
1C
1A
4A
2
7B
17E
8A
8B
1H
1F
6
17G
1G
17C
3
1E
17A
17D
17F
5
Participant code

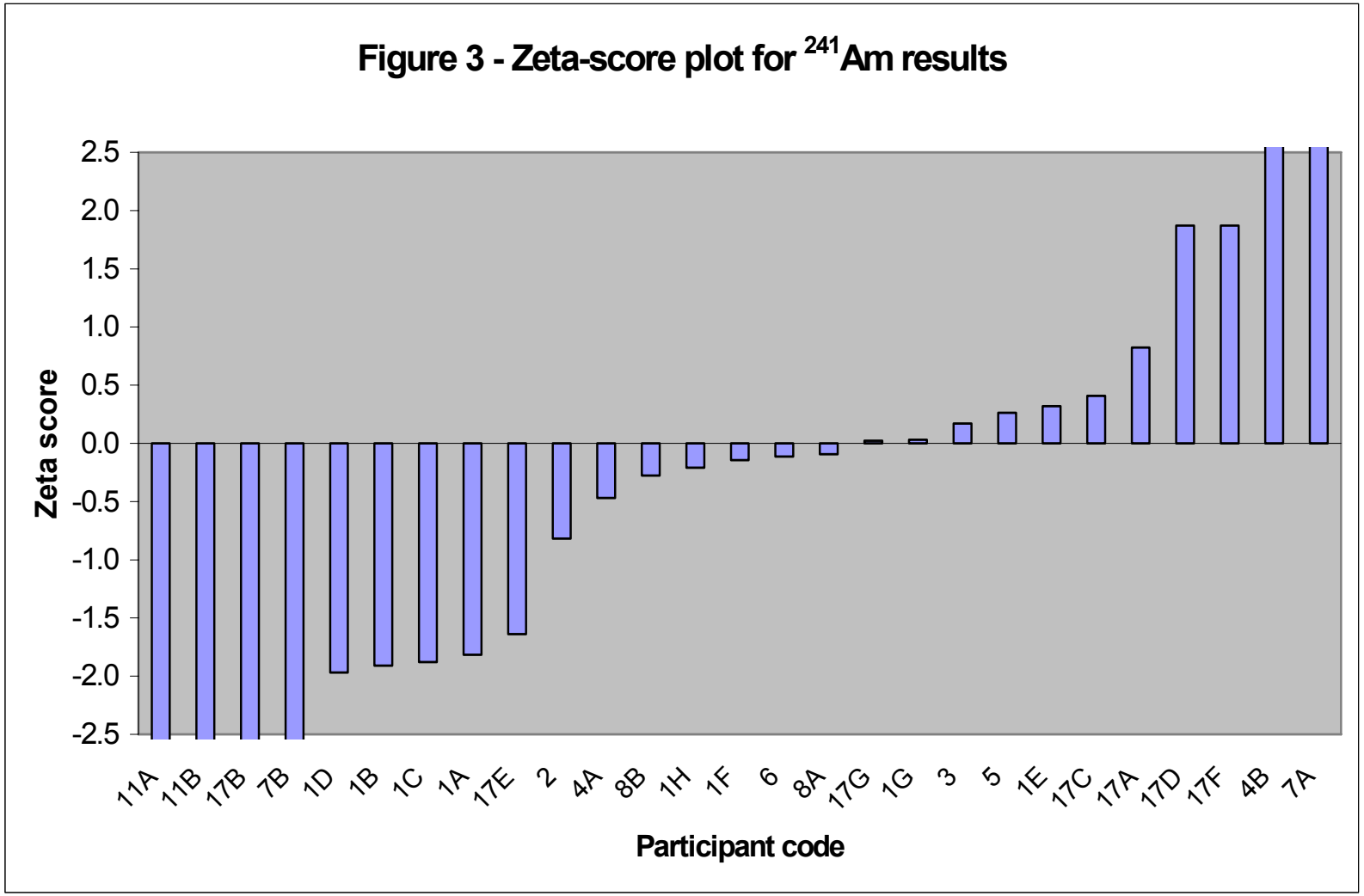


Figure 3 - Zeta-score plot for 241Am results
Zeta score
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
11A
11B
17B
7B
1D
1B
1C
1A
17E
2
4A
8B
1H
1F
6
8A
17G
1G
3
5
1E
17C
17A
17D
17F
4B
7A
Participant code

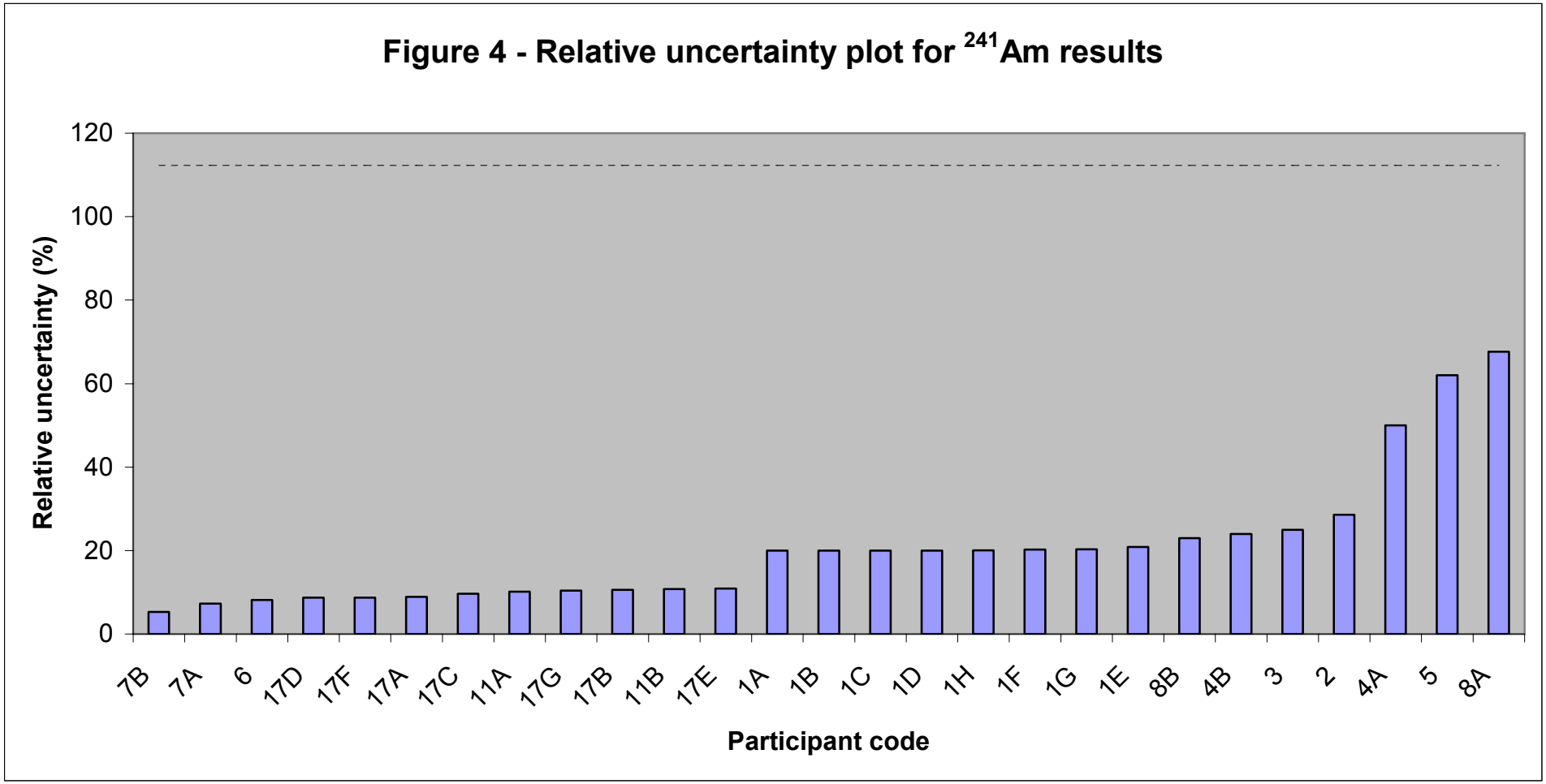


Figure 4 - Relative uncertainty plot for 241Am results
Relative uncertainty (%)
120
100
80
60
40
20
0
7B
7A
6
17D
17F
17A
17C
11A
17G
17B
11B
17E
1A
1B
1C
1D
1H
1F
1G
1E
8B
4B
3
2
4A
5
8A
Participant code

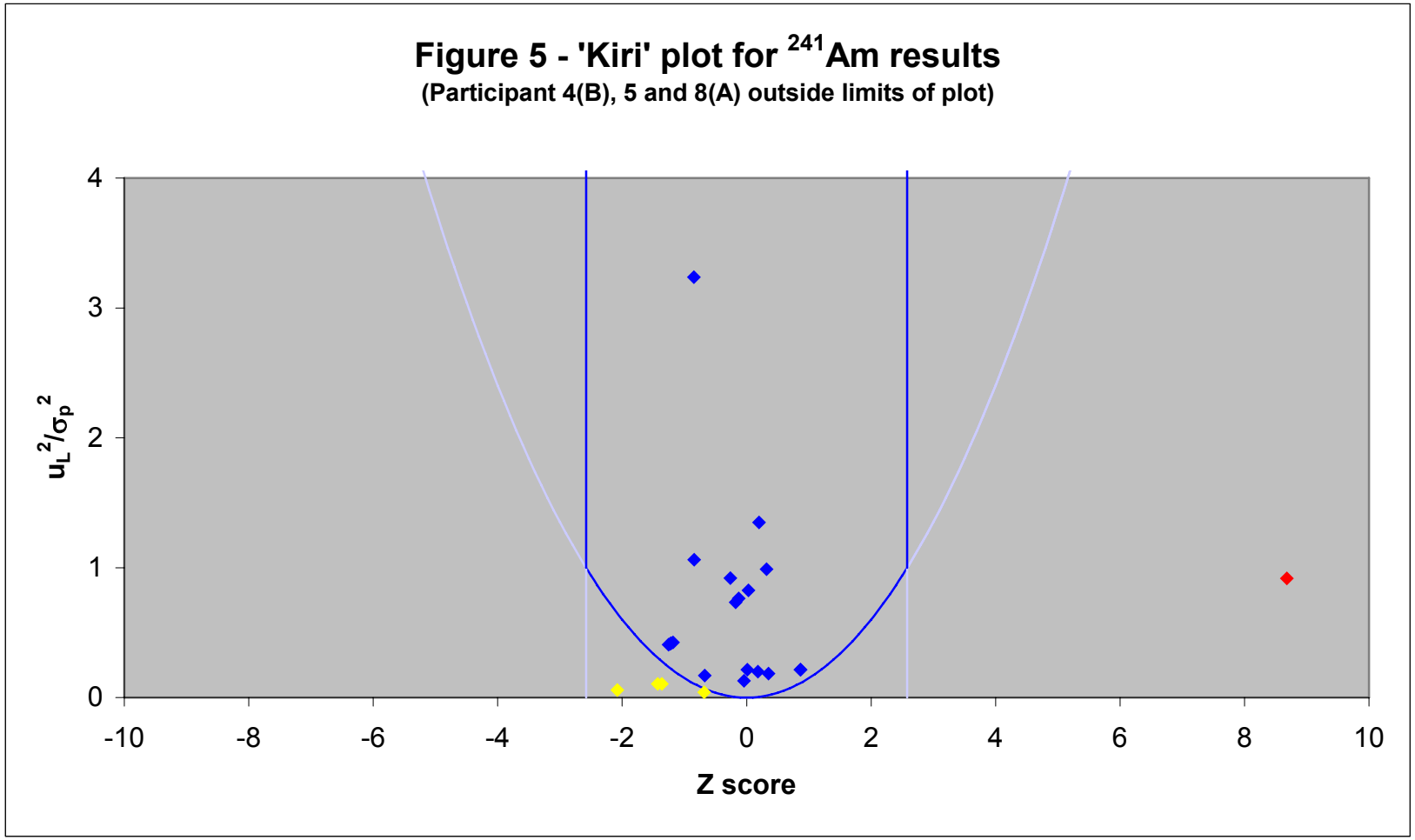


Figure 5 - 'Kiri' plot for 241Am results
(Participant 4(B), 5 and 8(A) outside limits of plot)
4
3
2
1
0
u_L^2/σ_p^2
-10
-8
-6
-4
-2
0
2
4
6
8
10
Z score

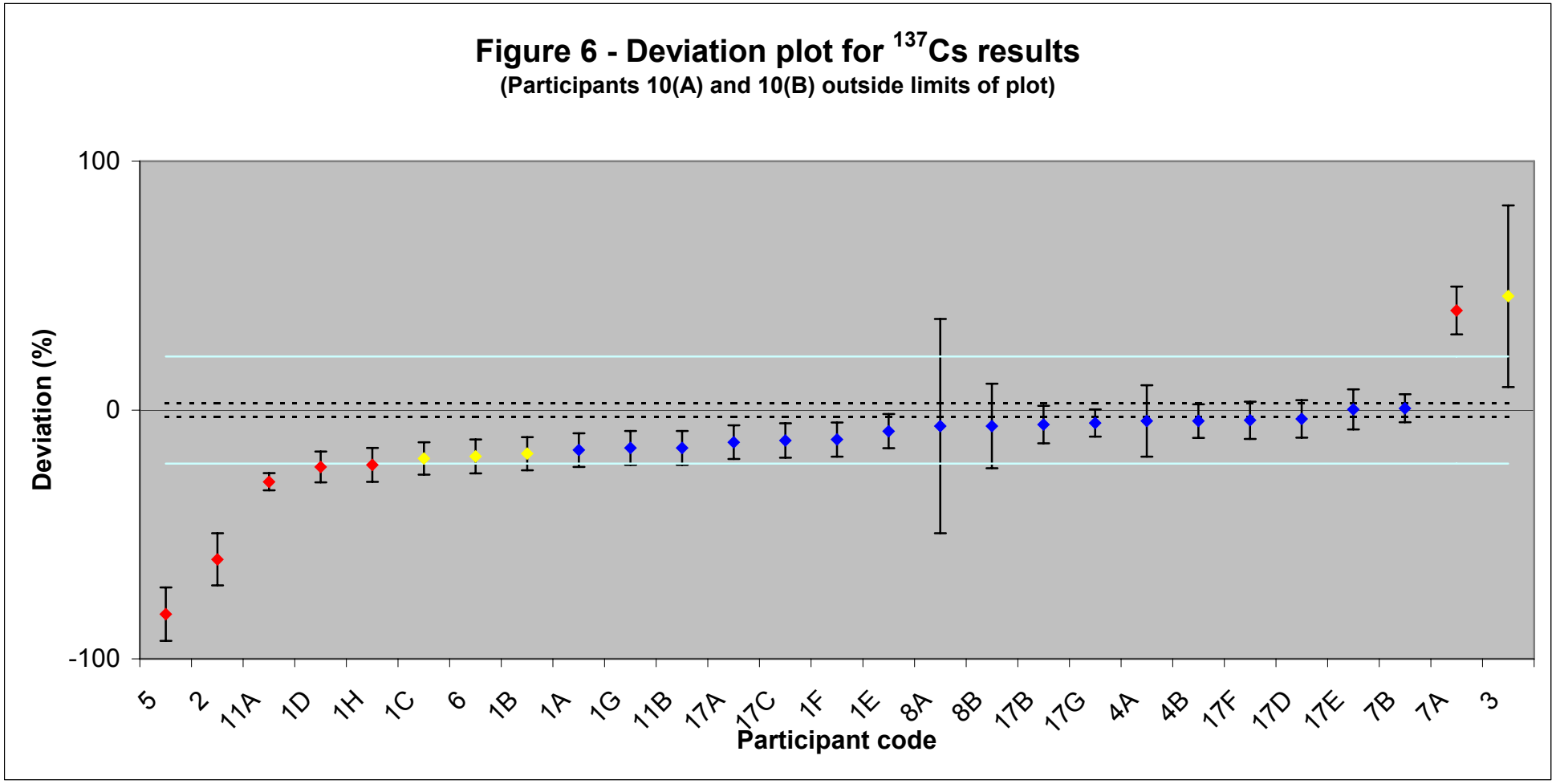


Figure 6 - Deviation plot for 137Cs results
(Participants 10(A) and 10(B) outside limits of plot)
Deviation (%)
100
0
-100
5
2
11A
1D
1H
1C
6
1B
1A
1G
11B
17A
17C
1F
1E
8A
8B
17B
17G
4A
4B
17F
17D
17E
7B
7A
3
Participant code

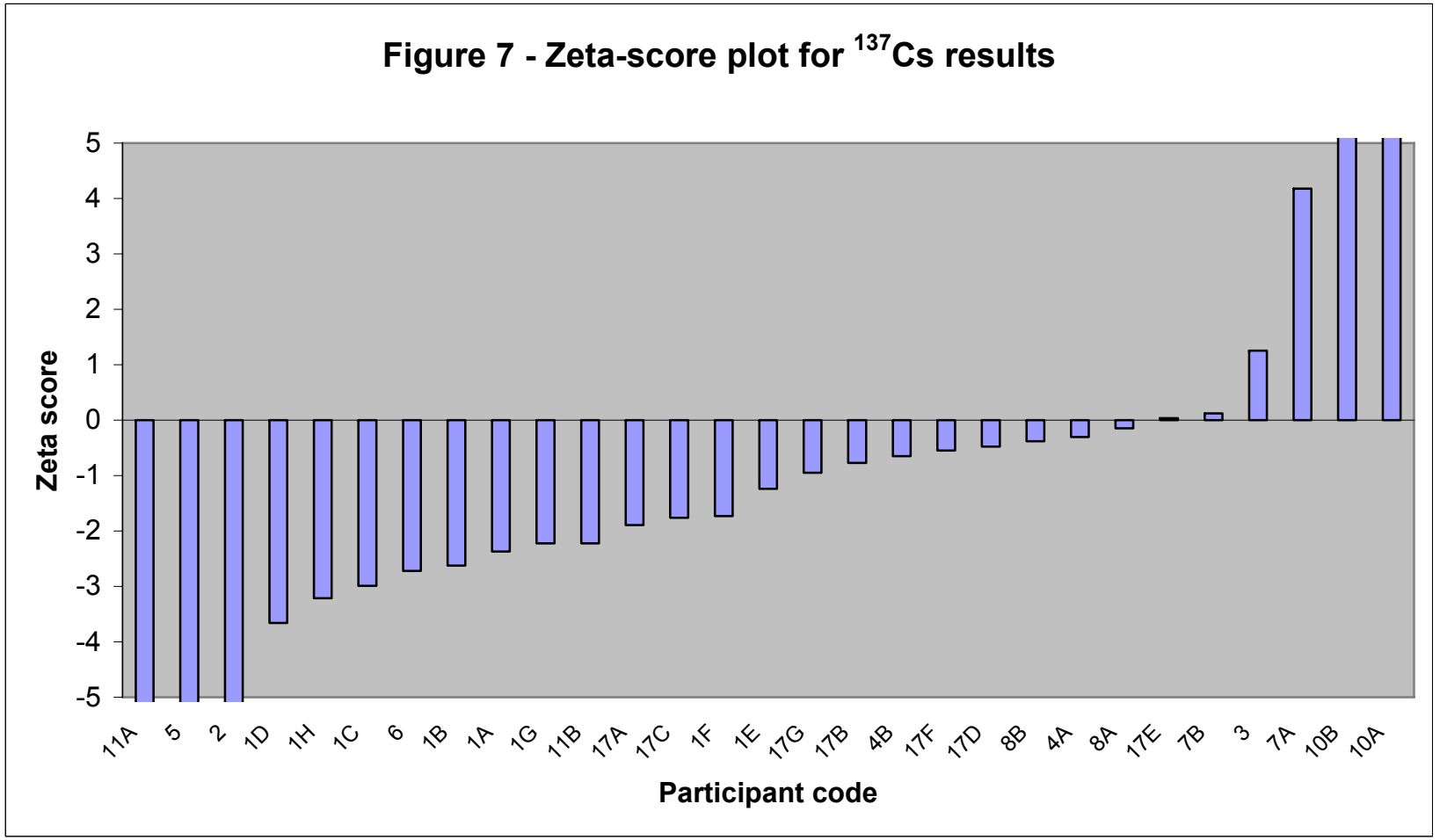


Figure 7 - Zeta-score plot for 137Cs results
Zeta score
5
4
3
2
1
0
-1
-2
-3
-4
-5
11A
5
2
1D
1H
1C
6
1B
1A
1G
11B
17A
17C
1F
1E
17G
17B
4B
17F
17D
8B
4A
8A
17E
7B
3
7A
10B
10A
Participant code

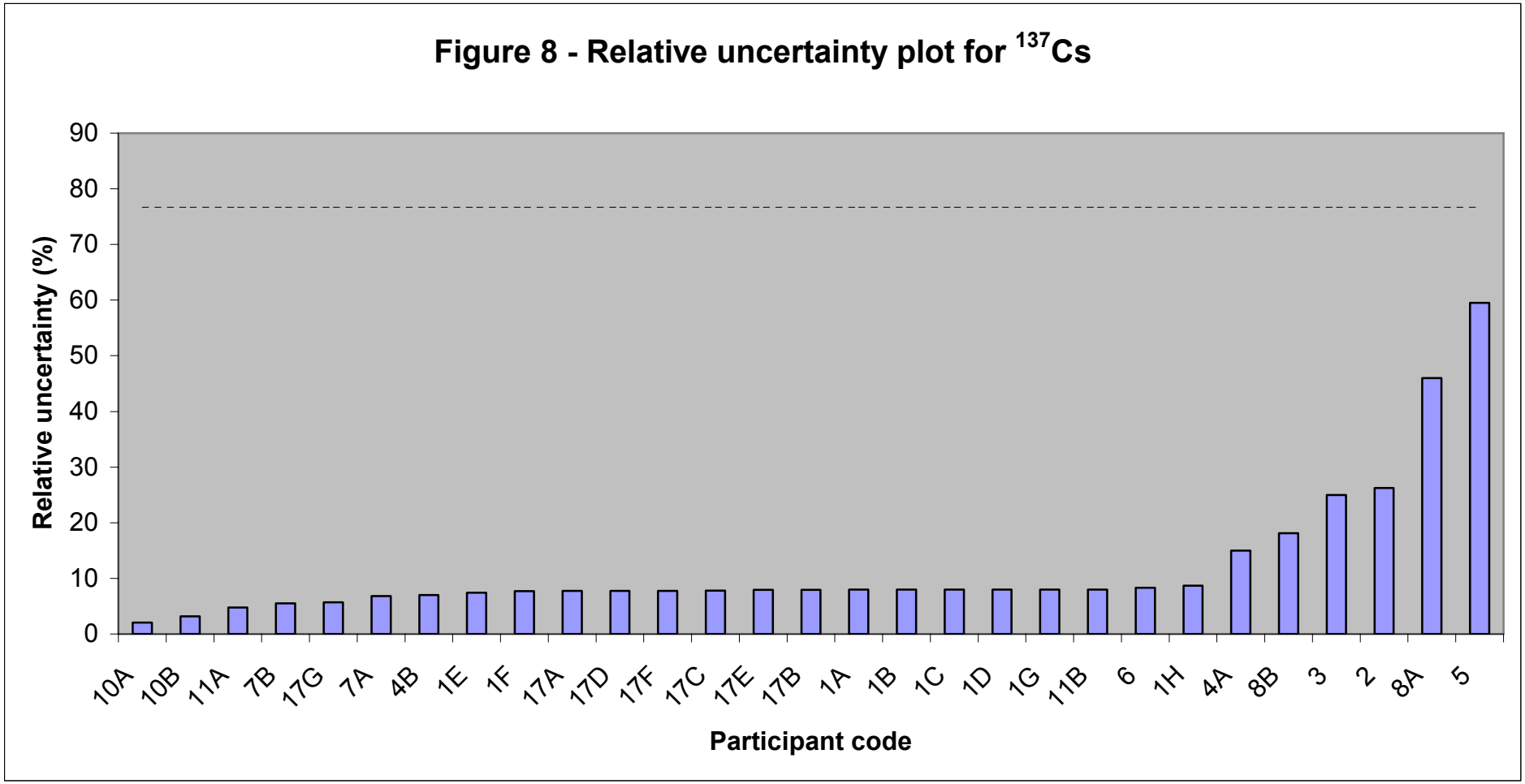


Figure 8 - Relative uncertainty plot for 137Cs
Relative uncertainty (%)
90
80
70
60
50
40
30
20
10
0
10A
10B
11A
7B
17G
7A
4B
1E
1F
17A
17D
17F
17C
17E
17B
1A
1B
1C
1D
1G
11B
6
1H
4A
8B
3
2
8A
5
Participant code

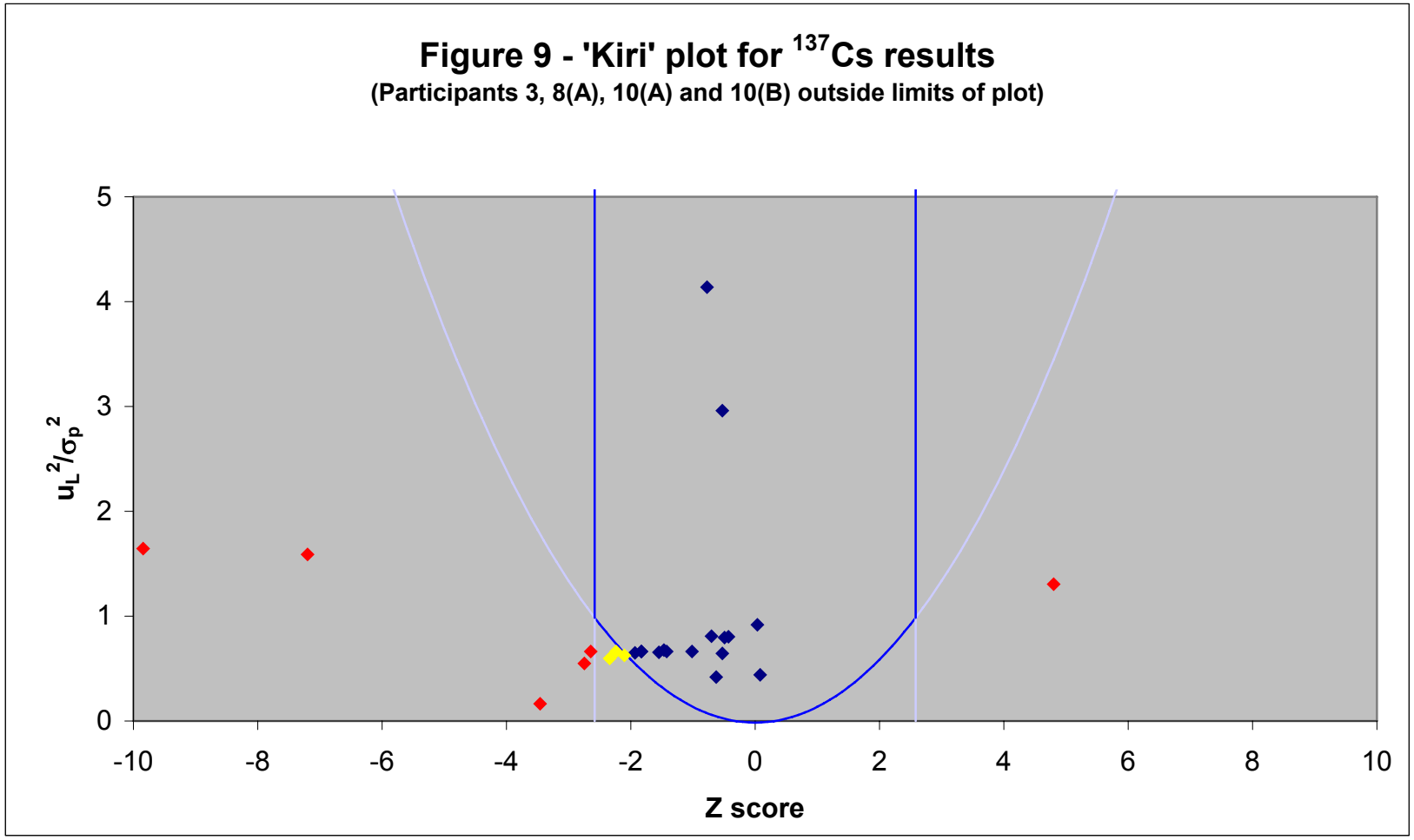


Figure 9 - 'Kiri' plot for 137Cs results
(Participants 3, 8(A), 10(A) and 10(B) outside limits of plot)
u_L^2/σ_p^2
Z score
0
1
2
3
4
5
-10
-8
-6
-4
-2
0
2
4
6
8
10

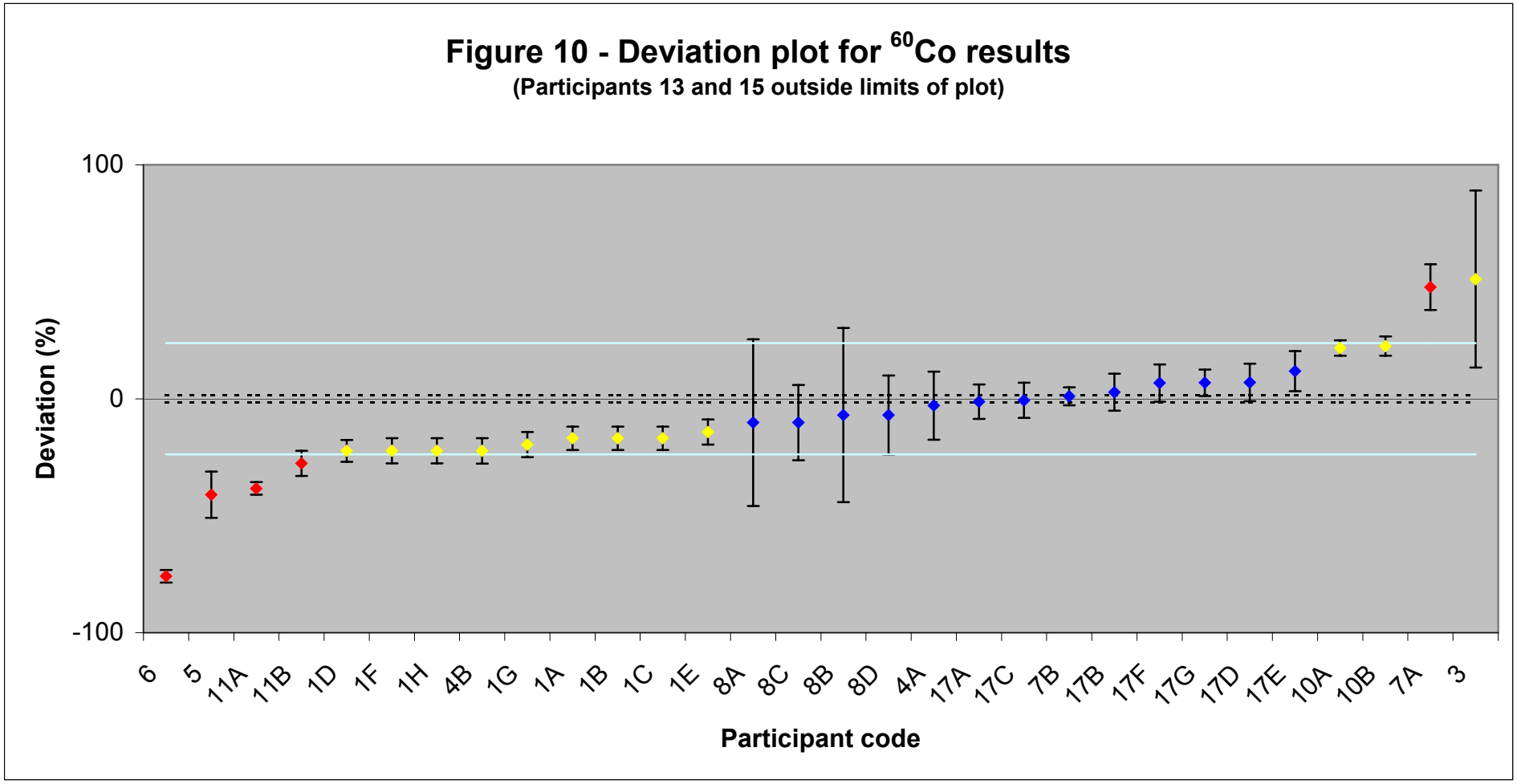


Figure 10 - Deviation plot for 60Co results
(Participants 13 and 15 outside limits of plot)
100
0
-100
Deviation (%)
6
5
11A
11B
1D
1F
1H
4B
1G
1A
1B
1C
1E
8A
8C
8B
8D
4A
17A
17C
7B
17B
17F
17G
17D
17E
10A
10B
7A
3
Participant code

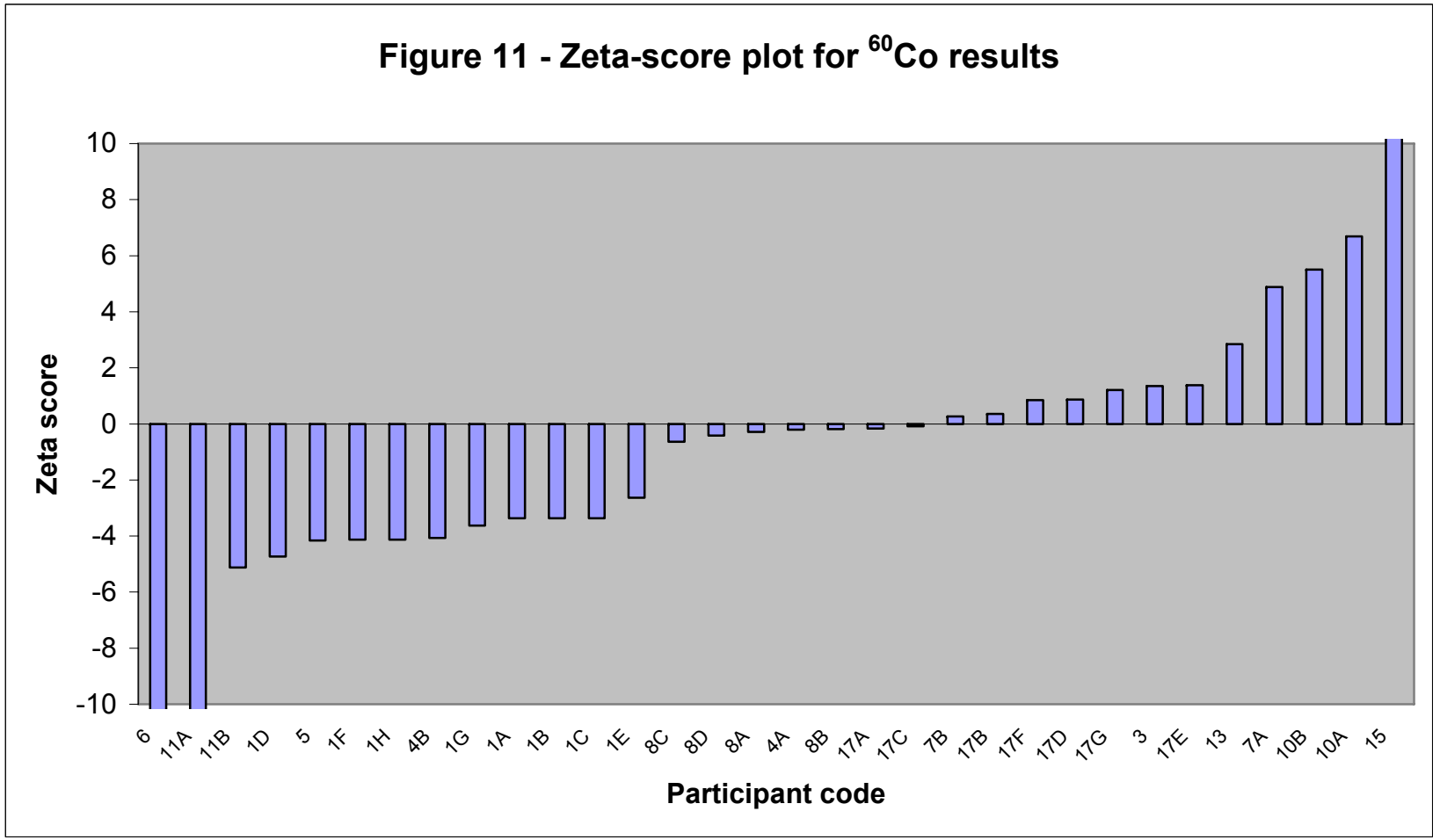


Figure 11 - Zeta-score plot for 60Co results
Zeta score
10
8
6
4
2
0
-2
-4
-6
-8
-10
6
11A
11B
1D
5
1F
1H
4B
1G
1A
1B
1C
1E
8C
8D
8A
4A
8B
17A
17C
7B
17B
17F
17D
17G
3
17E
13
7A
10B
10A
15
Participant code

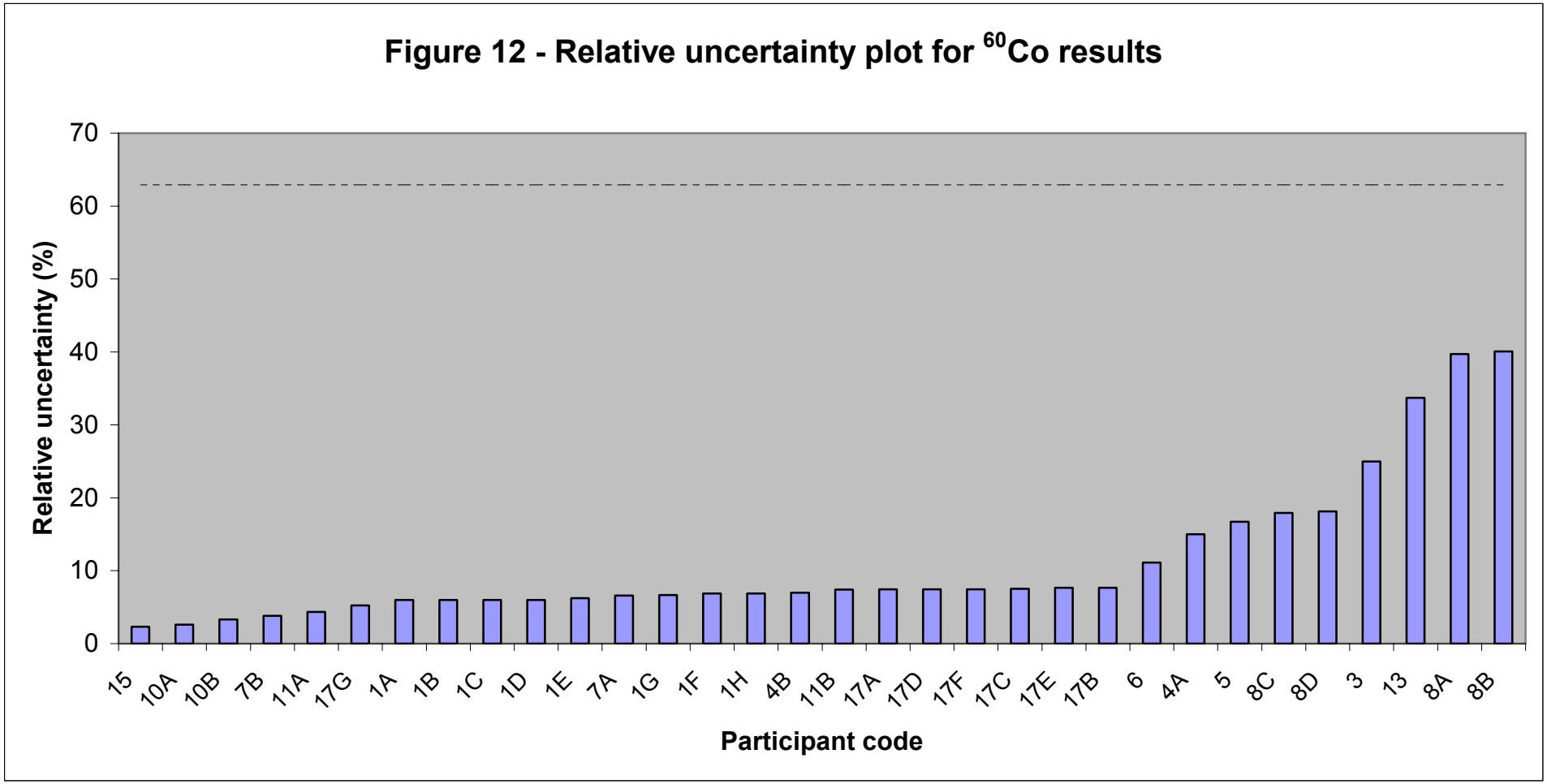


Figure 12 - Relative uncertainty plot for 60Co results
Relative uncertainty (%)
70
60
50
40
30
20
10
0
15
10A
10B
7B
11A
17G
1A
1B
1C
1D
1E
7A
1G
1F
1H
4B
11B
17A
17D
17F
17C
17E
17B
6
4A
5
8C
8D
3
13
8A
8B
Participant code

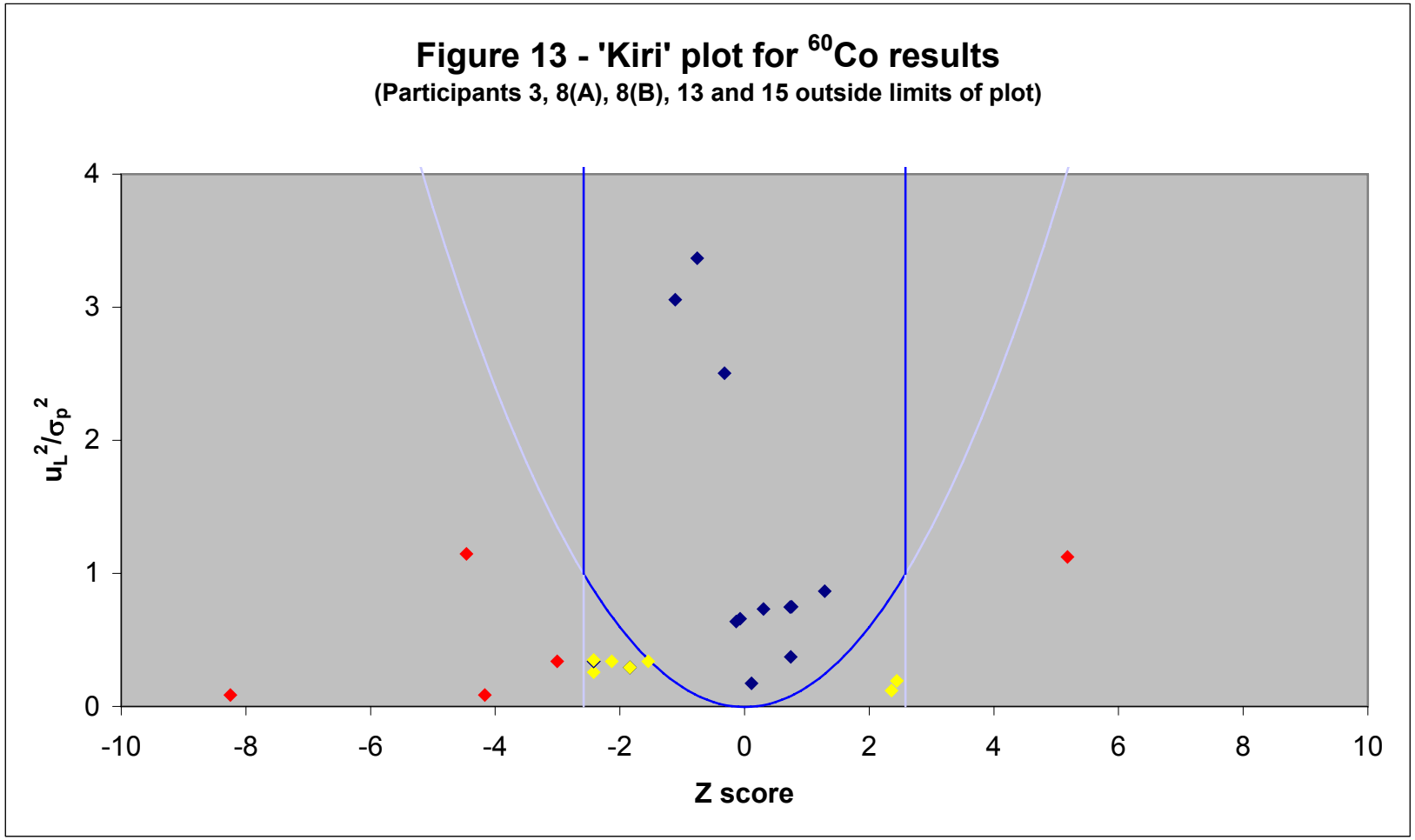


Figure 13 - 'Kiri' plot for 60Co results
(Participants 3, 8(A), 8(B), 13 and 15 outside limits of plot)
4
3
2
1
0
uL2/σp2
-10
-8
-6
-4
-2
0
2
4
6
8
10
Z score

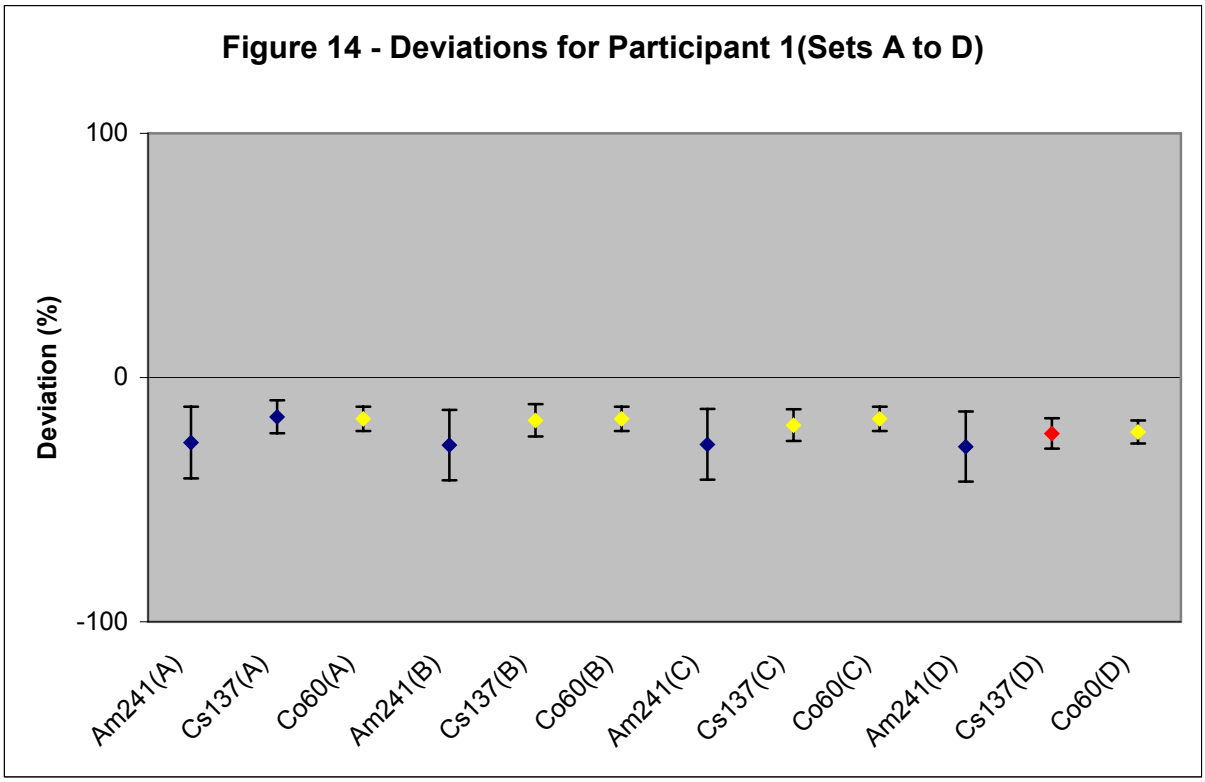


Figure 14 - Deviations for Participant 1(Sets A to D)
Deviation (%)
100
0
-100
Am241(A)
Cs137(A)
Co60(A)
Am241(B)
Cs137(B)
Co60(B)
Am241(C)
Cs137(C)
Co60(C)
Am241(D)
Cs137(D)
Co60(D)

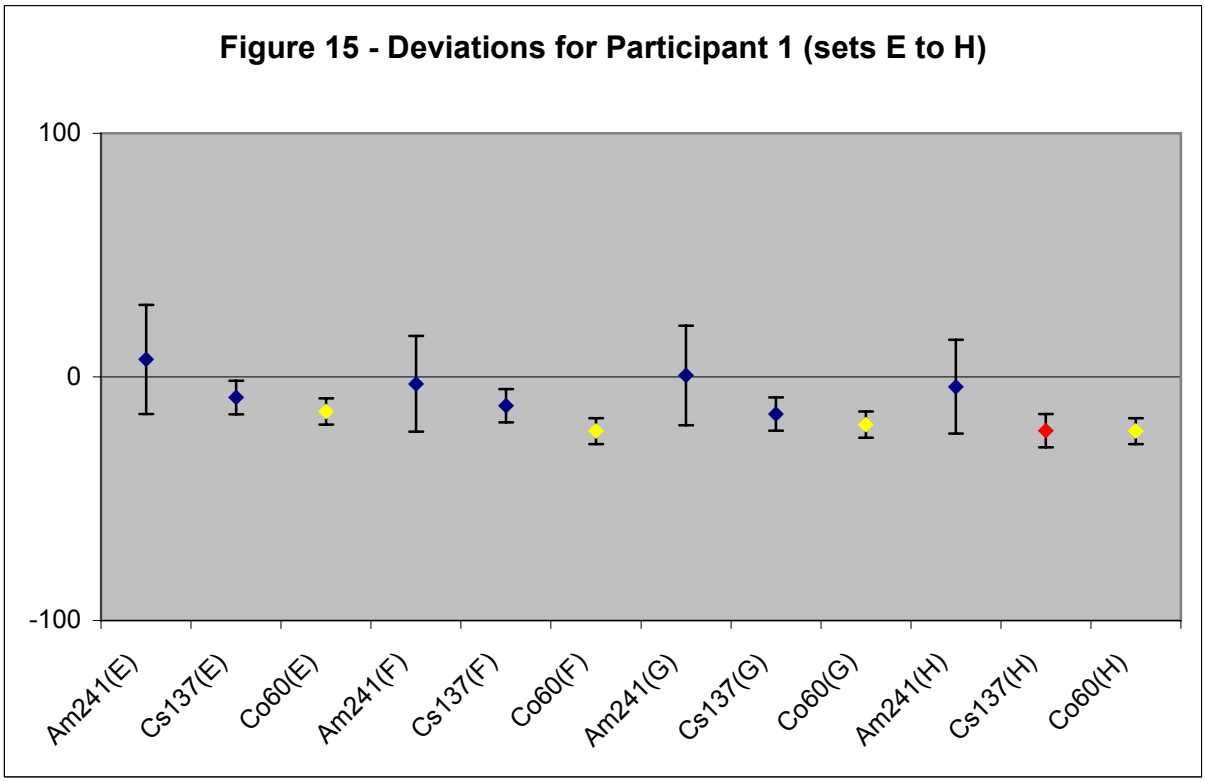


Figure 15 - Deviations for Participant 1 (sets E to H)
100
0
-100
Am241(E)
Cs137(E)
Co60(E)
Am241(F)
Cs137(F)
Co60(F)
Am241(G)
Cs137(G)
Co60(G)
Am241(H)
Cs137(H)
Co60(H)

Figure 16 - Devations for Participant 2

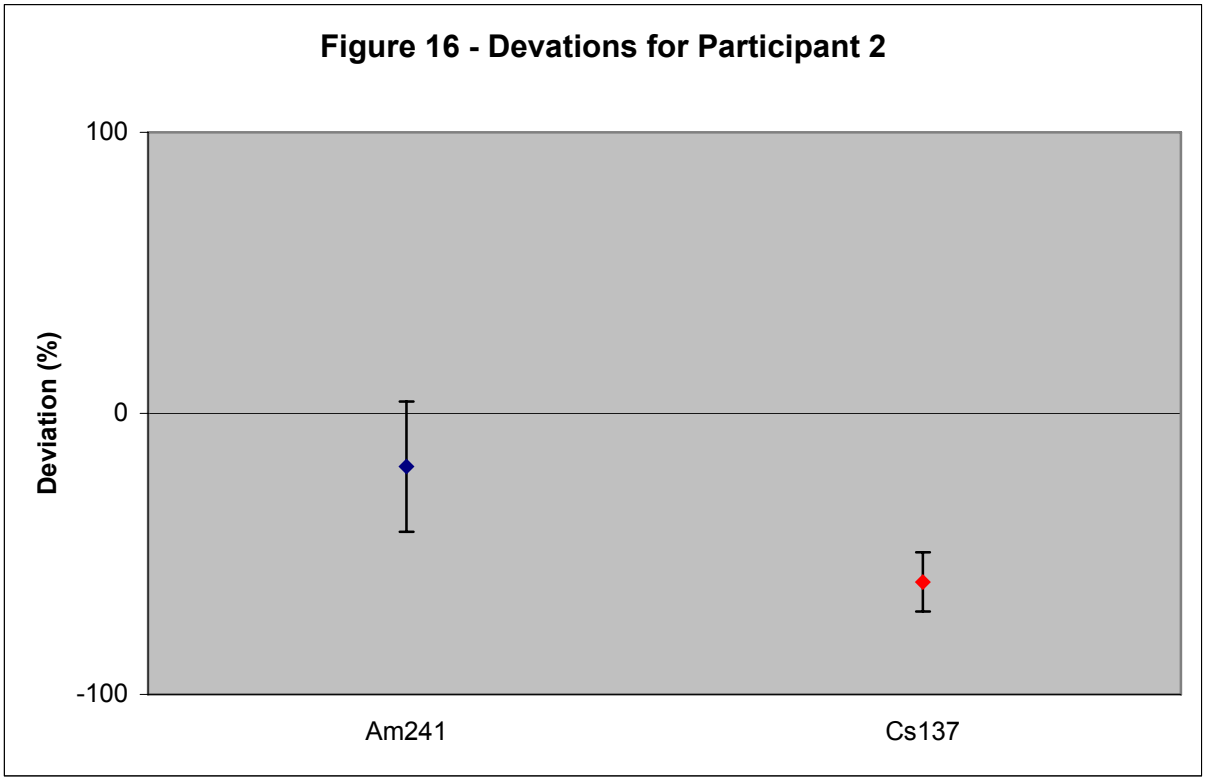


Figure 17 - Devations for Participant 3

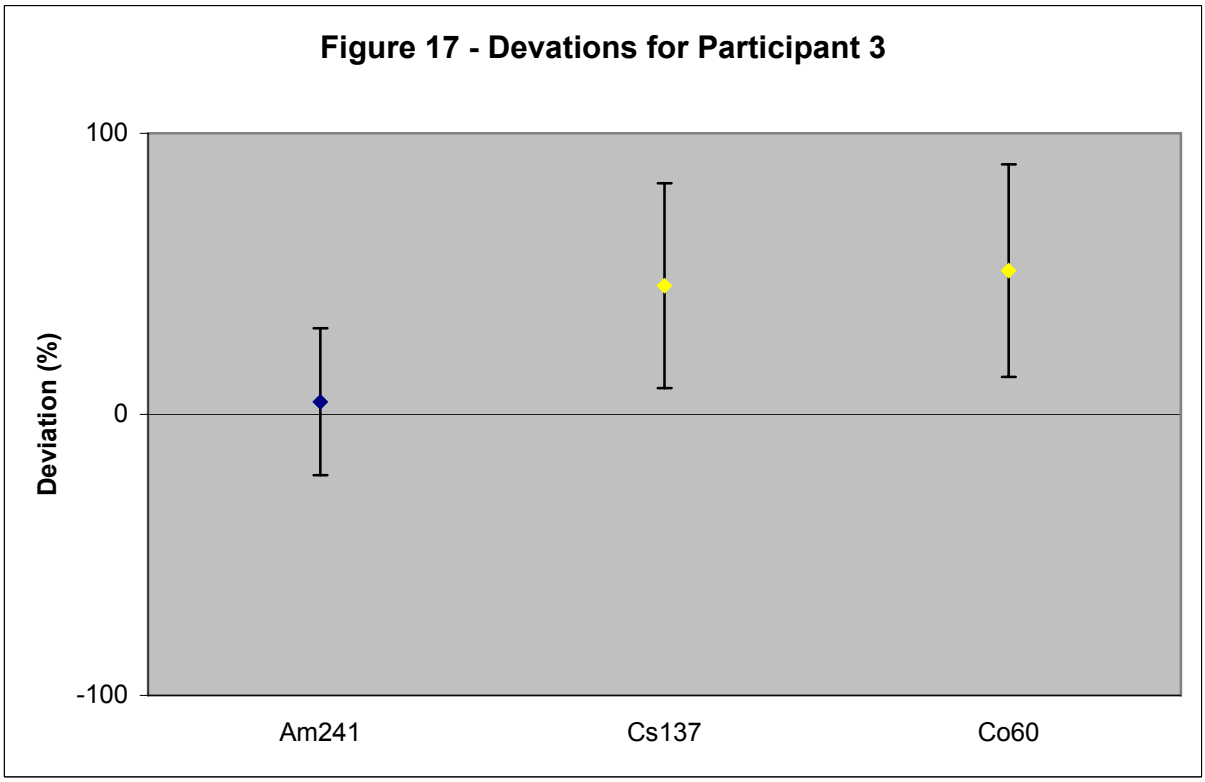


Figure 18 - Devations for Participant 4 (sets A and B) (Am241(B) outside limits of plot)

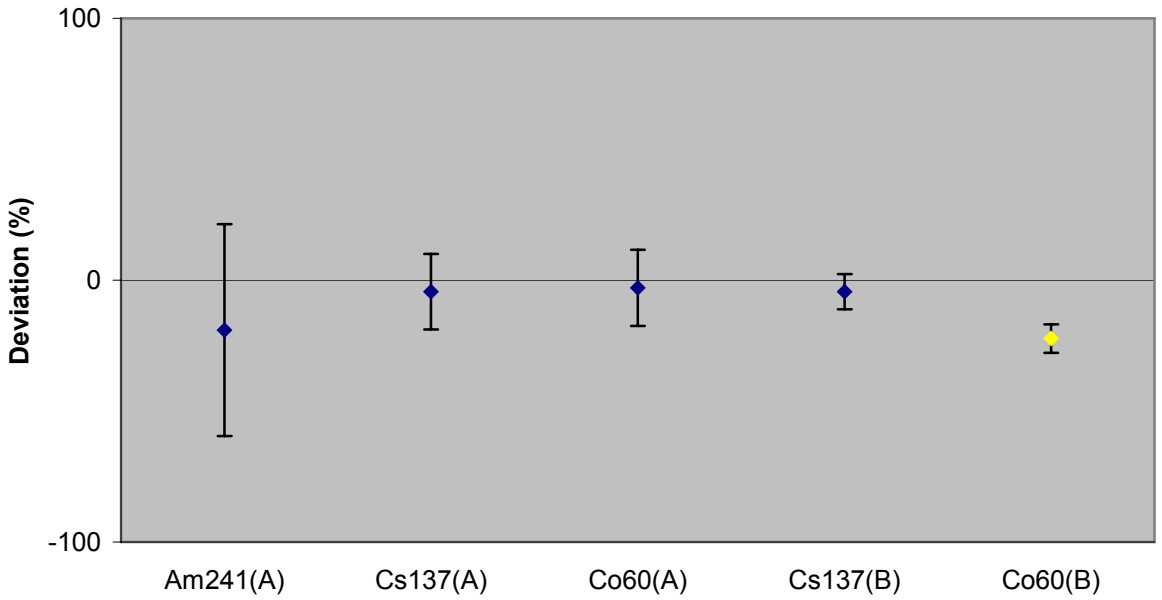


Figure 19 - Deviations for Participant 5

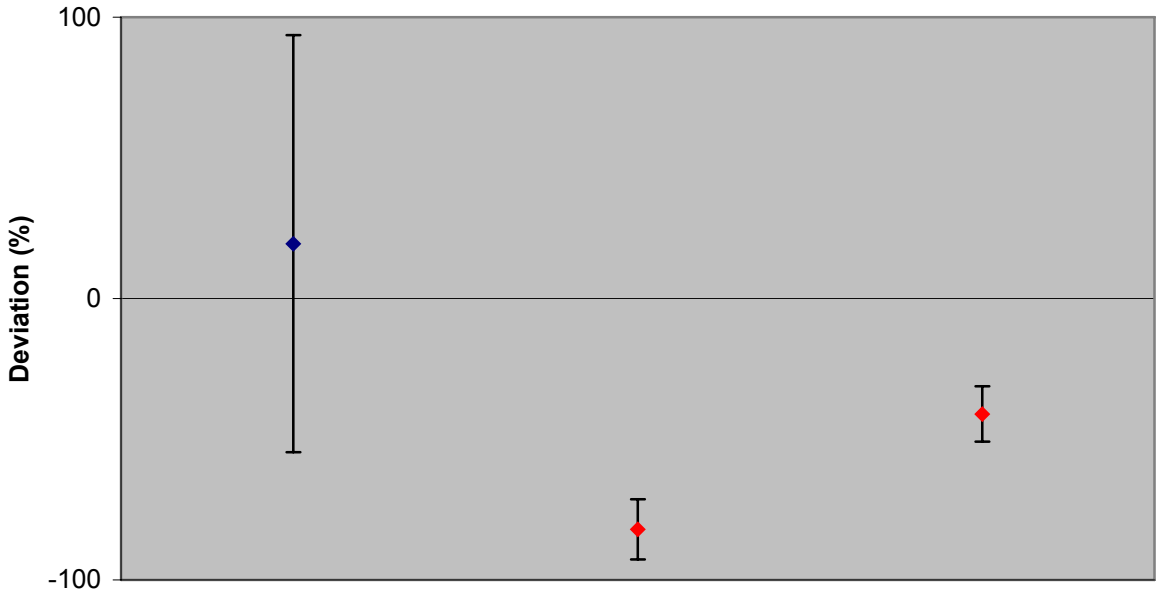


Figure 20 - Deviations for Participant 6

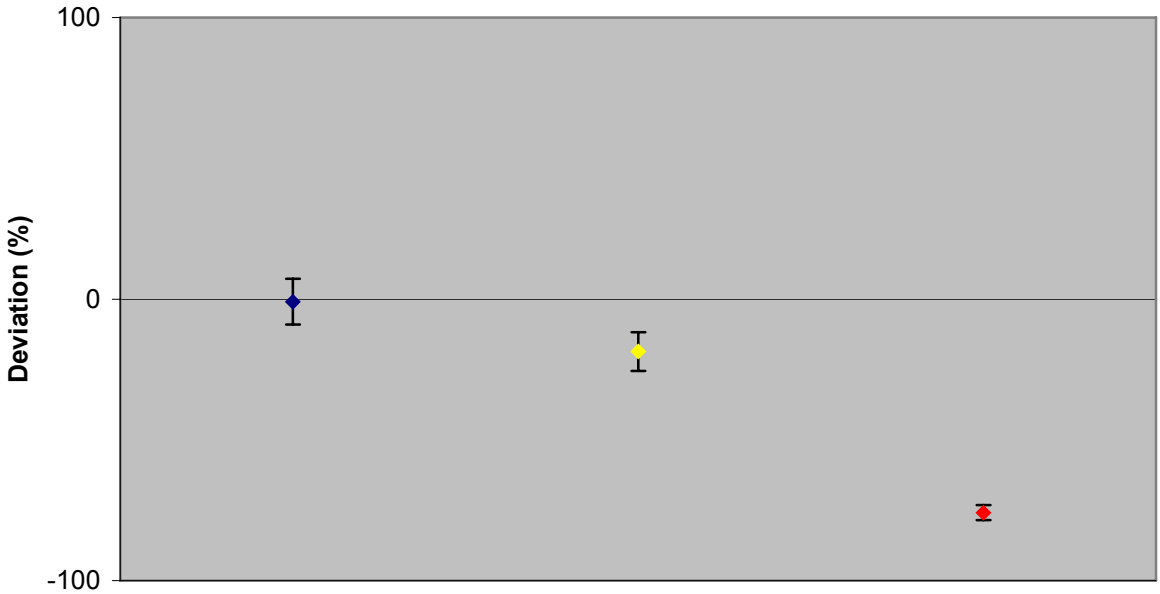
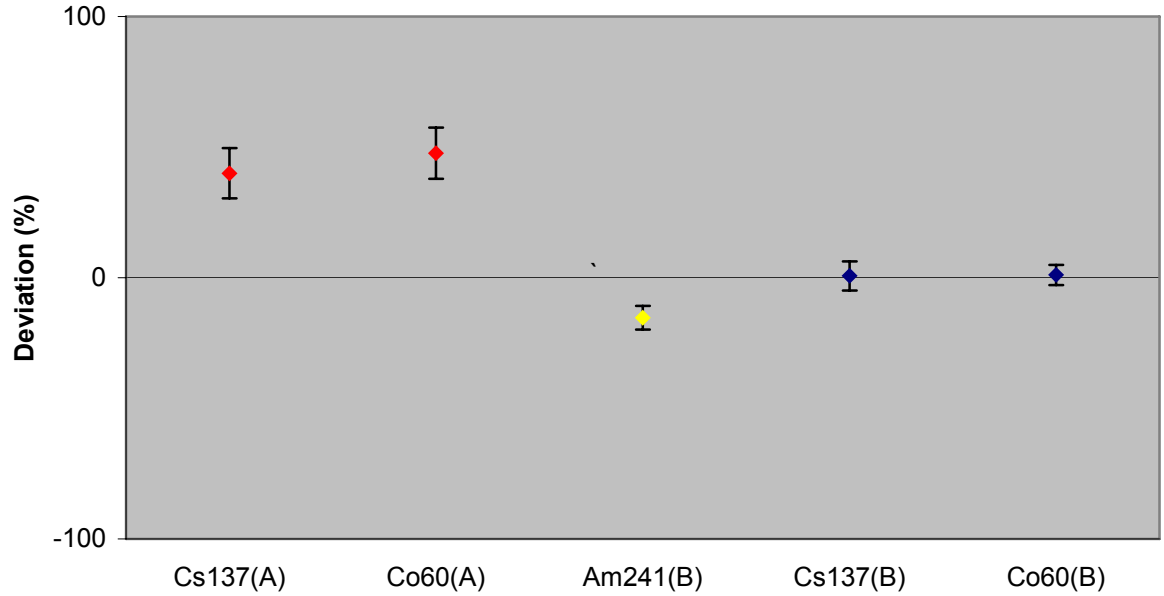


Figure 21 - Deviations for Participant 7 (Am241(A) outside limits of plot)



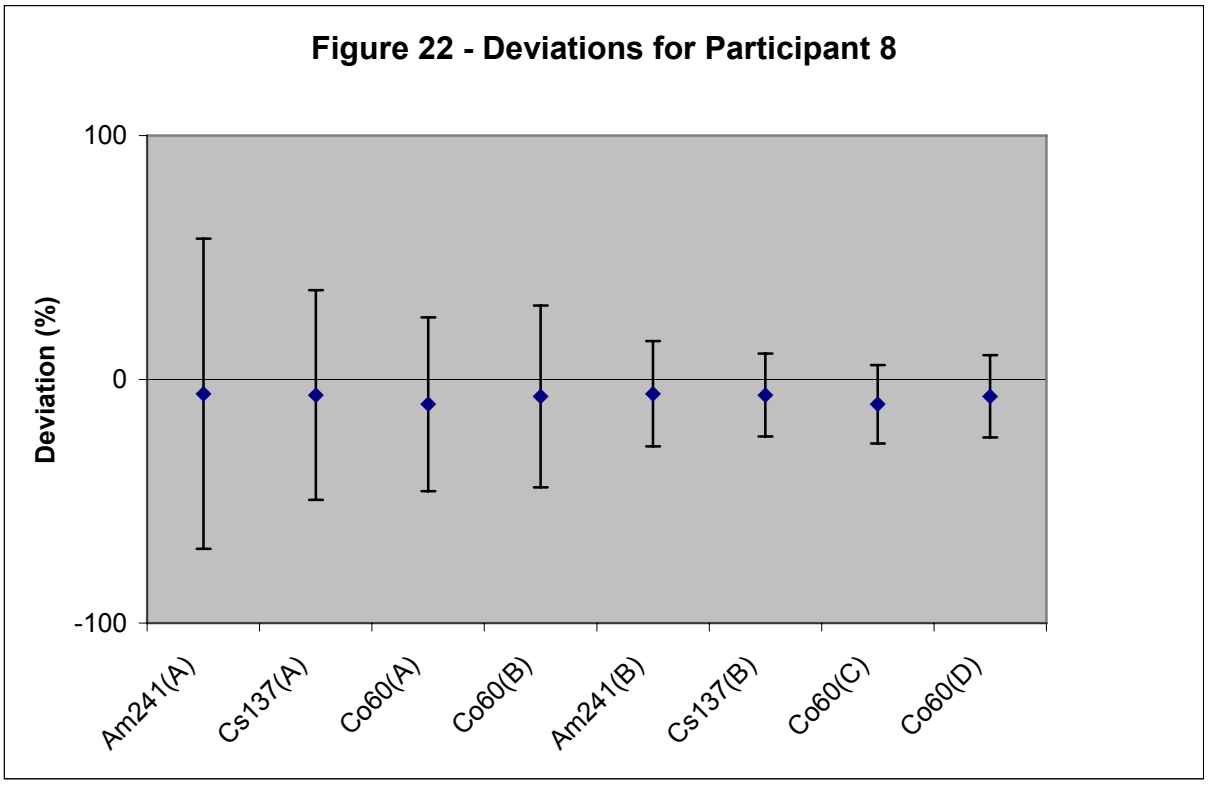


Figure 22 - Deviations for Participant 8
Deviation (%)
100
0
-100
Am241(A)
Cs137(A)
Co60(A)
Co60(B)
Am241(B)
Cs137(B)
Co60(C)
Co60(D)

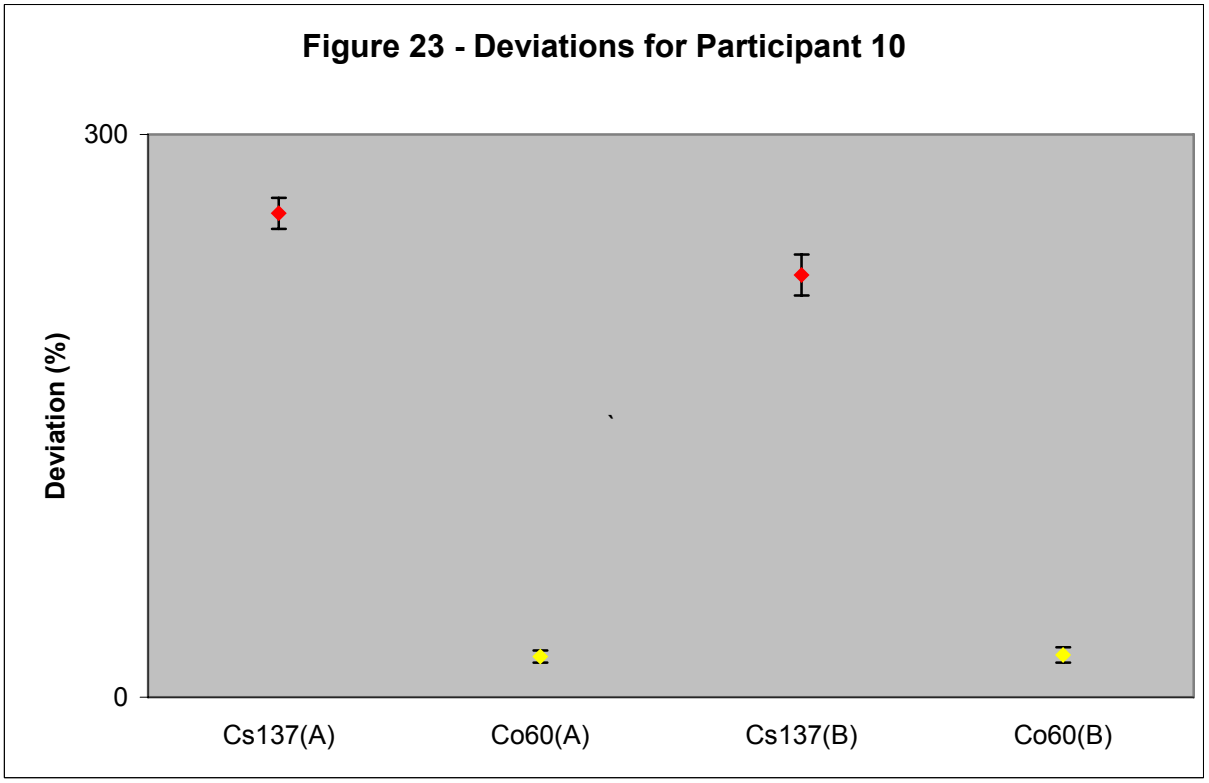


Figure 23 - Deviations for Participant 10
Deviation (%)
300
0
Cs137(A)
Co60(A)
Cs137(B)
Co60(B)

Figure 24 - Deviations for Participant 11

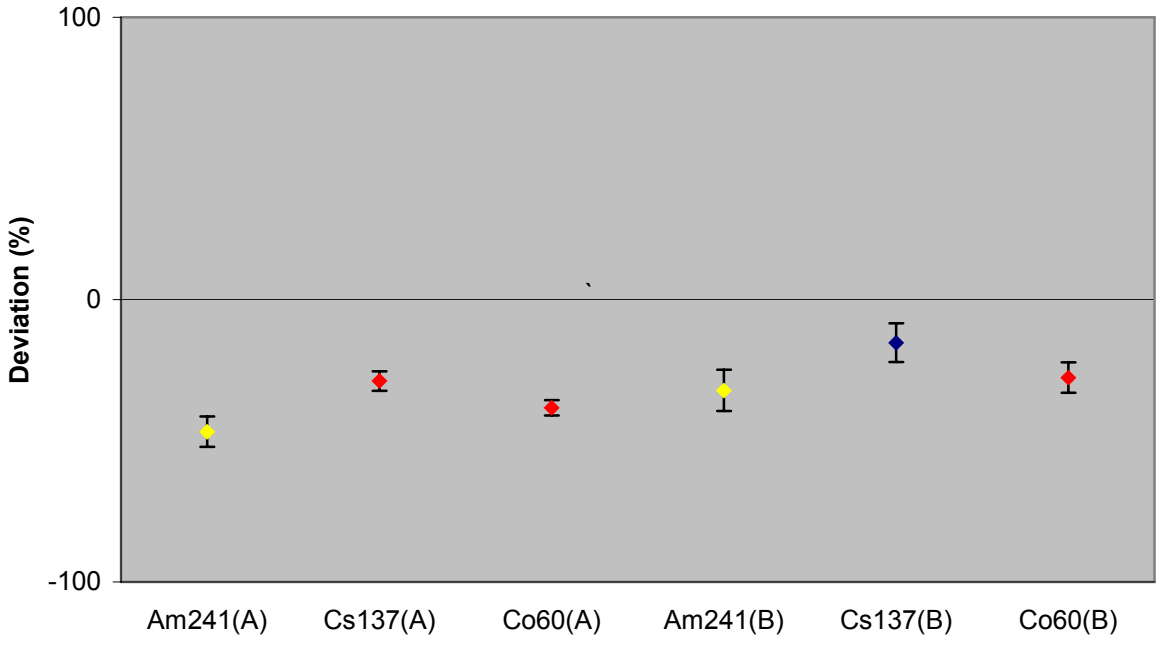


Figure 25 - Deviation for Participant 13

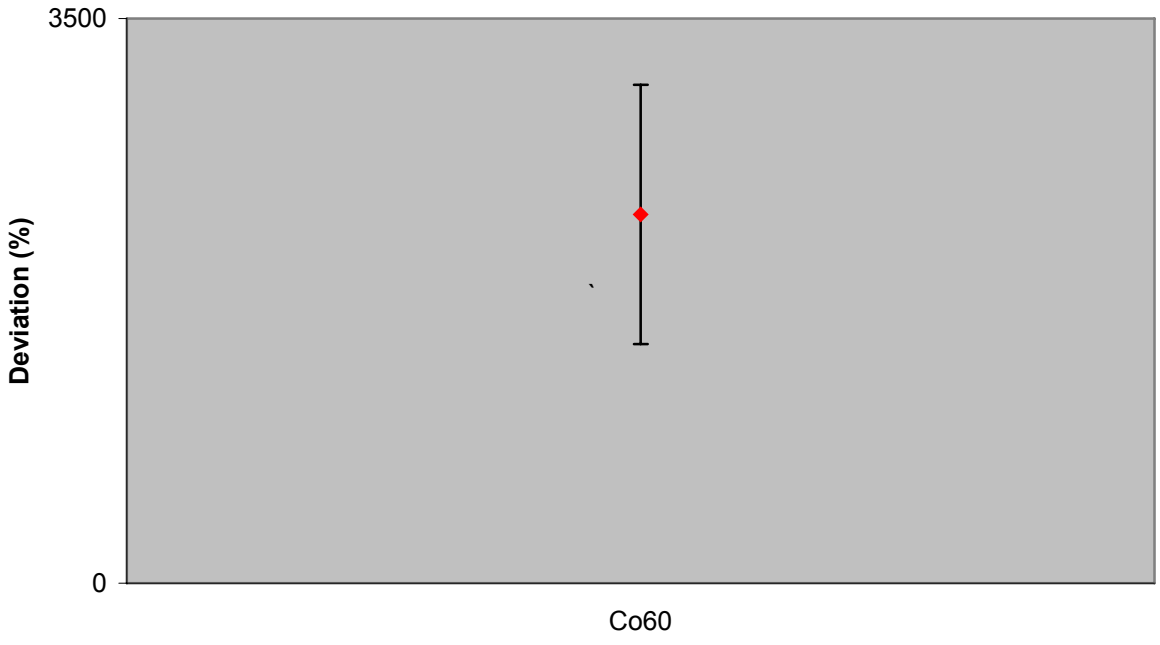


Figure 26 - Deviation for Participant 15

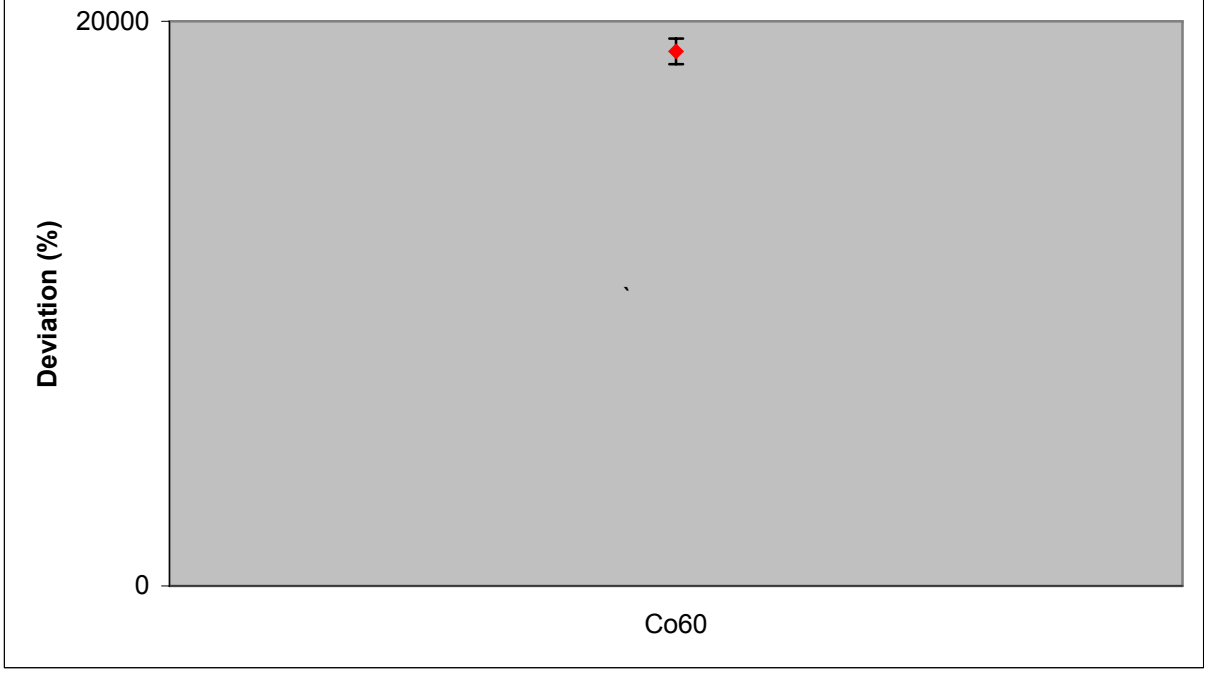


Figure 27 - Deviations for Participant 17 (sets A to C)

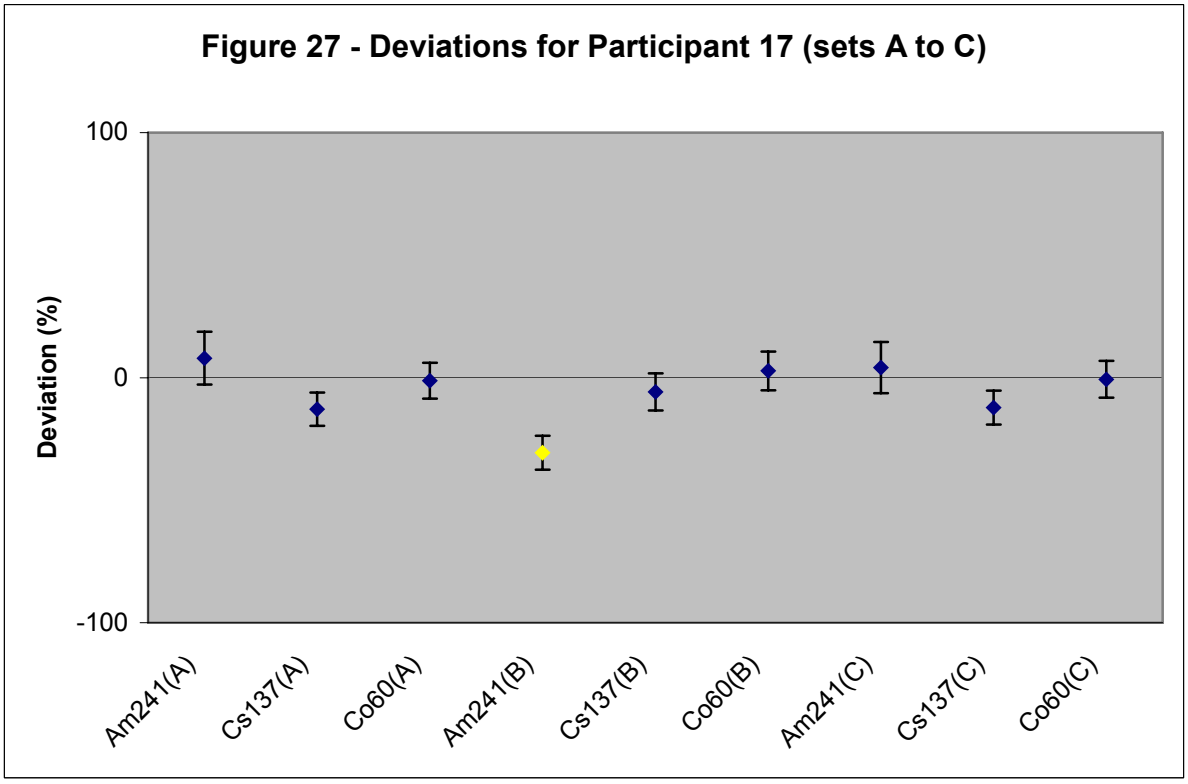


Figure 28 - Deviations for Participant 17 (sets D to F)

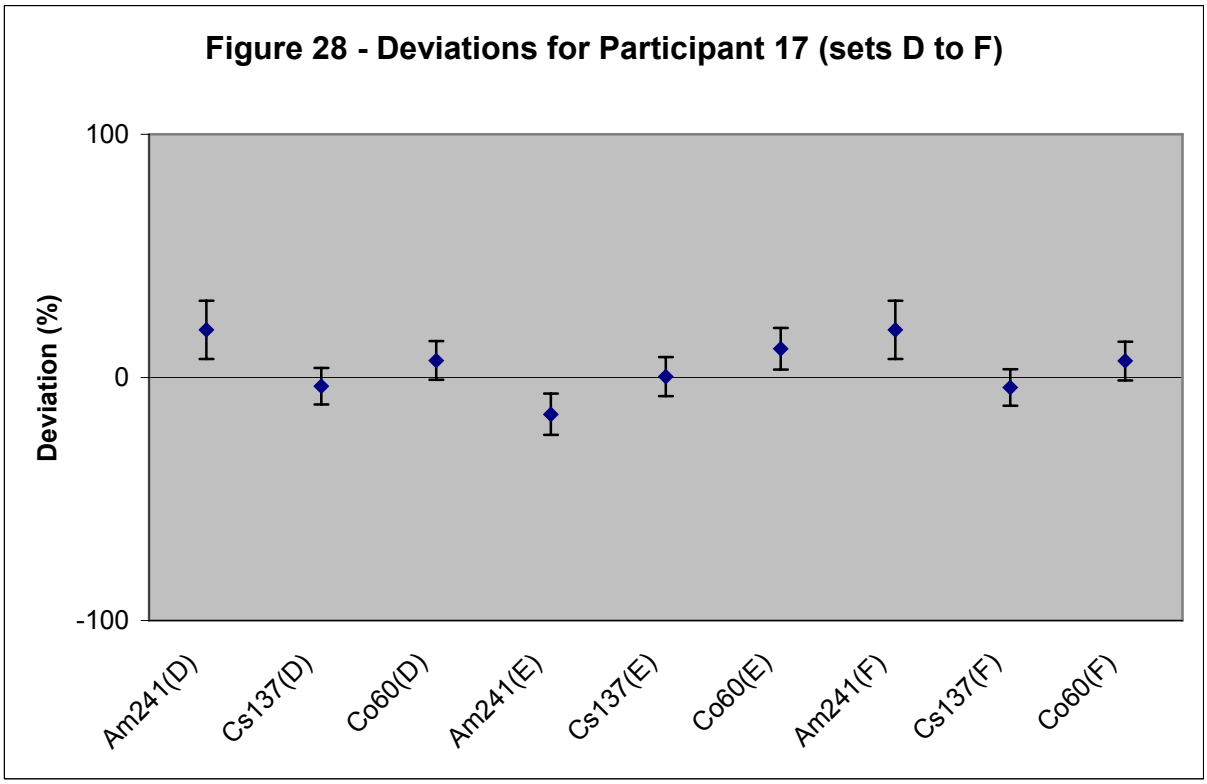
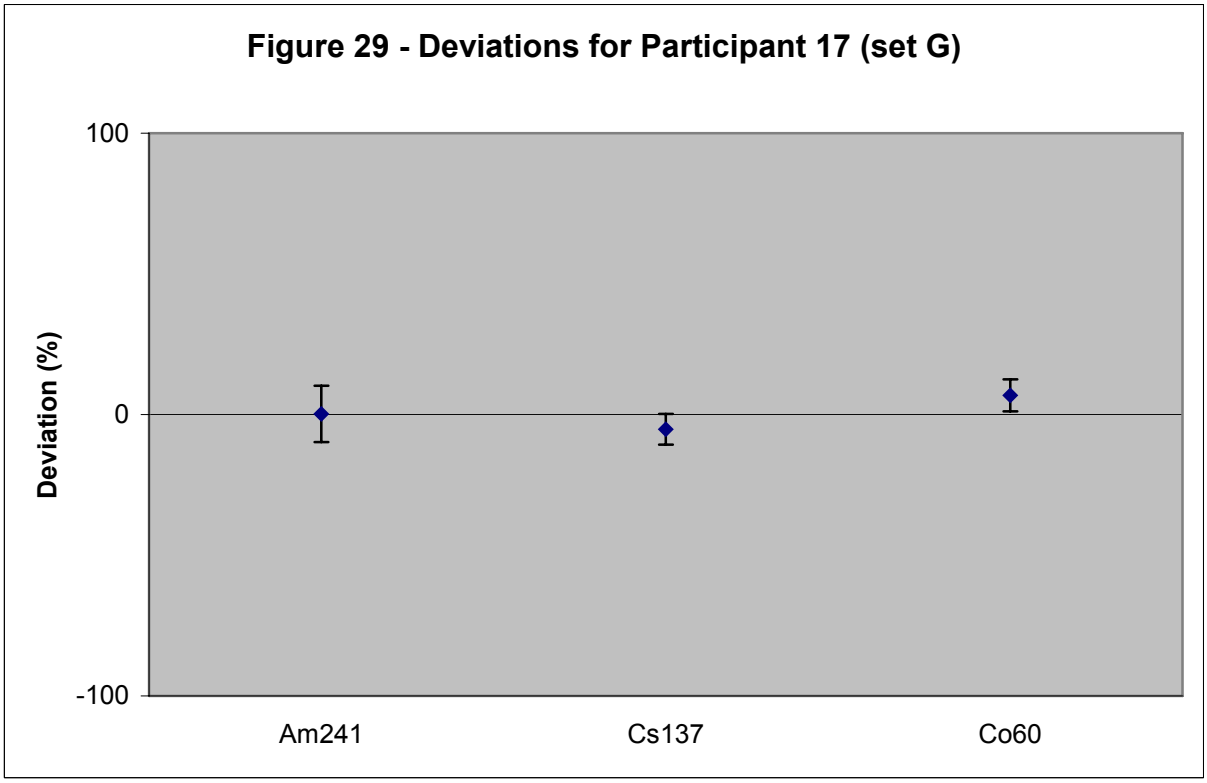


Figure 29 - Deviations for Participant 17 (set G)



APPENDIX A

Initial mailshot

Dear Colleague,

NPL 200 L DRUM γ COMPARISON

From November 2006, NPL will be running a comparison exercise to support metrology of low activity gamma-emitting waste in the UK.

This exercise will provide a unique opportunity to compare existing 200 L drum monitor γ calibrations with a standard drum, traceable to UK primary standards of radioactivity. Agreement with NPL would increase confidence in current measurements for waste sentencing, whereas a discrepancy from the NPL value would alert you to any problems with an existing calibration.

Briefly:

NPL will circulate a single drum as a blind sample and ask you to report your measurement results, along with details of current calibrations and the instrumentation used. The drum will be filled with a series of sample containers, each uniformly spiked with activity. The overall contents density will be 300 kg m^{-3} (nominal).

There will then be a follow-up workshop (next year) to:

- present the results (coded for anonymity), discuss and determine a forward plan for investigating any calibration or measurement problems arising;

- obtain your feedback on this 'multiple container' type of standard and where NPL should go next. For example, should we prepare a drum with a heterogeneous distribution of activity? Should the matrix be a soft waste simulant again, or perhaps concrete? Should we run a further comparison or provide standard drums for purchase or loan?

There is a nominal charge for participation to cover the costs of the materials and transport. The development of the reference material itself has been supported by the DTI as part of the National Measurement System.

continued……..…

The plan for the exercise is:

Action	Provisional dates
NPL to identify participants, arrange timetable for circulation of drum and confirm overall timetable	by end October 2006
NPL to prepare one standardised drum with following specification: Radionuclides: ^{241}Am, ^{60}Co and ^{137}Cs Activity concentration: < 0.4 Bq g^{-1} total Matrix: Ion-exchange resin in plastic bottles Overall density of drum contents: 300 kg m^{-3} (nominal)	by mid-November 2006
Participants to measure and return drum to NPL	within agreed dates between mid-November 2006 and mid-April 2007
Participants to return results to NPL	by mid-April
NPL to issue draft report	May
NPL to hold workshop	June
NPL to issue final report	July

If you are interested in taking part:

Please contact me by **Friday 29th September** (at julian.dean@npl.co.uk) indicating:

- Dates between **13th November 2006** and **13th April 2007** inclusive when it would **not** be possible for you to receive/measure/dispatch the drum;

- Your estimated maximum turnaround time for receipt, measurement and dispatch.

Important: If the exercise is oversubscribed we shall deal with requests for inclusion on a first-come-first-served basis, so please **do not** submit a Purchase Order at this stage. We shall contact you around the beginning of October to confirm whether or not we can accommodate you on this occasion. If so, we shall ask you to submit a Purchase Order at that stage.

The cost of participation would be £200 (plus delivery to your site). This charge would include attendance at the workshop but would not include the cost of returning the drum to NPL. For regulatory reasons, participants would have to arrange return transport of the drum but NPL would offer assistance in identifying a courier.

continued…….

This work is part of an initiative to establish a radioactivity measurement infrastructure for nuclear decommissioning and site clearance. We hope you will be able to participate and we look forward to hearing from you soon.

Regards

Yours faithfully

Julian Dean

APPENDIX B

List of participants

Mr W Allan
Environmental Safety Group
British Energy Generation Limited
Hunterston B Nuclear Power Station
West Kilbride
Ayrshire KA23 9QJ

Ms S J Allinson
Nexia Solutions
A709 Springfields
Salwick
Preston
Lancashire PR4 0XJ

Ms H Barton
British Energy
Hartlepool Power Station

Mr R K Bhanot
Springfields Fuels Limited
Springfields
Preston
Lancashire PR2 3LN

Mr G Callahan
British Nuclear Group
Bradwell Site
Bradwell On Sea
Southminster
Essex CM0 7HP

Mr P W Clarke
Magnox Electric Ltd
Oldbury Power Station
Oldbury Naite
Thornbury
South Gloucestershire BS35 1RQ

Mr C Dale
AMEC NNC Ltd
Building A512
Waste Quality Checking Laboratory
UKAEA
Winfrith

Dorchester
Dorset DT2 8WQ

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Devonport Royal Dockyard
Plymouth
Devon PL1 4SG

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Advanced Measurement Technology
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Wokingham
Berkshire RG41 2TZ

Mr S Holloway
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Reading
Berkshire RG7 4PR

Mr R Kelsey
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Mr L Malpass
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Dr T J Miller
AWE Aldermaston
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Mr I Pearman
NUKEM
Harwell International Business Centre

Harwell
Didcot
Oxfordshire OX11 0TA

Mr M Rushby
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Harwell International Business Centre
Didcot
Oxfordshire OX11 0TA

Mrs J Swan
Rm5, D2000
UKAEA
Dounreay
Thurso
Caithness KW14 7TZ

Mr R J Wicker
Magnox Electric Ltd
Dungeness A Power Station
Romney Marsh
Kent TN29 9PP

APPENDIX C

Reporting form

NPL 200 L DRUM COMPARISON EXERCISE 2007

Name:	
Organisation:	
Date of submission of results:	

Details of measurement method (please include, e.g., detector type/model, source-to-detector distance, background correction method, counting time, scan pattern, collimation, density correction routine, etc.)

Calibration method (please include, e.g., standard sources used, traceability of standards, uncertainties on standards, any geometrical correction factors used, all associated uncertainties, etc.)

Efficiency models (please include, e.g., details of any software used, and any validations carried out)

Any other information or comments

NPL 200 L DRUM COMPARISON EXERCISE 2007

Nuclide: **Am-241**

Reference time 1 December 2006 12:00 GMT

	(Bq/g)
Activity concentration	
Combined standard uncertainty (*k=1*)	

Uncertainty budget components	**Relative uncertainty (%)**
Uncertainty component associated with net count rate of nuclide	
Uncertainty component associated with detector counting efficiency	
Uncertainty component associated with emission probability	
Uncertainty component associated with decay/ingrowth correction	
Other uncertainty components (please specify)	
Combined standard uncertainty	

Nuclear data used	
Half-life (days)	
Emission probability (%)	keV
Emission probability (%)	keV

Limit of Detection	

NPL 200 L DRUM COMPARISON EXERCISE 2007

Nuclide: **Cs-137**

Reference time 1 December 2006 12:00 GMT

	(Bq/g)
Activity concentration	
Combined standard uncertainty (*k=1*)	

Uncertainty budget components	**Relative uncertainty (%)**
Uncertainty component associated with net count rate of nuclide	
Uncertainty component associated with detector counting efficiency	
Uncertainty component associated with emission probability	
Uncertainty component associated with decay/ingrowth correction	
Other uncertainty components (please specify)	
Combined standard uncertainty	

Nuclear data used	
Half-life (days)	
Emission probability (%)	keV
Emission probability (%)	keV

Limit of Detection	

NPL 200 L DRUM COMPARISON EXERCISE 2007

Nuclide: **Co-60**

Reference time 1 December 2006 12:00 GMT

	(Bq/g)
Activity concentration	
Combined standard uncertainty (*k=1*)	

Uncertainty budget components	**Relative uncertainty (%)**
Uncertainty component associated with net count rate of nuclide	
Uncertainty component associated with detector counting efficiency	
Uncertainty component associated with emission probability	
Uncertainty component associated with decay/ingrowth correction	
Other uncertainty components (please specify)	
Combined standard uncertainty	

Nuclear data used	
Half-life (days)	
Emission probability (%)	keV
Emission probability (%)	keV

Limit of Detection	

APPENDIX D

Minutes of post-comparison workshop

Date: Friday 21st September 2007

Location: National Physical Laboratory, Teddington, Middlesex TW11 0LW

Present

Ian Adsley	NUKEM Ltd
Sarah Allinson	Nexia Solutions
Pete Burgess	NPL
George Callahan	Bradwell Power Station
Phil Clarke	Oldbury Power Station
Chris Dale	AMEC
Julian Dean	NPL (Chairman)
Chris Gilligan	NPL
Steve Glover	Berkeley Centre
Arvic Harms	NPL
Trevor Hatt	Ortec/Ametek
Simon Jerome	NPL
Paul Knight	AWE
Bob Major	AMEC
Lee Malpass	Berkeley Centre
Tim Miller	AWE
Ian Pearman	NUKEM Ltd
Martin Rushby	Canberra UK Ltd
Jenny Swan	UKAEA Dounreay
Barbara Tawton	Project Services
Tim Twomey	Ortec/Ametek
Richard Wicker	Dungeness A Power Station
Colin Wilkins	Canberra UK Ltd

(n.b. Powerpoint slides from the formal presentations are given at the end.)

1.0 Session 1

The chairman welcomed the delegates and asked everyone to introduce themselves. Domestic issues were covered and the agenda was outlined.

1.1 Drum comparison: Background, results, discussion and actions required

Julian Dean described the background to the exercise and the basis for the source format used, described how the source was made, listed the participating laboratories, presented the results and proposed some conclusions and points for discussion.

(n.b. The details are given in the main body of the final report.)

JCJD asked if any of the apparent discrepancies (especially the underestimates) could be explained today, or by subsequent re-examination of stored data. He said if they could not, might they be indicative of 'real' waste measurement problems, and, if so, would it help if NPL were to, e.g., summarise any validations of ISOCS and/or ISOTOPIC, provide training and/or guidance on uncertainties, or run a further comparison or test.

None of the delegates said that the data suggested there was a problem with measuring actual waste and some said that the results not in agreement with NPL could be readily explained. JCJD asked for any such information to be sent to him for inclusion in the final report so that the report would illustrate standards of measurement in this user group as accurately as possible.

Three participants had used ISOCS to determine detection efficiencies (namely, Participants 1, 8 and 11). Participant 8, who had quoted by far the largest uncertainties of the three, pointed out that uncertainty budgets need to be carefully evaluated and that they would be happy to advise other ISOCS users on this matter. Participant 11, in preparing their model, had not allowed for the presence of the plastic bottles in the drum; similarly, Participant 1 had assumed the drum was full of resin. The three participants agreed it would be useful to compare their models of the NPL drum.

The above had illustrated the importance of a knowledge of the materials in a drum in the determination of detection efficiencies. This could be further aided by the use of techniques such as radiography, and Participant 4 had done exactly this. It was pointed out that a variety of systems and software had been used in this exercise and that the uncertainties on each needed to be carefully evaluated. Bob Major had a memo on possible uncertainties in drum monitoring and agreed to circulate it to the group. Pete Burgess felt that Measurement Good Practice Guide 34 (Non-Destructive Assay) needed to be revised to include a more thorough treatment of uncertainties than it provides at present.

Participants 2 and 12 pointed out that their waste monitors were located in the vicinity of stored radioactive materials and that background had therefore been a significant problem. Participant 12 also pointed out that their reported ^{241}Am value had been derived by the software from a radionuclide fingerprint, and was therefore not actually a measure of what was in the NPL drum.

Ian Adsley pointed out that there is a paper comparing Monte Carlo codes. There was interest in participation in an MC modelling discussion group or forum and NPL agreed to discuss with colleagues with relevant expertise with a view to setting up such a group.

There was interest in NPL running a second comparison, this time involving a drum with the activity distributed in a heterogeneous manner (perhaps with a 'hot spot' in one area). This could readily be achieved by modifying the current NPL drum. Apparently there are definitions of 'heterogeneous' for sample of this type and these would be sent to JCJD.

Tim Miller enquired as to the cost of making an NPL standard drum. JCJD agreed to provide a quote.

Arvic Harms suggested that it would be useful to include plots of deviations by participant (as well as by radionuclide) in the final report.

2.0 Session 2

2.1 Results of a recent NPL environmental proficiency test using a concrete reference material

Arvic Harms presented the results of a recent comparison exercise in which a neutron-irradiated concrete sample had been prepared by NPL and had been characterised by 27 laboratories. The assigned values for the activity concentrations of the individual radionuclides had been calculated by taking, in each case, the median of the participants results. NPL had carried out 'within-bottle' and 'between-bottle' repeat measurements of selected samples in order to quantify the heterogeneity of the material. Individual data were subjected to a z-test and a zeta test to determine the level of agreement with the median. 80 % of the overall results were found to be in agreement with the corresponding median.

2.2 ISO accreditation / Preparation of Tritiated cement

Simon Jerome outlined the steps NPL is taking to gain accreditation to ISO/IEC Guide 43-1, which defines the principles and described the factors which should be taken into account in the organisation and conduct of proficiency testing exercises. Such accreditation provides a 'seal of approval' for the test provider and gives the participants confidence in the test samples provided to them. The management system requirements and the technical requirements were outlined. The initial audit of the relevant NPL procedures and systems took place in July 2007 and an offer of accreditation to ISO/IEC 43-1 has been made subject to clearance of specific improvement actions. At this stage, the scope of the accreditation will cover radioactive standards solutions and concrete samples, but in due course this will be extended to include drum comparisons.

Simon also gave a separate, short talk on the preparation of Tritiated cement at NPL. This had been done to determine recoveries of Tritium from pyrolised 'real' samples of contaminated / activated cement samples. Producing such a reference material is problematic and raises as many problems as it solves. The chemical form and the 'chemical location' of the Tritium are important and must be stated in any certification of such a reference material.

2.3 Overview of radioactivity projects in the AIR programme 2007 - 2010

JCJD gave a very brief introduction to the new NPL Acoustics and Ionising Radiation Programme and outlined the content of the radioactivity projects, These were:

- Primary measurement standards and systems;
- Infrastructure for secondary measurement standards of radioactivity;
- Provision of measurement infrastructure for nuclear medicine;
- Infrastructure for environmental radioactivity standards;
- Measurement infrastructure for radiation protection;
- Measurement infrastructure for nuclear decommissioning;
- Radioactivity knowledge transfer.

The decommissioning project would consist of four sub-projects:

- Production and certification of two Certified Reference Materials (which is a 'flexible' definition and can mean a standard source, or a comparison exercise – the proposed second drum comparison could therefore be accommodated here);
- Compilation of a Measurement Good Practice Guide on mathematical modelling for measuring radioactivity in waste;
- A consultancy and audit service on use of such models;
- The production of an NPL Report on characterisation of surface contamination monitors for radioactivity in different materials;
- Ongoing support to the Clearance and Exemption Working Group and Nuclear Industry Code of Practice.

2.4 Discussion on requirements for NPL calibration services for γ-assays

PHB led a short discussion on needs for standards and calibration services in this field. Much of this had been raised in the morning session.

There seemed to be more interest in standard contaminated articles (e.g. toolboxes) for checking the responses of box monitors, rather than Certified Reference Materials. A larger article (e.g. a bag of material) might be a useful 'compromise' between a toolbox and a drum and enable a wider range of monitors to be checked. A suitable activity level for a small article would be of the order of tens of Bq of ^{60}Co.

If CRMs are to be prepared for 'Free Release' monitors, then they should really be prepared in larger volumes than a drum - a 1m^3 'builders' bag' might be more suitable (e.g. containing "soil" at around the 0.1 Bq g^{-1} (gamma) level).

One delegate suggested that standards like the NPL resin drum could be used as a 'master' drum for users to compare with 'rod' drums (i.e. drums of inactive matrix with standard mixed-radionuclide rods inserted); the latter could then be used as a working standard.

George Callahan (Bradwell) mentioned that there was a Magnox Health Physicists' meeting at Trawsfynydd coming up very soon and that he would ask them for their input.

2.5 Summary of workshop

JCJD summarised the actions, which were:

- Any participants with discrepant/questionable results to send explanatory information (with supplementary data if they wish) to JCJD by 5 October;
- JCJD to issue final report in mid-October;
- RM to issue his uncertainties memo to the participants;
- NPL staff to revise the uncertainties section of GPG 34;
- PHB and JCJD to speak to relevant NPL staff re: setting up a discussion forum for MCNP of waste detectors;
- NPL staff to consider a repeat comparison using a 'heterogeneous' drum in the next NMS programme;
- Any particants with a definition of 'heterogeneous' to forward to JCJD;
- JCJD to provide AWE with a quote for a standard drum;
- JCJD to include plots of deviation by participant in the final report;
- GC to send JCJD feedback from the Magnox Health Physicists' meeting at Trawsfynydd.

He finished by thanking the participants, and the NPL staff involved, for their contributions to the comparison and the workshop.

Julian Dean

5th October 2007

Welcome to the 2007 NPL Drum Comparison Workshop

NPL

Today's agenda

10-45	**Session 1**
10-45	*Welcome, domestic issues, introductions and agenda*
11-10	**Drum comparison: Background, results, discussion and actions required - JCJD**
12-40	**Lunch**

NPL

Today's agenda

13-40 Session 2

13-40 Results of a recent NPL environmental proficiency test using a concrete reference material – Arvic Harms

14-10 ISO accreditation – Simon Jerome

14-25 Overview of NMS Acoustics and Ionising Radiation programme 2007 - 2010 - JCJD

NPL

Today's agenda

Session 2 (continued)

14-55 Discussion on requirements for NPL calibration services for γ-assays - Pete Burgess

15-25 Summary of workshop – JCJD

15-30 Close - Tea/coffee available

NPL

The National Physical Laboratory

- One of the world's leading National Measurement Institutes (NMIs)
- Around 600 staff including 450 Graduate/PhD scientists
- Operated by SERCo for DTI/DIUS since 1995

NPL

Nationally…

…at head of the National Measurement System

- Standards
- Related research
- Measurement services
- Knowledge Transfer activities

NPL

Internationally…

…works with other NMIs under, e.g., the Bureau International des Poids et Mesures (BIPM):

- Sharing resources
- Harmonising standards

NPL

Structure

Two scientific divisions, providing measurement capability across a wide range of scientific and engineering areas:

1. Industry and Innovation Division

2. Quality of Life Division
   - ➢ Acoustics and Ionising Radiation Team
     - ❑ Radioactivity and Neutrons Group

NPL

Funding

- Mostly from National Measurement System Programmes Unit (NMS-PU) of DIUS
- NMS-funded work carried out in consecutive 3-year 'Knowledge-base' programmes (e.g. Acoustics and Ionising Radiation)
- Next AIR programme October 2007 – September 2010
  - ➢Input to projects welcomed!

NPL

NPL
National Physical Laboratory

Concrete samples in the NPL Environmental Radioactivity Proficiency Test Exercise 2007

NPL Drum Comparison Workshop

Arvic Harms

21 September 2007

Introduction

Since 1989 NPL has organised 13 Environmental Radioactivity Proficiency Test Exercises (mostly aqueous solutions)

Most recent exercise (2007):
8 sample types including a solid matrix (C; neutron-irradiated concrete)

AL and AH:	7 nuclides each
BL and BH:	6 nuclides each
B2:	4 nuclides
GL and GH:	10 nuclides each

C: ^{3}H, ^{14}C, ^{40}K, ^{41}Ca, ^{55}Fe, ^{60}Co, ^{63}Ni, ^{133}Ba, ^{137}Cs, ^{152}Eu & ^{154}Eu

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2007 Exercise

Started in April 2007

Deadline for submission of results: 16 June 2007

Workshop held: 19 September 2007

65 participants (32 UK and 33 overseas) and 245 samples

1295 results (1159 PTE results and 136 C results)

70% of the PTE results were in agreement

NPL

C samples

C samples not a proficiency test but a comparison (with 27 participants)

Assigned values are the medians of the participant values

C samples originate from samples taken from a concrete bioshield of a decommissioned nuclear reactor which ceased operation ~25 years ago after ~20 years of operation.

The concrete contains nuclides formed by neutron activation of concrete components

NPL

Sample preparation

The concrete core samples were crushed, mixed and sieved to <0.5 mm to form a homogeneous powder (~2.7 kg)

The powder was then heated overnight to 150 °C to remove ^{3}H present as mobile tritiated water

52 samples (50 g each) were prepared

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C composition as determined with neutron activation analysis

Ca	26.0(3) %	Ca-41
Si	15(3) %	
Al	1.21(3) %	
Fe	0.680(8) %	Fe-55
K	0.53(2) %	K-40
Mg	0.44(3) %	
Na	0.222(3) %	
Ba	192(12) ppm	Ba-133
Co	2.70(6) ppm	Co-60
Eu	0.372(11) ppm	Eu-152 and Eu-154

and 26 other elements (including Au, Cs, Th and U)

NPL

Homogeneity testing (Co-60, Ba-133, Eu-152 and Eu-154)

15 randomly selected bottles (29% of the bottles) were kept at NPL

14 bottles were measured once — s_{bb} (%)

1 bottle was measured five times — s_{meas} (%)

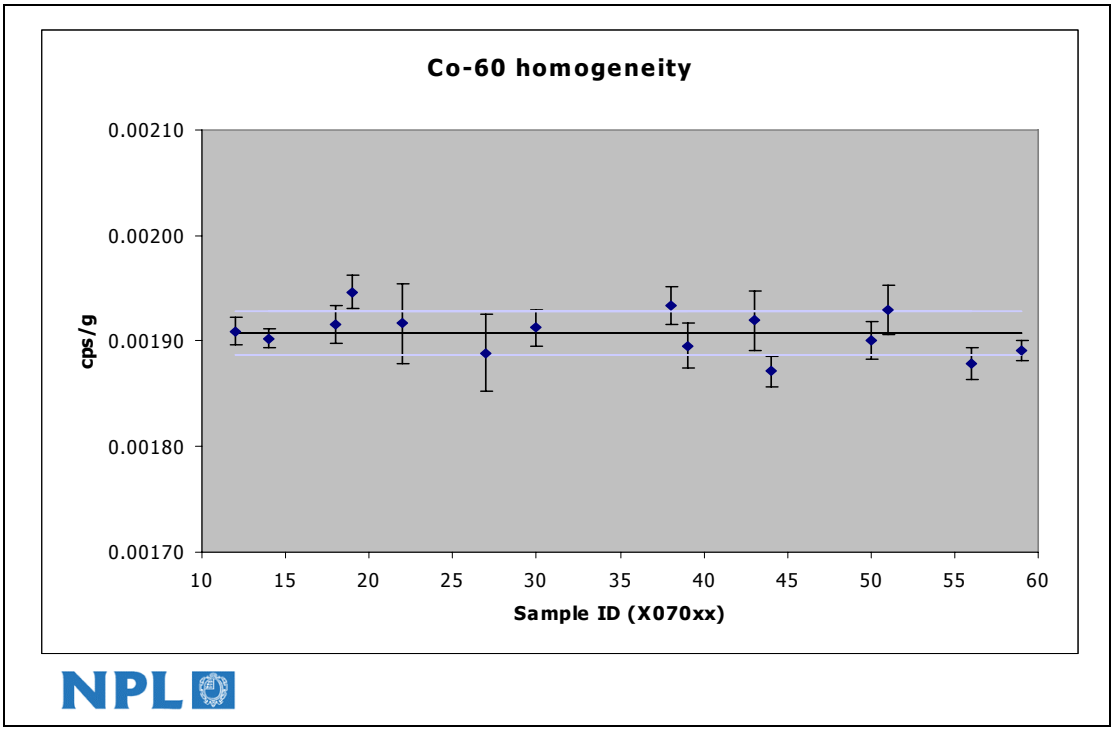
$$u_{bb}^2 = u_{meas}^2 + u_{inho}^2$$

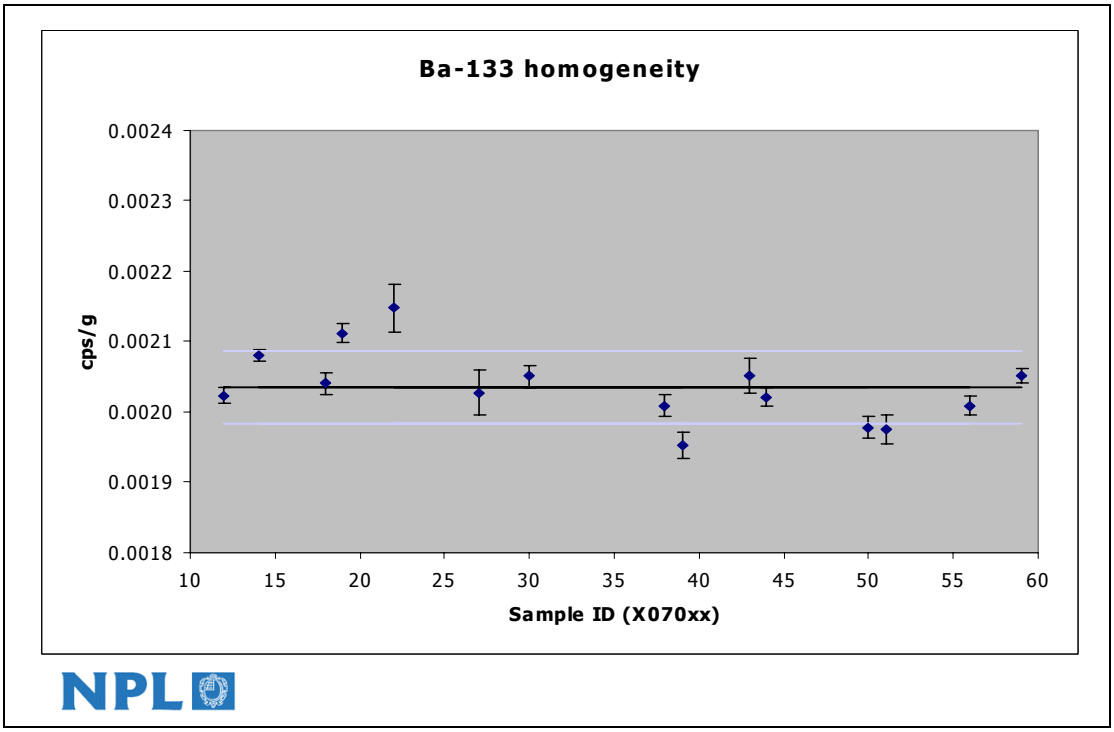
$$u_{inho}^2 = u_{bb}^2 - u_{meas}^2 = s_{bb}^2 - \frac{s_{meas}^2}{5}$$

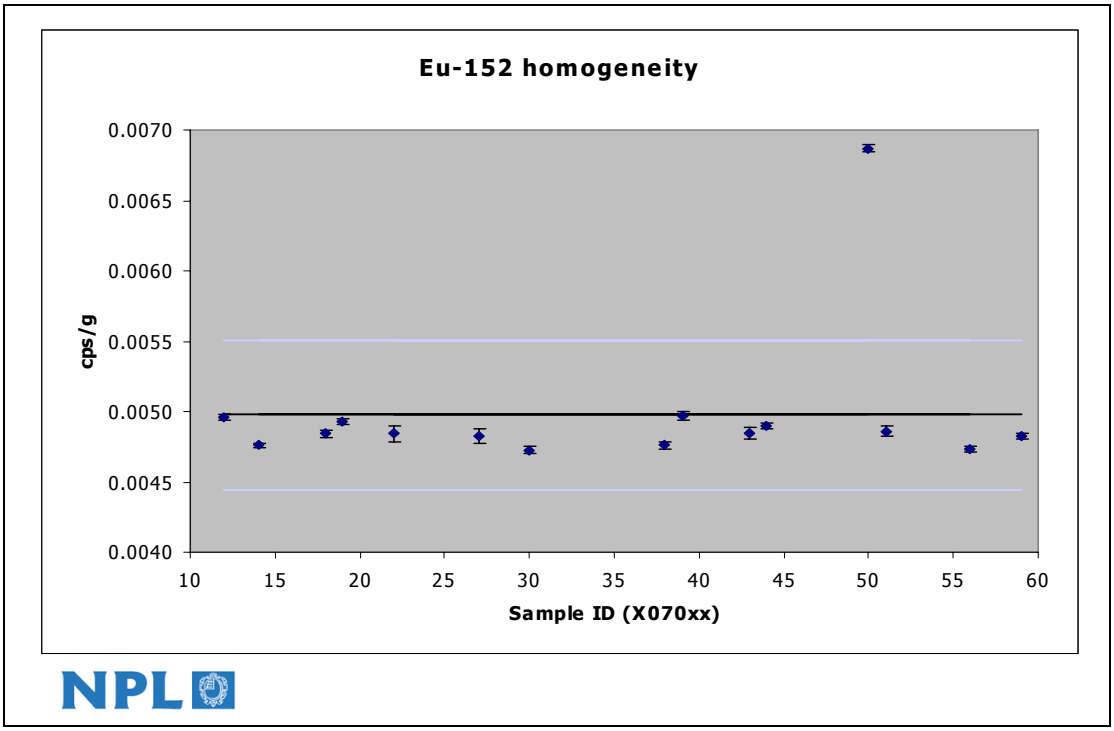
(ideally $u_{inho} = 0$)

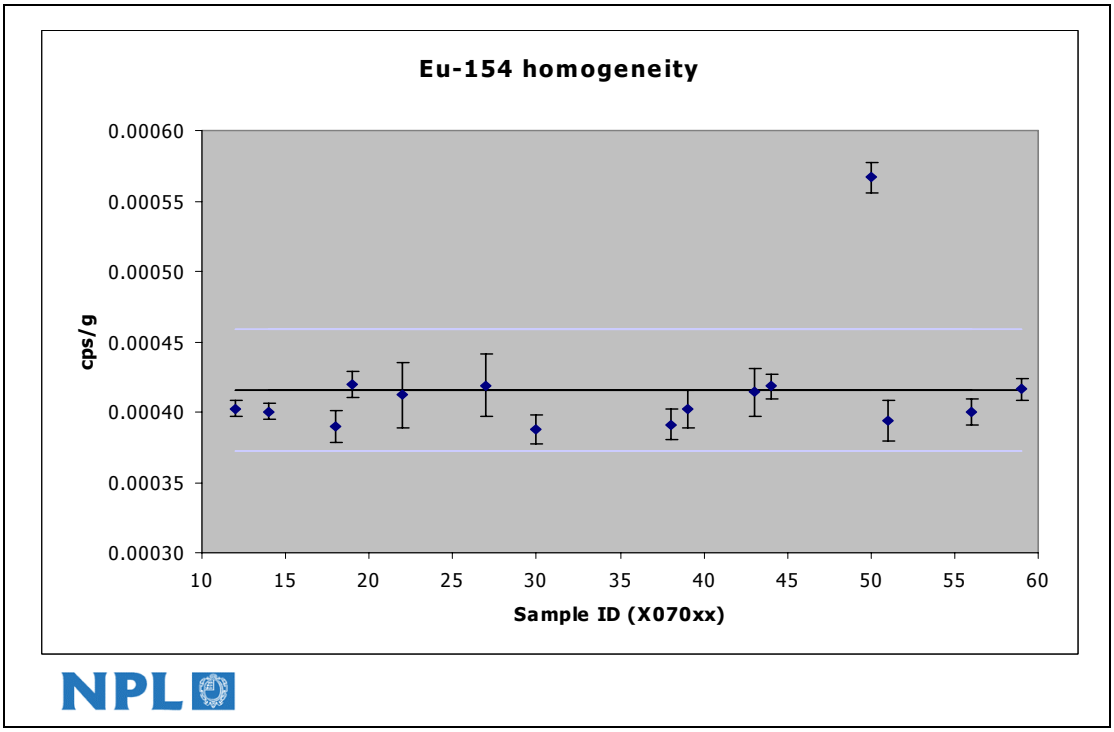
$$u_N^2 = u_{med}^2 + u_{inho}^2 = u_{med}^2 + s_{bb}^2 - \frac{s_{meas}^2}{5}$$

NPL


Co-60 homogeneity
0.00210
0.00200
0.00190
0.00180
0.00170
cps/g
10
15
20
25
30
35
40
45
50
55
60
Sample ID (X070xx)
NPL


Ba-133 homogeneity
0.0024
0.0023
0.0022
0.0021
0.0020
0.0019
0.0018
cps/g
10
15
20
25
30
35
40
45
50
55
60
Sample ID (X070xx)
NPL


Eu-152 homogeneity
cps/g
0.0070
0.0065
0.0060
0.0055
0.0050
0.0045
0.0040
10
15
20
25
30
35
40
45
50
55
60
Sample ID (X070xx)
NPL


Eu-154 homogeneity
cps/g
0.00060
0.00055
0.00050
0.00045
0.00040
0.00035
0.00030
10
15
20
25
30
35
40
45
50
55
60
Sample ID (X070xx)
NPL

Between-bottle uncertainty (in %)

	u_{bb}	u_{meas}	u_{inho}	u_{med}	u_N
Co-60	1.09	0.92	0.59	*2.48*	**2.55**
Ba-133	2.52	0.79	2.40	*4.41*	**5.02**
Eu-152	10.64	0.58	10.62	*4.62*	**11.59**
Eu-154	10.41	1.96	10.22	*2.67*	**10.57**

(without X07050)

	u_{bb}	u_{meas}	u_{inho}	u_{med}	u_N
Co-60	1.12	0.92	0.65	*2.48*	**2.56**
Ba-133	2.48	0.79	2.35	*4.41*	**5.00**
Eu-152	1.62	0.59	1.51	*4.62*	**4.86**
Eu-154	2.86	1.96	2.08	*2.67*	**3.39**

NPL

Treatment of data (I)

There is no assigned NPL value; instead the median value of the returned results was assigned as *N*

u_{med} was calculated according:

$$u_{med} = \frac{1.858 \ \mathrm{MAD}}{\sqrt{n-1}}$$

MAD *(median of the absolute deviation)*

Only zeta and z tests were performed

z test was modified for all nuclides except ^{60}Co and ^{133}Ba

Acceptance criteria were made nuclide specific (because there are a function of the degrees of freedom)

NPL

Treatment of data (II)

(i) Zeta test

pass if Abs(zeta) ≤ t value $_{P = 0.01}$

$$\zeta = \frac{L - N}{\sqrt{u_L^2 + u_N^2}}$$

(iii) z test

pass if Abs(z test) ≤ t value $_{P = 0.01}$

$$z = \frac{L - N}{u_N}$$

(^{60}Co and ^{133}Ba only)

$$z = \frac{L - N}{R_{med} N}$$

NPL

Treatment of data (III)

zeta test	z test	
pass	pass	'In agreement'
fail	pass	'Questionable'
pass	fail	'Questionable'
fail	fail	'Discrepant'

NPL

Results (I)

	(Bq g^{-1})	Results	In agreement
^{3}H leachable	0.9(7)	5	60%
^{3}H total	9.0(19)	9	100%
^{14}C	0.16(12)	5	100%
^{40}K	0.18(4)	6	67%
^{41}Ca	0.39(19)	3	100%
^{55}Fe	0.037(22)	3	100%
^{58}Co	-	3	-
^{60}Co	0.0750(19)	26	73%
^{63}Ni	0.0170(24)	3	67%
^{133}Ba	0.054(3)	24	71%
^{137}Cs	0.00110(23)	2	100%

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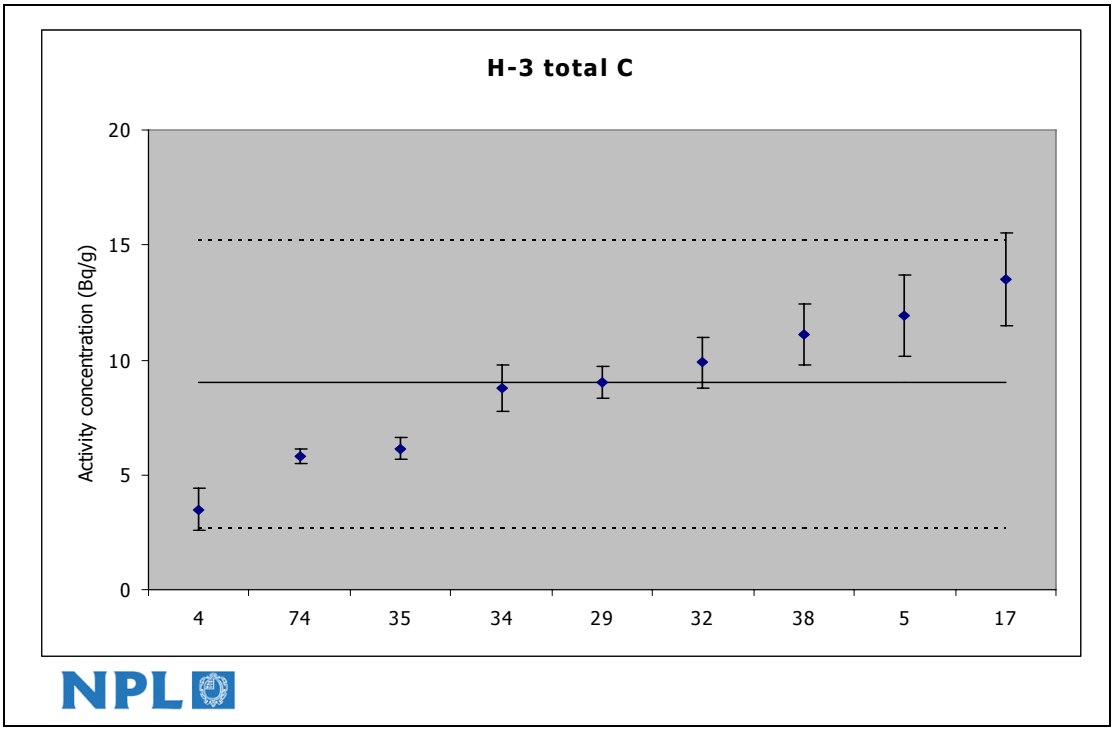
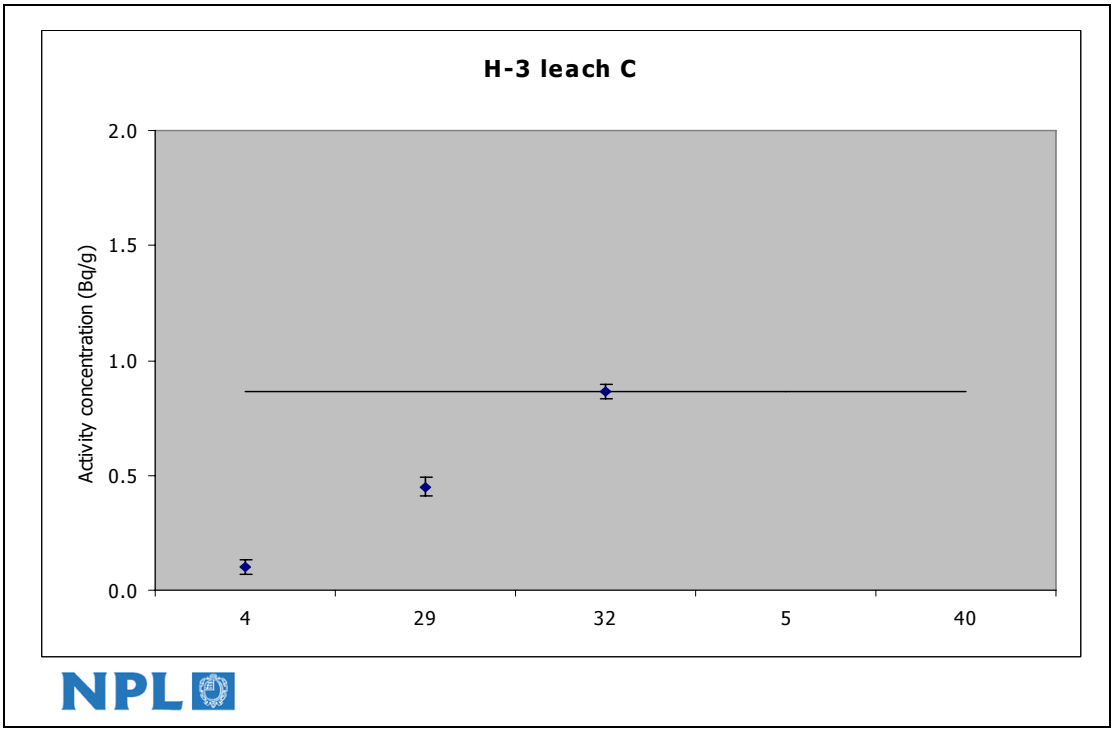
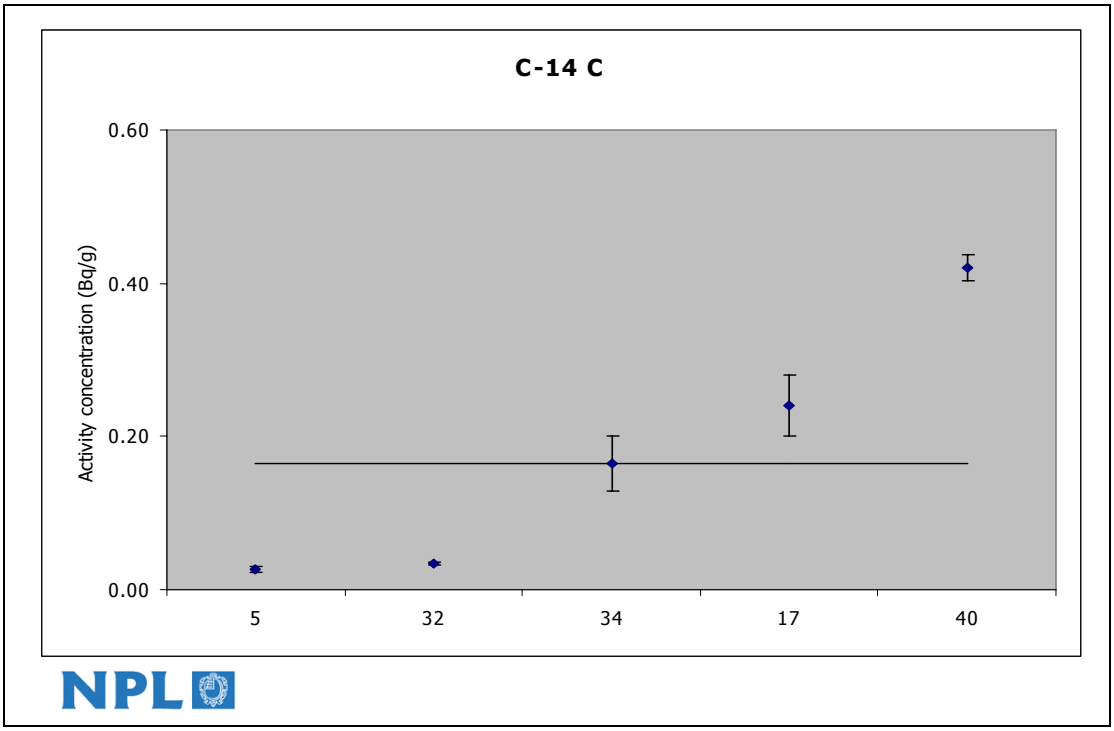
Results (II)

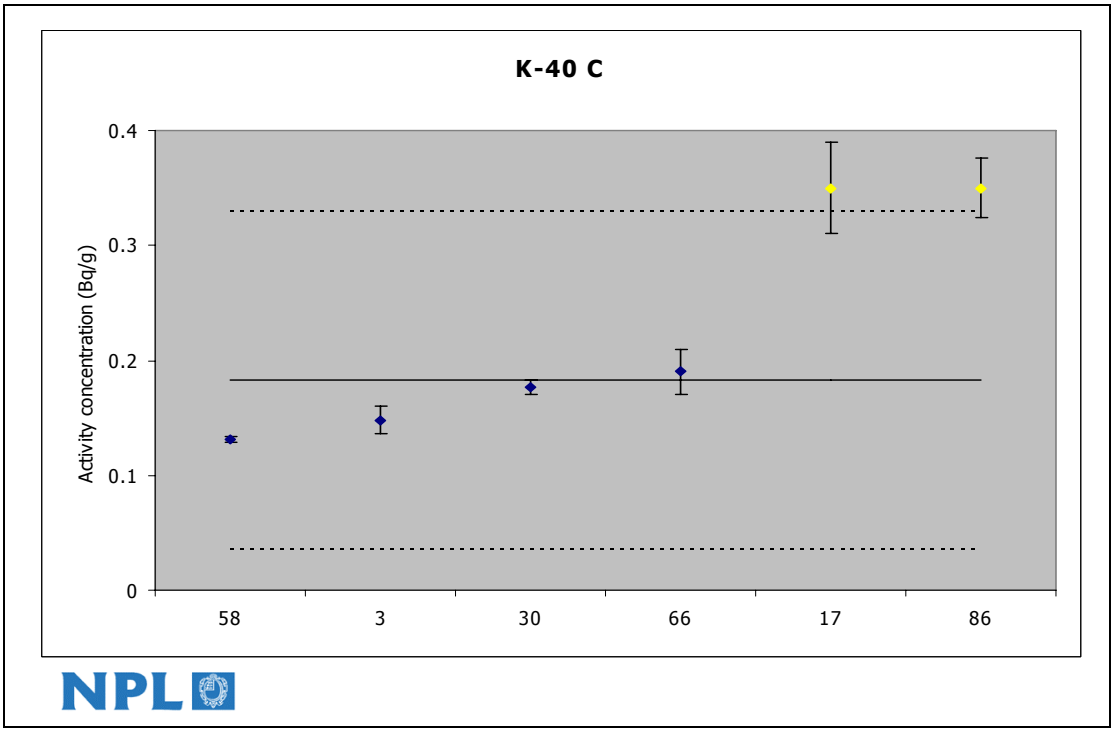
	(Bq g^{-1})	Results	In agreement
^{152}Eu	1.16(13)	25	88%
^{154}Eu	0.048(5)	21	86%
^{210}Pb	0.60(3)	1	-
^{226}Ra	0.05020(19)	2	100%
^{228}Ra	0.0102(23)	2	100%
^{228}Th	0.0060(3)	1	-
^{234}Th	0.037(4)	1	-

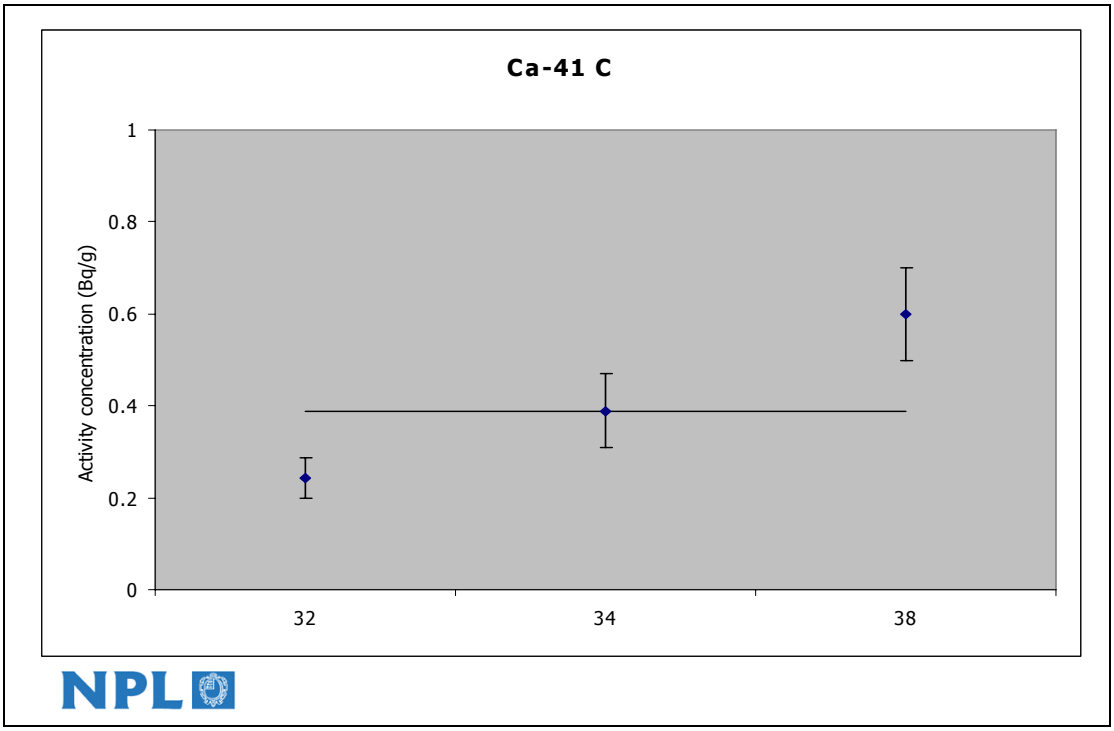
NPL

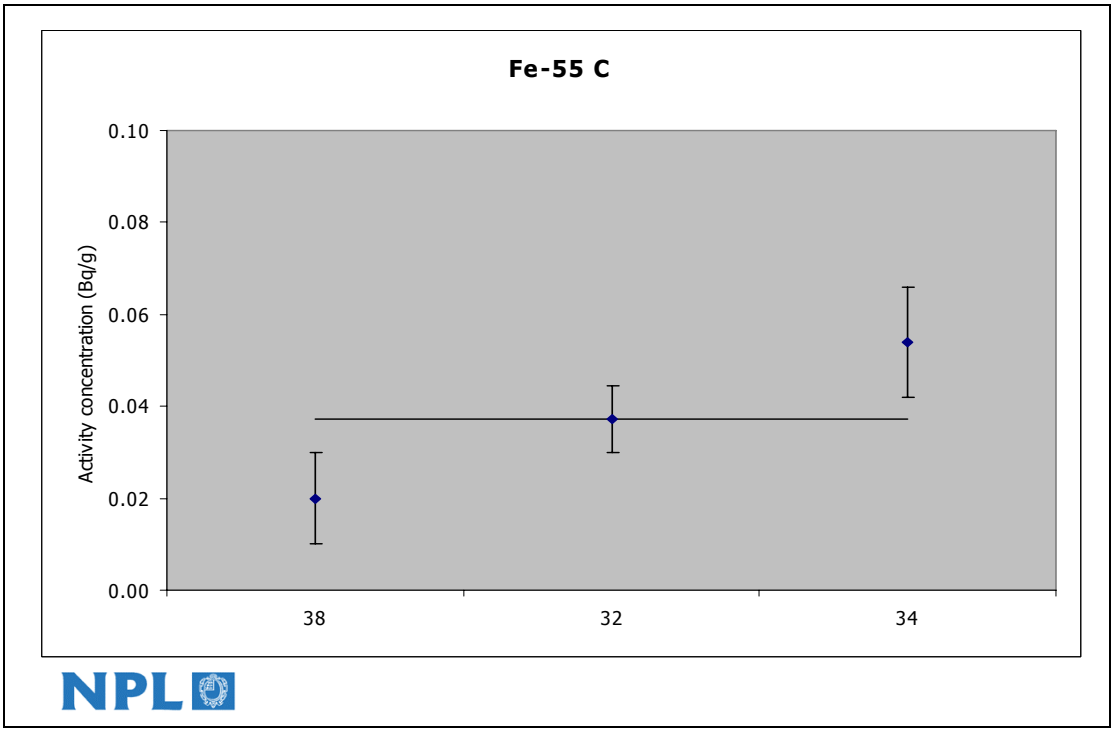

H-3 total C
Activity concentration (Bq/g)
20
15
10
5
0
4
74
35
34
29
32
38
5
17
NPL

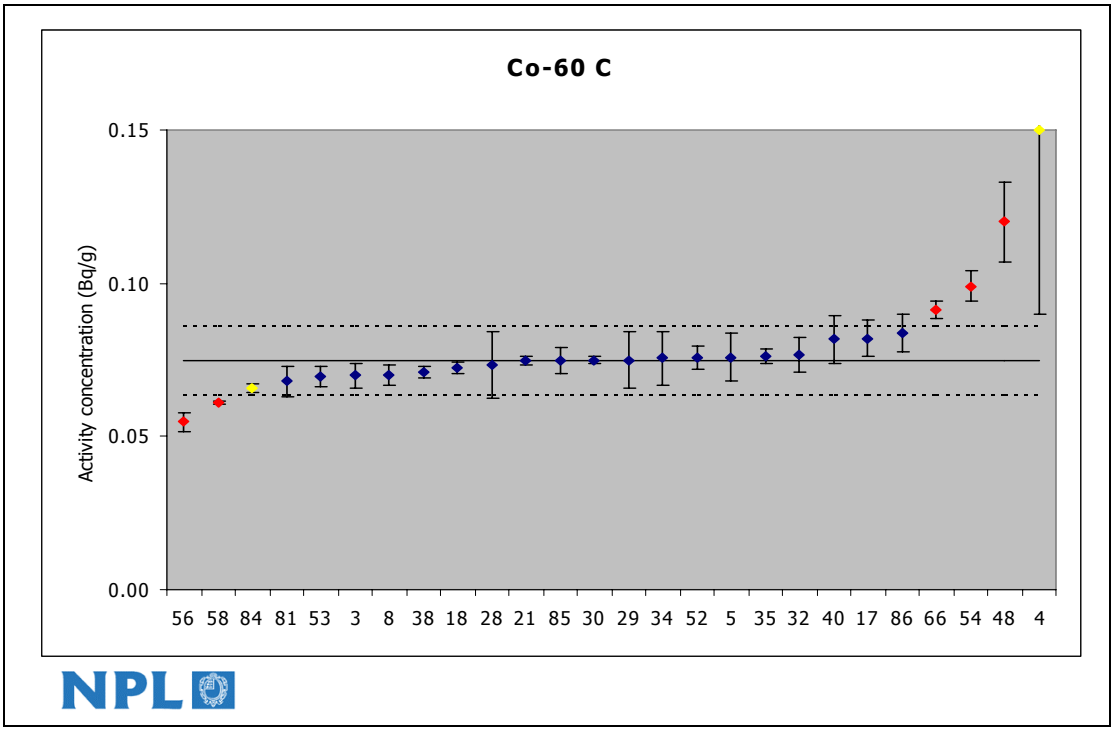

H-3 leach C
Activity concentration (Bq/g)
2.0
1.5
1.0
0.5
0.0
4
29
32
5
40
NPL

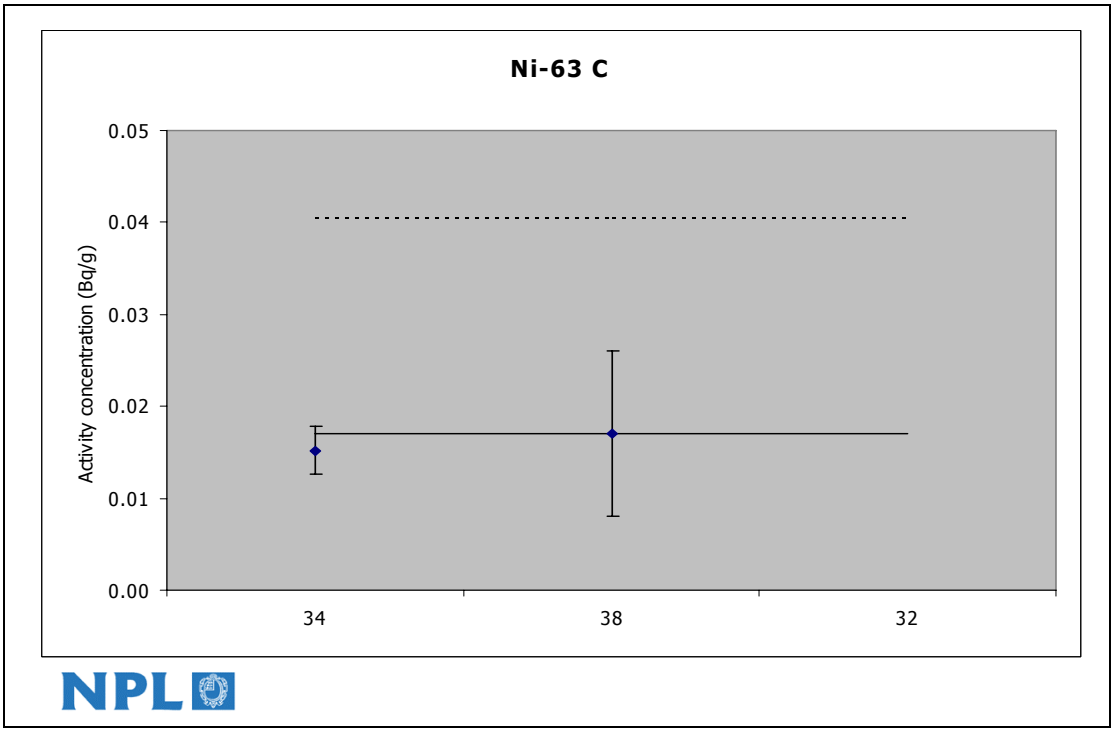

C-14 C
Activity concentration (Bq/g)
0.60
0.40
0.20
0.00
5
32
34
17
40
NPL

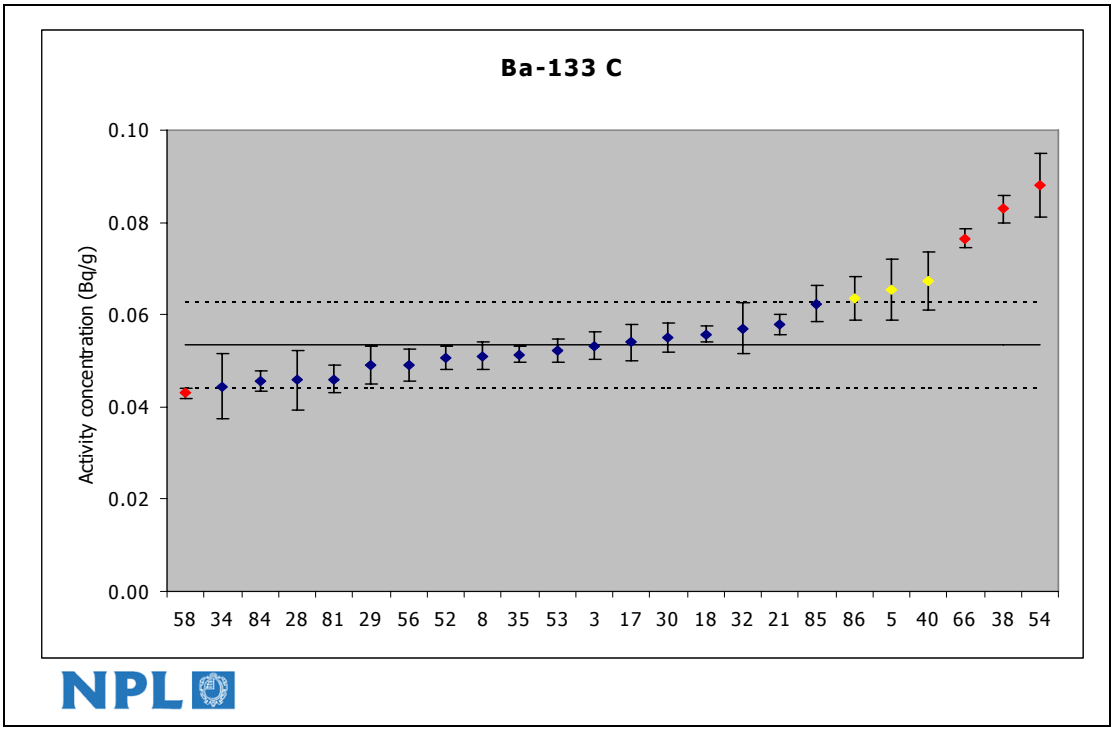

K-40 C
Activity concentration (Bq/g)
0.4
0.3
0.2
0.1
0
58
3
30
66
17
86
NPL

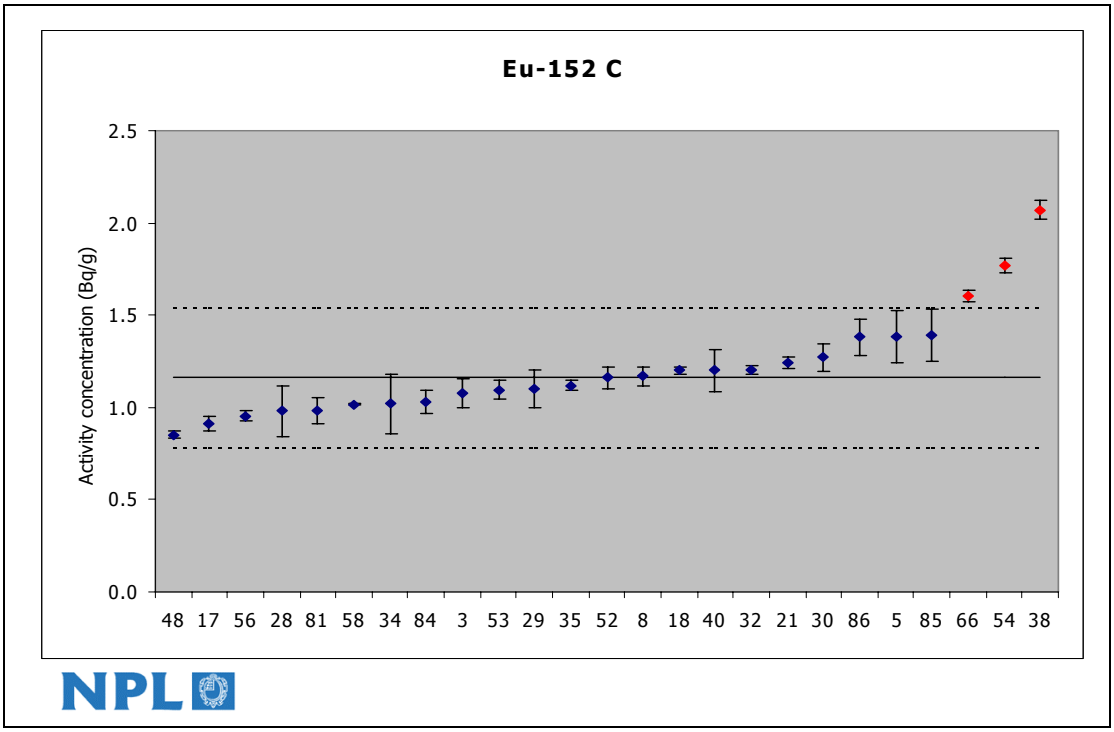

Ca-41 C
Activity concentration (Bq/g)
1
0.8
0.6
0.4
0.2
0
32
34
38
NPL

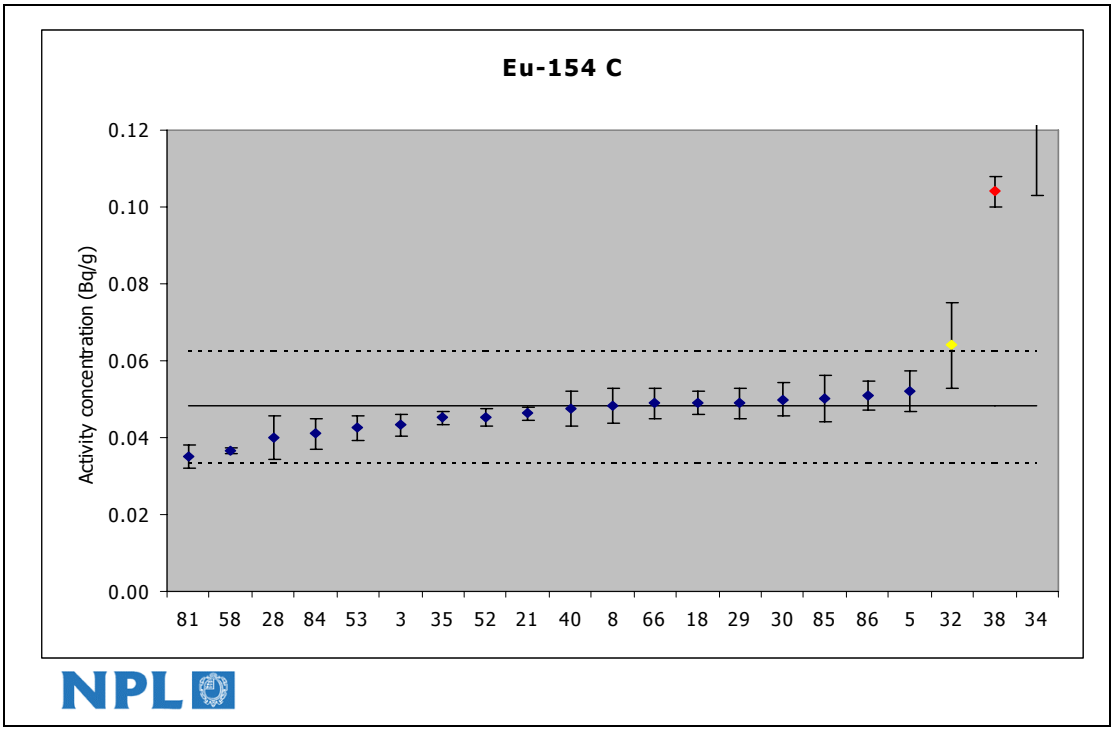

Fe-55 C
Activity concentration (Bq/g)
0.10
0.08
0.06
0.04
0.02
0.00
38
32
34
NPL

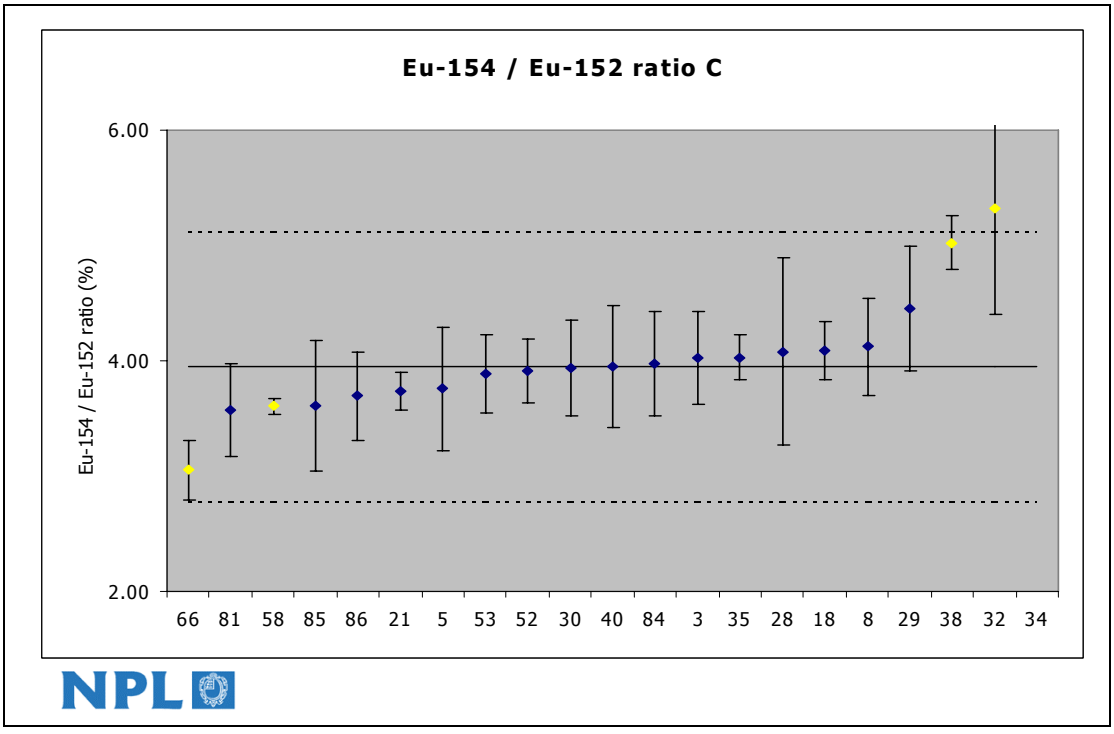

Co-60 C
Activity concentration (Bq/g)
0.15
0.10
0.05
0.00
56 58 84 81 53 3 8 38 18 28 21 85 30 29 34 52 5 35 32 40 17 86 66 54 48 4
NPL

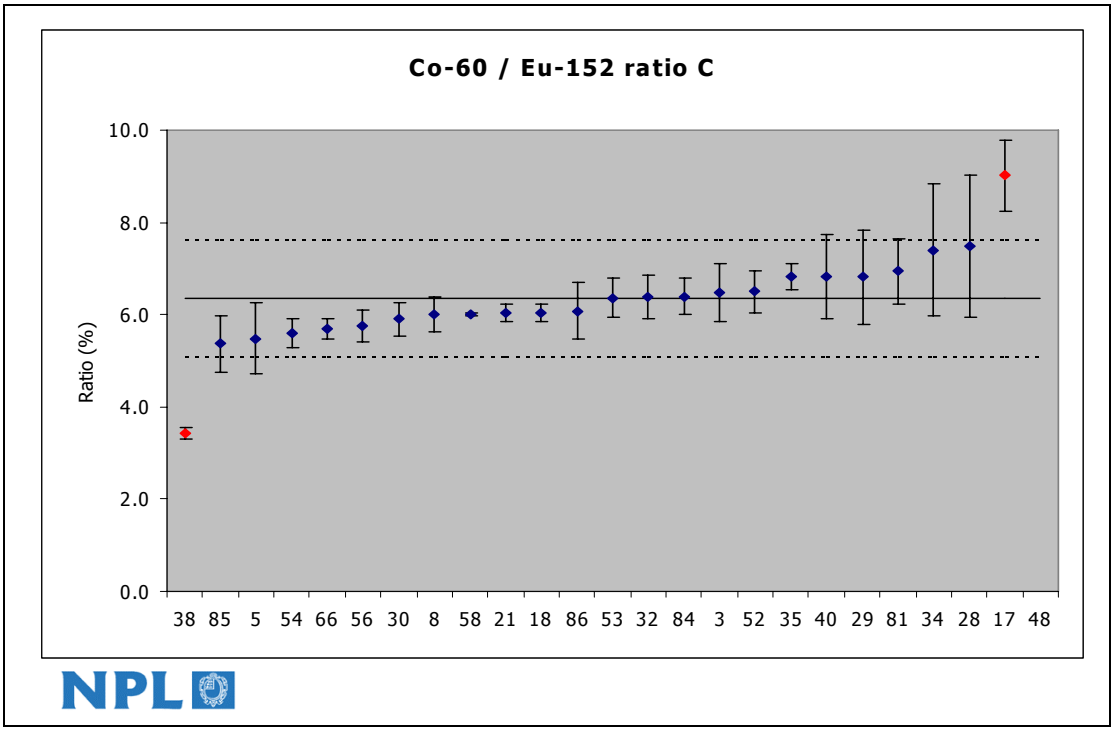

Ni-63 C
Activity concentration (Bq/g)
0.05
0.04
0.03
0.02
0.01
0.00
34
38
32
NPL

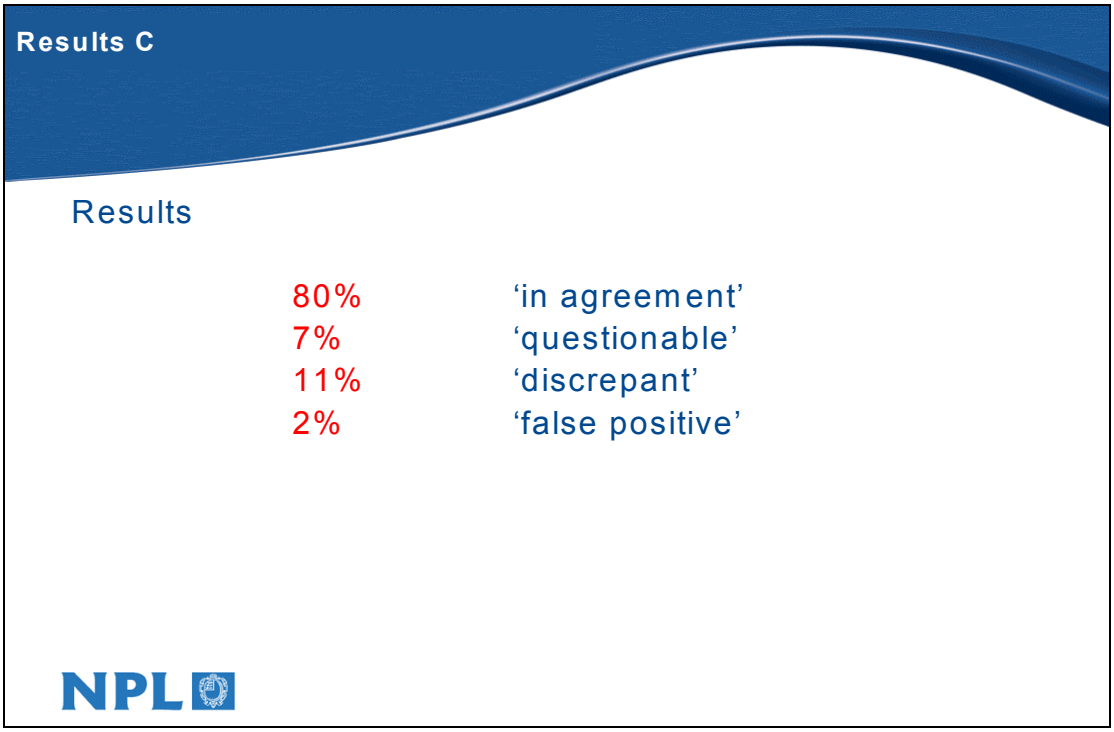

Ba-133 C
Activity concentration (Bq/g)
0.10
0.08
0.06
0.04
0.02
0.00
58 34 84 28 81 29 56 52 8 35 53 3 17 30 18 32 21 85 86 5 40 66 38 54
NPL


Eu-152 C
Activity concentration (Bq/g)
2.5
2.0
1.5
1.0
0.5
0.0
48 17 56 28 81 58 34 84 3 53 29 35 52 8 18 40 32 21 30 86 5 85 66 54 38
NPL


Eu-154 C
Activity concentration (Bq/g)
0.12
0.10
0.08
0.06
0.04
0.02
0.00
81 58 28 84 53 3 35 52 21 40 8 66 18 29 30 85 86 5 32 38 34
NPL


Eu-154 / Eu-152 ratio C
Eu-154 / Eu-152 ratio (%)
6.00
4.00
2.00
66 81 58 85 86 21 5 53 52 30 40 84 3 35 28 18 8 29 38 32 34
NPL


Co-60 / Eu-152 ratio C
Ratio (%)
10.0
8.0
6.0
4.0
2.0
0.0
38 85 5 54 66 56 30 8 58 21 18 86 53 32 84 3 52 35 40 29 81 34 28 17 48
NPL


Results C
Results
80% 'in agreement'
7% 'questionable'
11% 'discrepant'
2% 'false positive'
NPL

Results C (Co-60, Ba-133, Eu-152 and Eu-154 only)

Results

78%	'in agreement'
7%	'questionable'
15%	'discrepant'

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Eu-152/154 inhomogeneity affecting the exercise?

One sample (X07050, which was kept at NPL) had a different composition than the other 14 samples tested (containing a "hot" Eu-152/154 particle?)

If similar samples were sent-out (~7% chance) then this may explain the "Q" and "D" Eu-152/154 results for Labs 32, 34, 38, 54 and 66

However, the Eu ratios for Labs 32, 34, 38 and 66 are all "Q"
Lab 54 did not report Eu-154 and had "D" results for Co-60 and Ba-133 as well

Sample X07051 (which was prepared directly after X07050) was normal

Labs 32, 34, 38, 54 and 66 analysed X07053, X07035, X07040, X07052 and X07032, respectively

The inhomogeneity component was incorporated in u_N

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NPL National Physical Laboratory

Tritium in Concrete

Pete Burgess, María García-Miranda, John Gisby , Arvic Harms, Simon Jerome, Selina Woods

simon.jerome@npl.co.uk

NPL Radioactivity Comparison, 19th September 2007

Tritium in Concrete

- The UK 'nuclear legacy' from Harwell to Sizewell B will need to be decommissioned over the next century
- Total expected cost (2005 prices) ~£50 Billion over the next century (that's ~£10 million ***per week***)
- Currently, the boundary between 'free release' and low level radioactive waste is 0.4 Bq/g, summed over all anthropogenic radionuclides, irrespective of radiotoxicity
- In reactor concrete, this effectively means tritium limits the disposal route

NPL

Tritium in Concrete

Source term

- Neutron activation:

$^{6}Li(n,\alpha)^{3}H$ (~580 b)

$^{10}B(n,2\alpha)^{3}H$ (<10 mb)

$^{11}B(n,^{9}Be)^{3}H$ (<10 mb)

$^{2}H(n,\gamma)^{3}H$ (<10 mb)

- Fission:

Fission yields 0.01 to 0.02%

- Contamination

Ingress of water from elsewhere

NPL

Tritium in Concrete

- Tritiated cement made by making commercially available cement with tritiated water
- Concrete/cement setting is complex and takes years to complete; water loss is important in this process
- Water is incorporated in two ways:
  - Within pores and channels within the concrete matrix
  - Within Calcium Silicate Hydrate ($Ca_2SiO_4.xH_2O$) gel
- Isotopic fractionation is not expected

NPL

Tritium in Concrete

- Tritiated cement prepared as a single bulk mixture and set in:
  - Closed polystyrene pots (150 cm^3)
  - Open polystyrene pots (150 cm^3)
  - Open aluminium pyrolyser boats (~20 cm^3)
- Allowed to cure in a sealed glass tank with a water reservoir
- Activity concentration based on mass balance from mixing and any evaporation losses

NPL

Tritium in Concrete

- Mass Balance:

W_1 = dry container + dry mixer

W_2 = dry concrete + W_1

W_3 = water + W_2

W_4 = $W_3 - W_1$ (= mass of wet concrete)

W_5 = cured concrete + W_1

W_6 = $W_5 - W_1$ (= mass of cured concrete)

W_7 = $W_6 - (W_2 - W_1)$ (= mass of water in cured concrete)

P = $W_7/(W_3 - W_2)$ (= proportion of water retained)

NPL

Tritium in Concrete

- Activity concentration in cured concrete

A_1 = Bq/g of tritium in mixing water

$A_2 = A_1 \times (W_3 - W_2)/ W_4$ (= Bq/g of tritium in wet concrete)

$A_3 = A_1 \times W_7/W_4$ (= Bq/g of tritium in cured concrete)

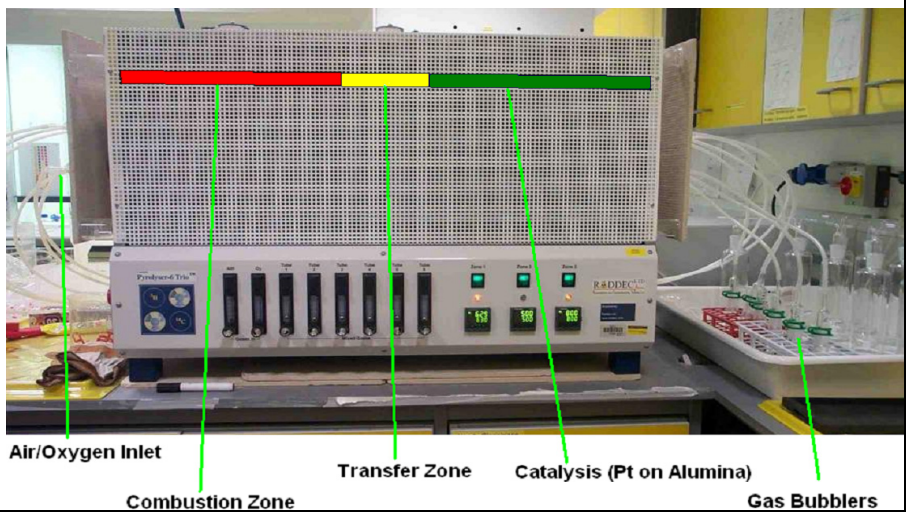
- Cannot carry out a meaningful direct measurement
- Have to rely on mass balance data only

Closed polystyrene pots	1446 ± 0.70% Bq/g(*k=1*)
Open polystyrene pots	1424 ± 0.73% Bq/g (*k=1*)
Open aluminium pyrolyser boats	1363 ± 0.91% Bq/g (*k=1*)

NPL

Tritium in Concrete

- Analysed with RADDEC Pyrolysis Furnace
- Six tube furnace for volatile radionuclides



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Tritium in Concrete

- Samples measured by loading into combustion boats
- Oxygen passed through system
- Off-gas trapped in bubblers
- Ignition by increasing temperature to 900 ºC
- Maintain temperature for at least 6 hours
- Weigh and distil water in bubblers
- Mix with Ultima Gold AB
- Measure on suitable counter

NPL

Tritium in Concrete

- Initial measurements with combustion at 900 ºC gave good recoveries – 69.5 (± 8.5)% (*k=1*)
- Assumed (at this stage) that losses were due to poor gas flow through the system and losses from the gas bubblers
- Temperature profiled release indicated that tritium released at ~200 ºC and at ?6-900 ºC
- Two releases of tritium indicate that water in concrete pores released at lower temperatures but matrix bound tritium requires more aggressive treatment
- Similar observation made independently by another laboratory

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Tritium in Concrete

- All very successful, but……
- Combustion yields dropped to very low levels
- Only operational difference was to grind the concrete prior to analysis
- Surface area increased
- Diffusion paths decreased
- May lead to rapid loss of tritium

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Tritium in Concrete

- Setting reactions are slow and balance between pore and matrix water may change
- Material may not be stable, depending on the sample pre treatment
- Should it be prepared with low surface to volume ratio
- How is this to be presented to users?
- Many laboratories use crushing/grinding/sieving techniques for sample preparation

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Tritium in Concrete

Conclusion

- Tritiated concrete can be prepared and the tritium activity concentration derived from experimental data
- Tritium is present as pore and crystalline water in a dynamic system
- Presenting such material as a powder limits its usefulness
- As with organically bound tritium, certification will need to cover chemical form as well as activity concentration
- Work so far has raised more questions than it has solved
- Compliance with ISO Guide 34 is not yet possible

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ISO Guide 43, Part 1

Simon Jerome
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NPL Drum Comparison, 21st September 2007

What is it?

- ISO Standard ISO 43 '***Proficiency testing by interlaboratory comparisons***'
- Part 1: '*Development and operation of proficiency testing schemes*'
- In reality…….
- ILAC Guide G13:2000 '***Guidelines for the Requirements for the Providers of Proficiency Testing Schemes***'

International Laboratory Accreditation Cooperation

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Why do it?

PT Providers

- Valuable tool for Laboratories and UKAS
- PTs/Comparisons must be reliable
- Participants need confidence in the PT provider's competence.
- Accreditation allows for an independent assessment of competence.
- PT providers requested accreditation.

ISO/IEC 17025:2005

- Requires that suppliers of critical services are evaluated.
- Requires participation in suitable PTs/Comparisons

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How is it done?

PT Providers Assessment Criteria

- Combination of Assessment Standards
- ISO/IEC Guide 43-1:1997
- ILAC G13:2000
- ISO/IEC 17025:2005

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Outcomes

PT Providers - Feedback

- Positive feedback received from organisations
- Laboratories have noted an improvement in the service provided

Technical Assessors have noted:

- Better clarity in reporting
- Increased awareness in laboratory staff

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Management System Requirements

- Quality Management System
- Organisation and Management
- Document and Information Control
- **Request, Tender or Contract Review**
- Use of Collaborators (Subcontractors)
- Procurement of Services and Supplies
- **Client Feedback**
- Control of Non-conforming Materials
- Corrective/Preventive Action
- **Records**
- **Internal Audits/Management Reviews**

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Technical Requirements

- General
- Management, Staffing and Training
- Collaborators (Subcontractors)
- **Organisation and Scheme Design Logistics**
- *Choice of Method or Procedure*
- **Conduct of Proficiency Testing Scheme**
- **Data Analysis and Interpretation of Scheme Results**
- **Communication with Participants**
- **Confidentiality**
- **Collusion and Falsification of Results**

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At NPL

Seeking accreditation for proficiency test provision

- Initial assessment July 2007
- Assessment team:
  - Assessment Manager (QMS Issues)
  - Technical Assessor 1 (Technical Issues)
  - Technical Assessor 2 (Statistical Analysis)
- Currently working through improvement actions

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NPL Outcome

Offer of accreditation is subject to clearance of improvement actions

- Should complete October 2007
- UKAS review on submission
- Surveillance visit 3 months after accreditation offered
- Will cover
  - Assigned value scheme: Multiple radionuclides in solution
  - Assigned value scheme: Single radionuclide in solution
  - Consensus value scheme: Multiple γ emitters in concrete

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The future

Complete initial accreditation

- Extend to other PTs/Comparisons
- Will (eventually) include drum comparisons as
  - Assigned value scheme: Multiple γ emitters in variable density drummed waste
- Intend migrating to flexible scope

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Overview of Radioactivity Projects in AIR Programme 2007 - 2010

Julian Dean
National Physical Laboratory
NPL Drum Comparison Workshop, 21st September 2007

Background

- Programme runs October 2007 – September 2010
- Based on extensive user consultation process
- Will cover:
  - Acoustics
  - Radiation dosimetry
  - Neutron metrology
  - Radionuclide metrology
  - Knowledge Transfer
  - Programme Management and Formulation

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Overall purpose of programme

- "The aim of the programme is to enable all users of ionising radiation and acoustical measurement instrumentation in the UK to carry out measurements of acoustic fields, radiation dosimetry, radioactivity and neutrons to an accuracy that is fit for purpose and at the forefront of good practice internationally.To that end, the programme seeks to provide appropriate primary measurement standards, associated services and knowledge transfer mechanisms, and to support UK industry and user communities in the innovation of instrumentation and measurement methodologies in line with government policy."

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Radioactivity theme - projects

- Primary Measurement Standards and Systems
- Infrastructure for Secondary Measurement Standards of Radioactivity
- Provision of Measurement Infrastructure for Nuclear Medicine
- Infrastructure for Environmental Radioactivity Standards
- Measurement Infrastructure for Radiation Protection
- Measurement Infrastructure for Nuclear Decommissioning
- Radioactivity Knowledge Transfer

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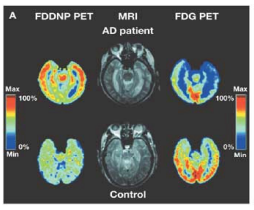
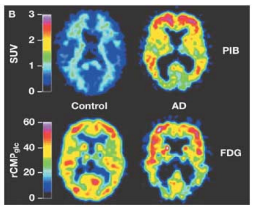
Primary Measurement Standards and Systems

- Compliance with Mutual Recognition Agreement
- Upgrading of primary systems
- Nuclear data evaluations
- Gas standards (including PET gas monitors)





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Infrastructure for Secondary Measurement Standards of Radioactivity

- Development and validation of secondary standards
- Tritiated water comparison
- Source preparation facilities upgrade and chemistry support

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Provision of Measurement Infrastructure for Nuclear Medicine

- New primary standards (e.g. ^{177}Lu)
- Measurement service for ^{125}I brachytherapy seeds
- Development of ion-chamber based procedures
- Radionuclide Calibrator Users' Forum, GPGs

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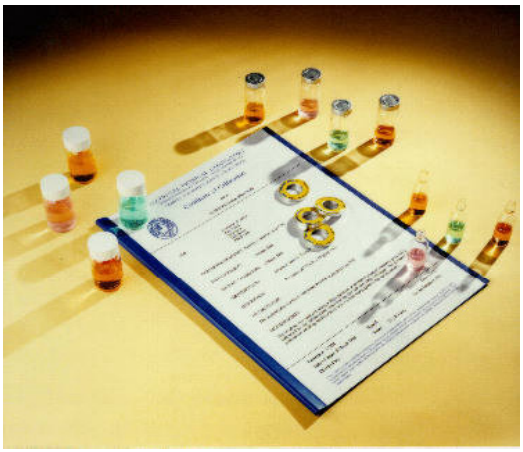
Infrastructure for Environmental Radioactivity Standards

- Primary standardisations of ^{208}Po or ^{209}Po, ^{241}Pu and ^{227}Ac
- Development of two non-aqueous Reference Materials for radioactivity monitoring
- Annual Environmental Radioactivity Proficiency Tests
- Environmental KT



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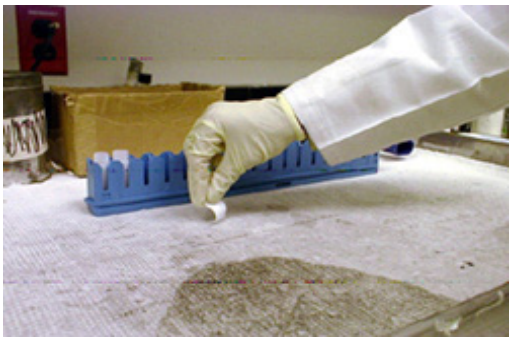
Measurement Infrastructure for Radiation Protection

- Photon-emitting large-area reference source standard
- Microfluidic devices for rapid radiochemical assays
- Comparison of true and apparent activities on filters and wipes
- Response of instruments to different forms of Tritium
- User fora (IRMF, ARMUG)



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Measurement Infrastructure for Nuclear Decommissioning

- Production and certification of two Certified Reference Materials
- GPG on mathematical models for measuring radioactivity in waste
- Consultancy and audit service on use of models
- NPL Report on characterisation of surface contamination monitors for radioactivity in different materials
- Support to CEWG and NICoP

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Large volume gamma standards – what next?

Pete Burgess

Questions 1

- Two standards or one intercomparison and one standard?
- Views on the plastic bottle approach
- Homogeneous or not?

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Questions 2

- Different nuclide mix?
- Radium?
- Activity level?
- Package size – drum again, smaller, bigger?
- Matrix – concrete, brick, with or without naturals?

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Anyone want to buy one?

- We can probably finance a small number of standards for loan
- We can make bespoke standards – contaminated pipes, surface contaminated box etc

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