The Abdus Salam
International Centre for Theoretical Physics

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1833-3

Workshop on Understanding and Evaluating Radioanalytical Measurement Uncertainty

5 - 16 November 2007

ALMERA 2006 Proficiency Test on the determination of gamma emitting radionuclides in soil, grass and water

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IAEA-CU-2006-04 ALMERA Proficiency Test on the determination of gamma emitting radionuclides

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International Atomic Energy Agency
Agency's Laboratories Seibersdorf

4th ALMERA coordination meeting, 5-7 November 2007

ICTP, Trieste, ITALY

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Introduction

40 years tradition at the Chemistry Unit at the Agency's laboratories in Seibersdorf

- organization of proficiency tests,
- production and distribution of reference materials, and
- the provision of training

- Proficiency testing is a traditional activity in CU.

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Introduction

- ALMERA members recommended that at least one Proficiency Test should be organised per year.
- Soil, water, vegetation and air filter matrices were proposed.
- Reporting time within 3 working days

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Introduction

The quality of a PT depends mainly on :

- How the property value for the test item is established;
- Which performance indicators are used;
- How the acceptance criteria are established

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PT approaches

I- How the property value for the test item is established

Unknown target value

Consensus values from the participants (retroactively).

Uncertainty

Known target value

pure substance or spike

certified reference materials

Consensus values from expert laboratories

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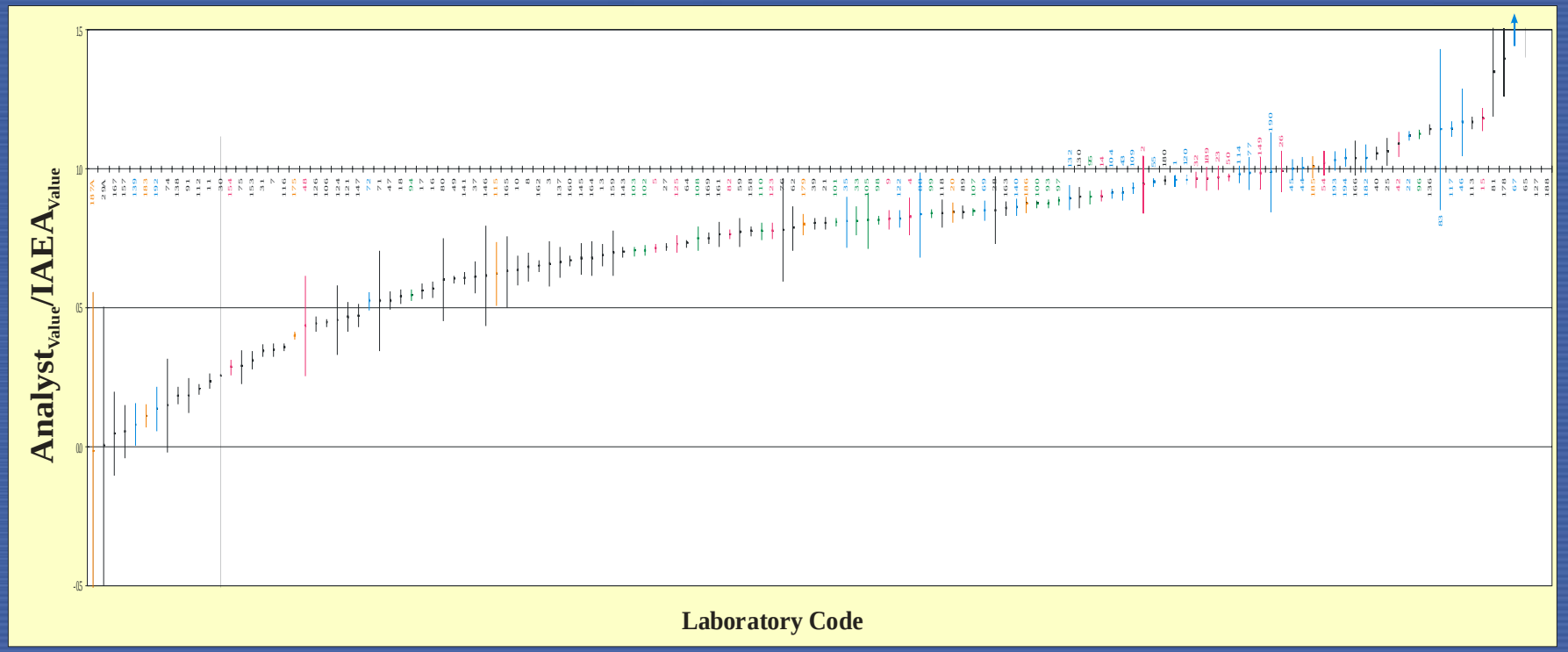
Relative distribution of participants' results for 5.4 Bq of ^{90}Sr in a 50g sample



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Establishing property value

- The Chemistry Unit at Agency's laboratories uses either:
  - spiked matrix reference materials
  - or matrix reference materials characterized by expert laboratories.
- To illustrate CU approach, the preparation of the spiked soil used in ALMERA PT is presented.

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Preparation of spiked soil

- The Chemistry Unit at Agency's laboratories developed a spiking procedure for RN in soil,
- Improving the particle size and particle distribution of the blank material,
- Improving the homogenization process,
- Drying process,

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Preparation of spiked soil

- Homogeneity testing,
- Estimate the heterogeneity uncertainty (ISO Guide 35),
- Trend check, stability test.
- Checking the property values,
- Quality control of spiked materials

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Trend check

- 38 bottles were counted for 3600 sec and 7 bottles for 57000 sec by gamma-spectrometer
- Slope calculated
- Uncertainty slope estimated
- Check for significance of trend performed.
- Table 1 shows summary of trend check results

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Trend check

	^{210}Pb	^{241}Am	^{109}Cd	^{134}Cs	^{137}Cs	^{54}Mn	^{65}Zn	^{60}Co
Slope	1.303 E-05	3.667 E-05	-1.110 E-05	3.196 E-06	-9.595 E-06	-3.755 E-06	-1.336 E-05	7.996 E-06
u-Slope	1.230 E-05	2.045 E-05	2.295 E-05	1.122 E-05	9.391 E-06	9.891 E-06	1.073 E-05	7.121 E-06
df	44	44	44	44	44	44	44	44
Slope/u	1.058	1.792	-0.484	-0.323	-1.021	-0.379	-1.224	1.122
T-critical (0.05, 44)	2.01	2.01	2.01	2.01	2.01	2.01	2.01	2.01

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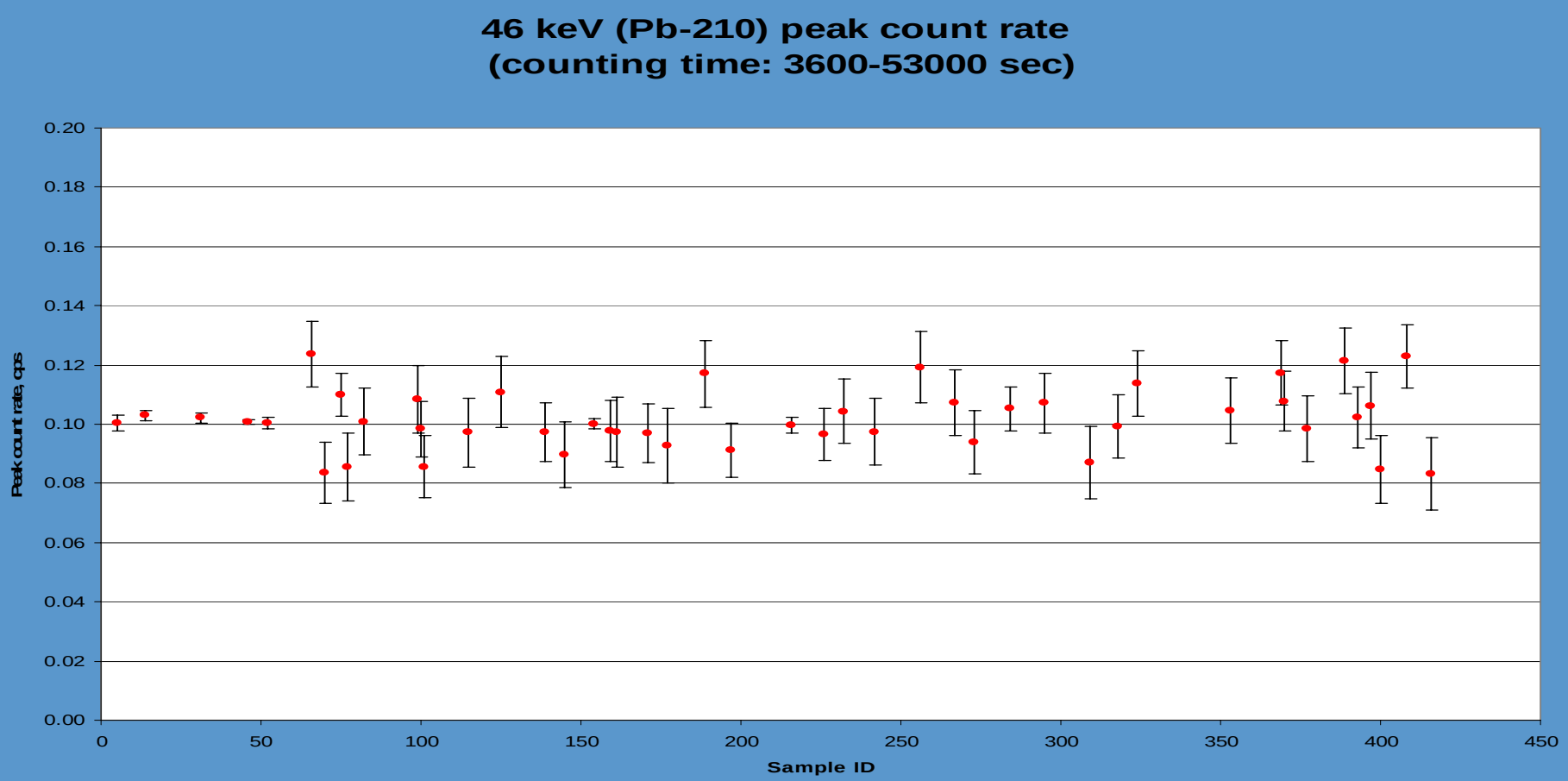
Trend check



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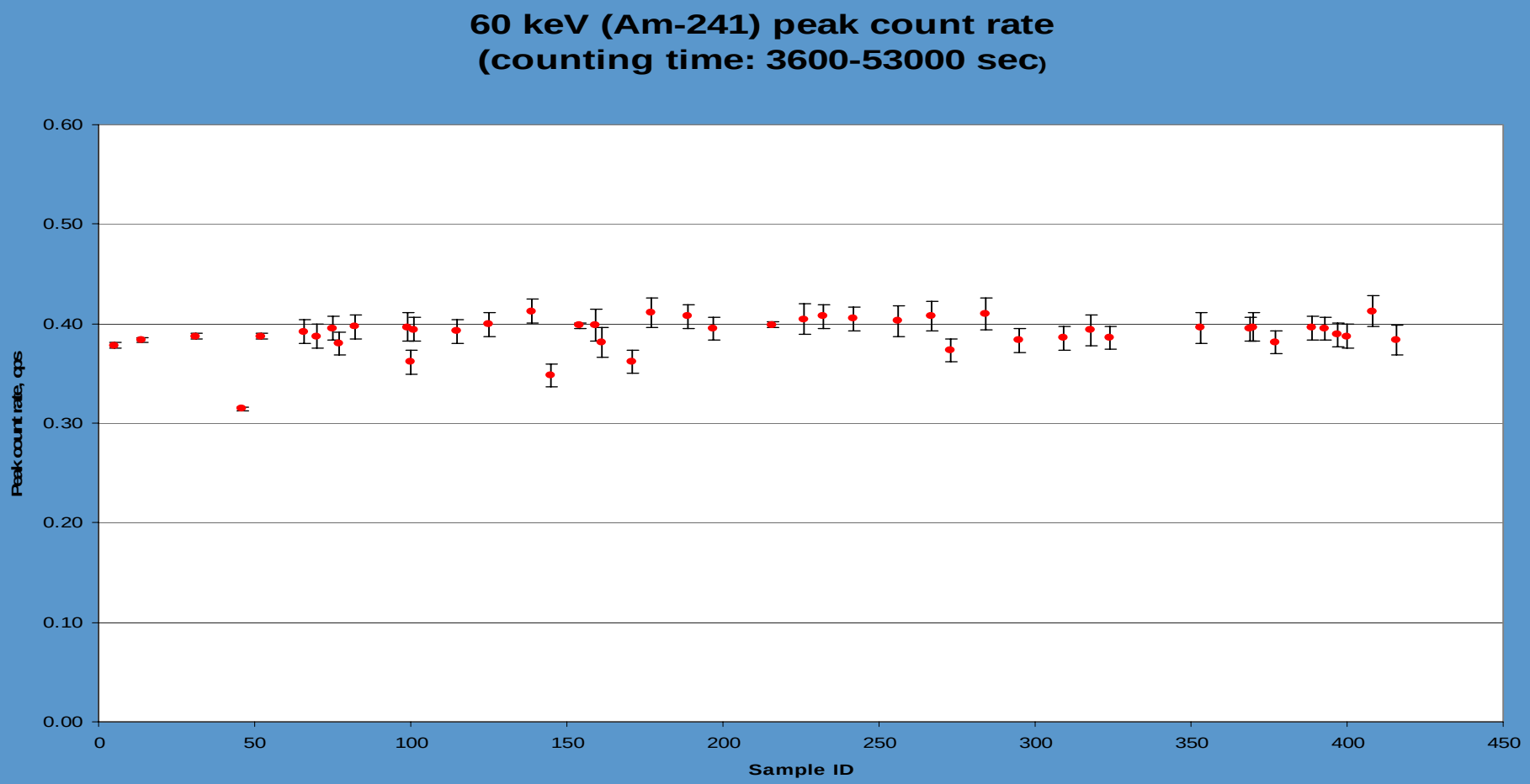

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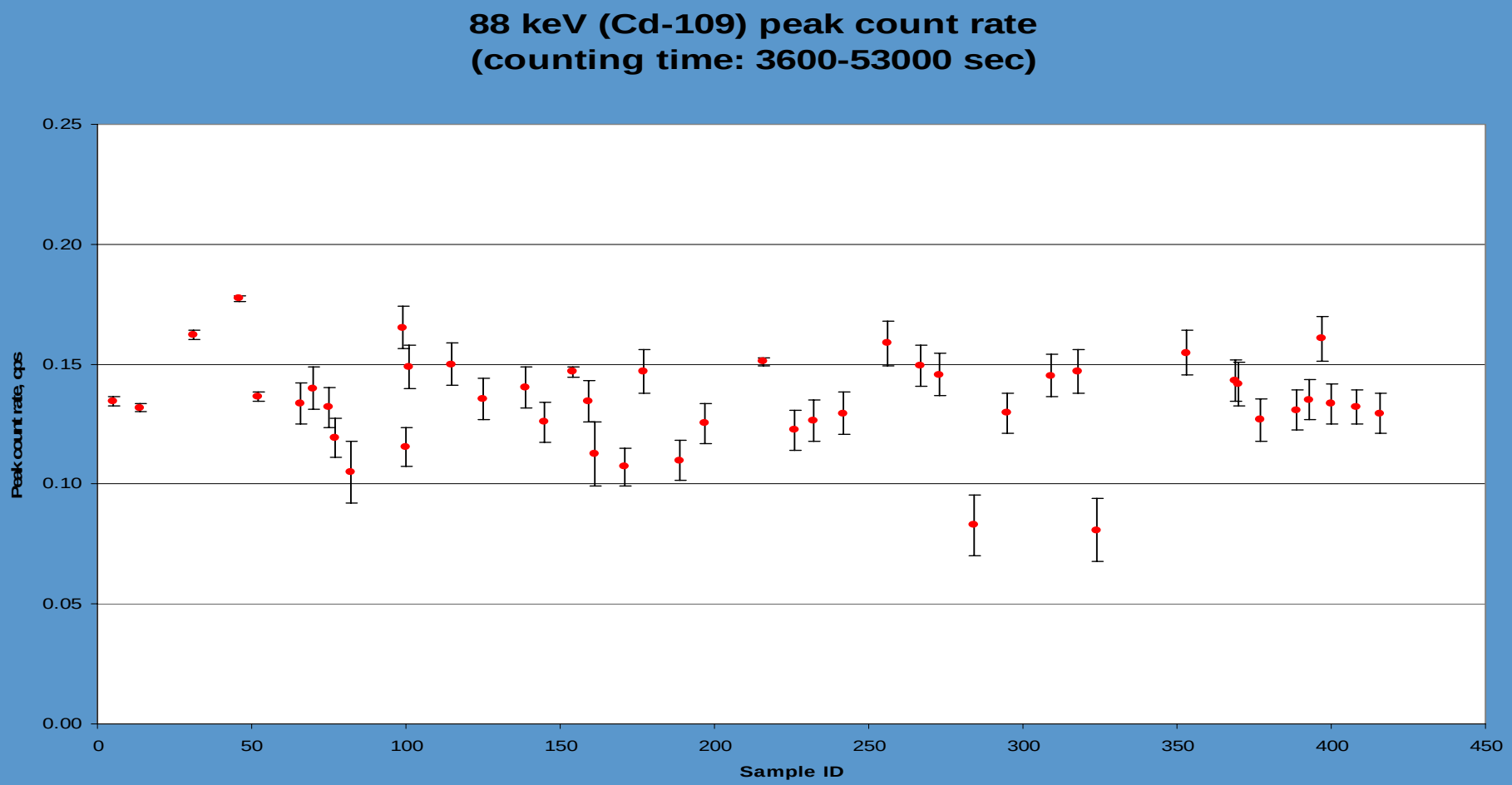

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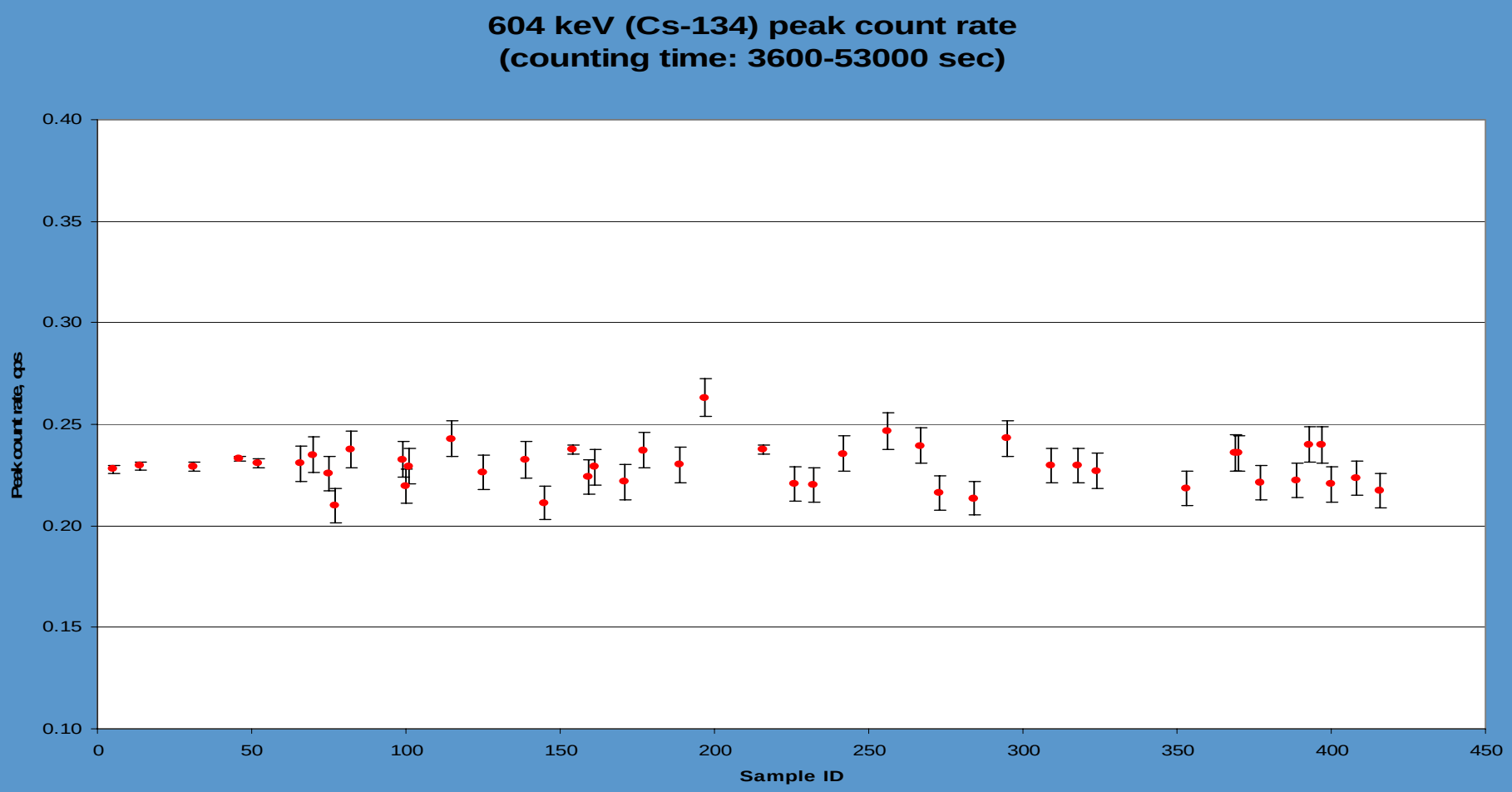

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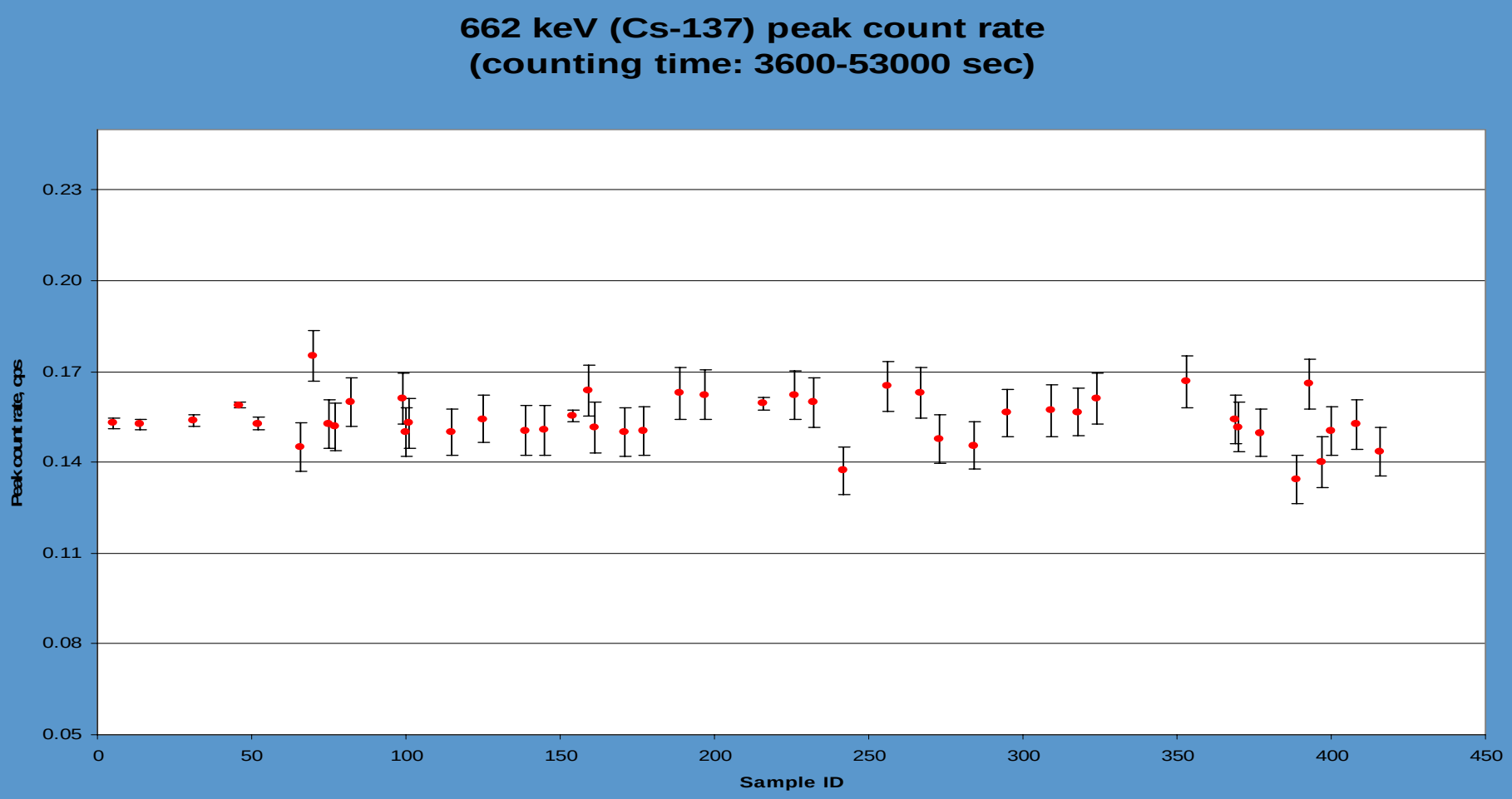

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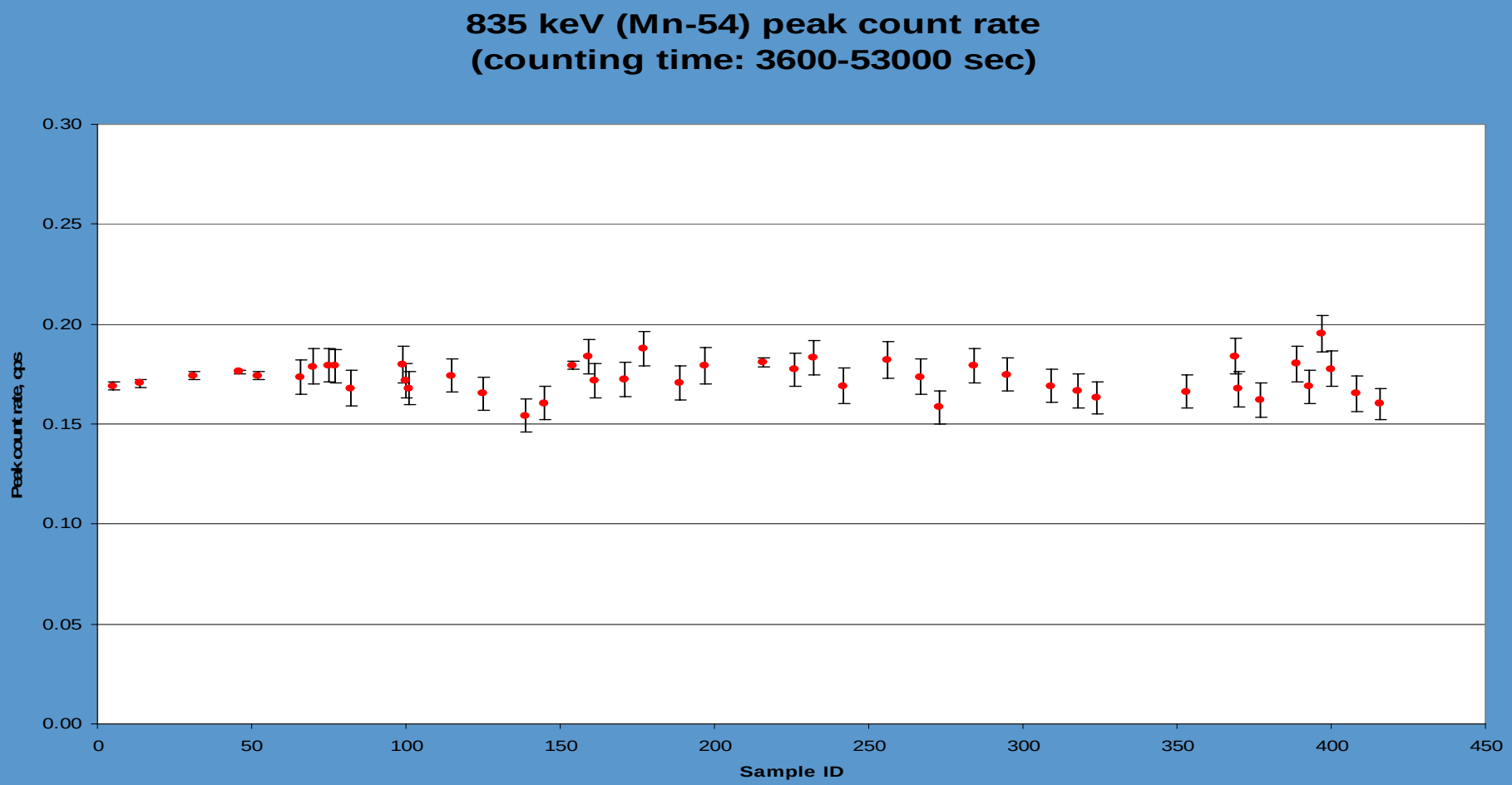

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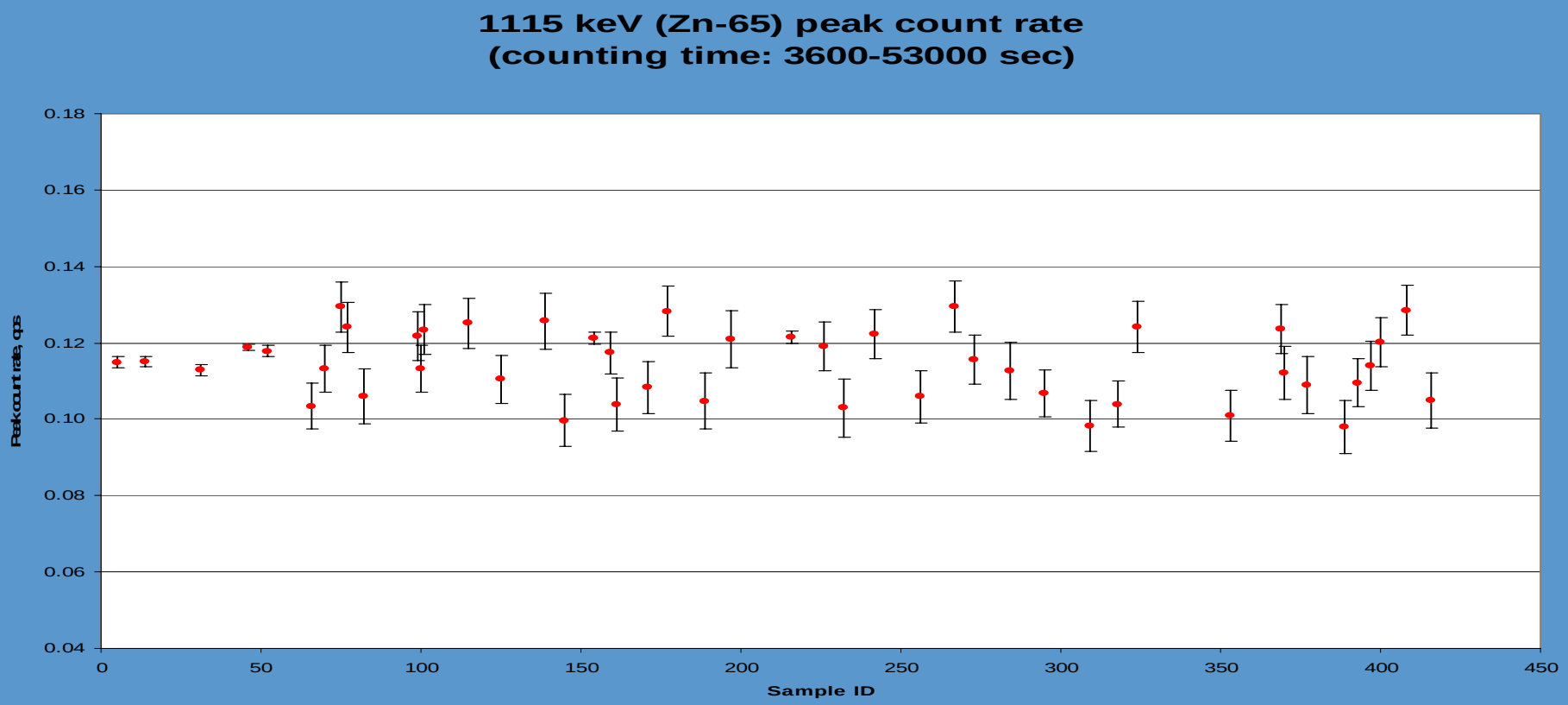

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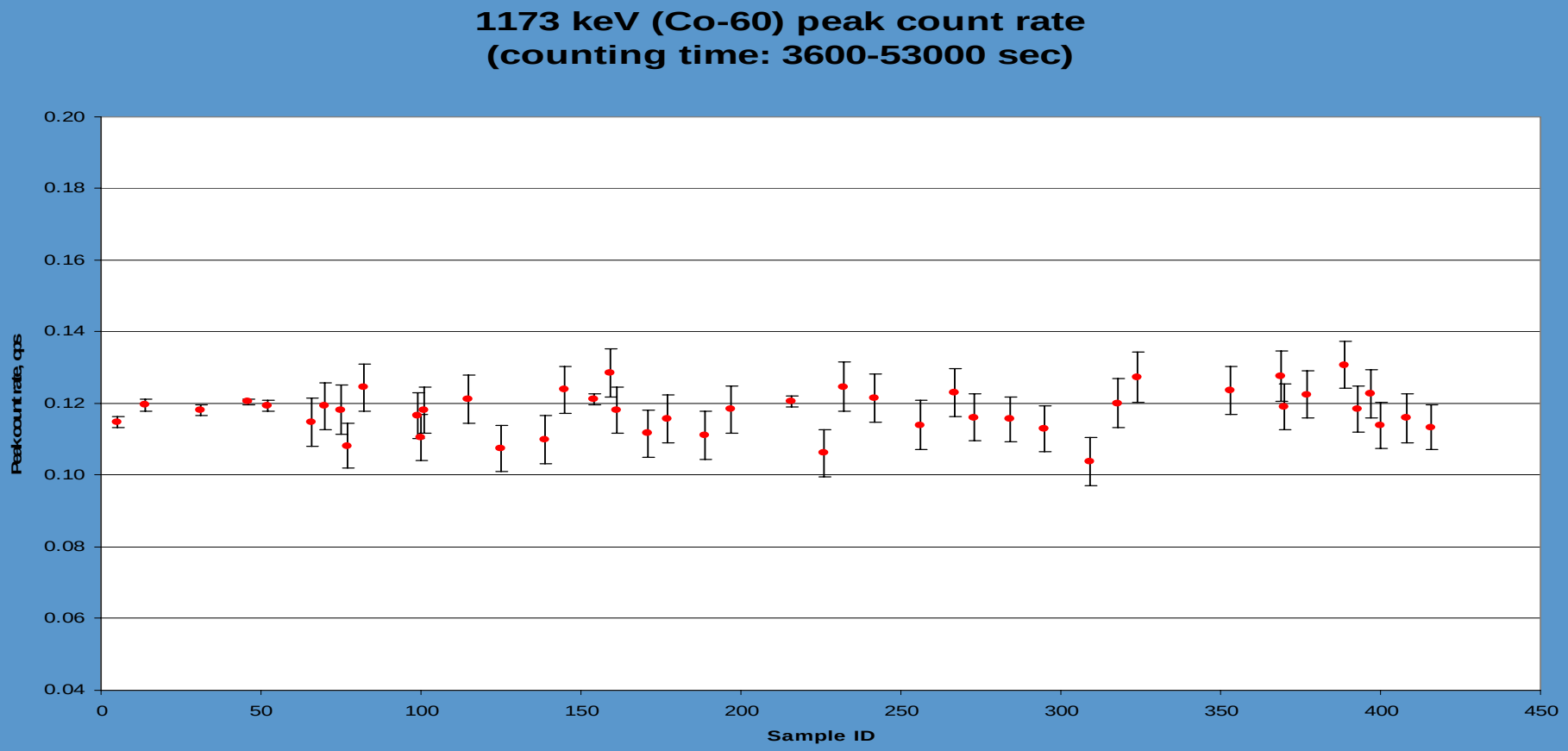

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Homogeneity testing

•To estimate within and between bottles uncertainty associated with the heterogeneity 3 bottles were analysed in triplicate at sample mass of 50 g.

• Single way ANOVA was applied according to the formulas stated in ISO Guide 35

$$s_{wb}^2 = MS_{within}$$

$$s_{bb}^2 = \frac{MS_{amon\,g} - MS_{within}}{n_0}$$

$$u^*_{bb} = \sqrt{\frac{MS_{within}}{n}} \sqrt[4]{\frac{2}{\nu_{MS_{within}}}}$$

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Homogeneity testing

- Table 2 summarize the homogeneity testing results:

RN	^{210}Pb	^{241}Am	^{109}Cd	^{134}Cs	^{137}Cs	^{54}Mn	^{65}Zn	^{60}Co
u^*_{bb} (%)	0.60	0.30	1.22	0.24	0.36	0.29	0.43	0.50

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Quality control of spiked material

• All spiked material were counted on gamma-spectrometer to insure consistency and to detect any gross error during the preparation.

•401 samples were measured.

• The following pictures show the results of these measurements

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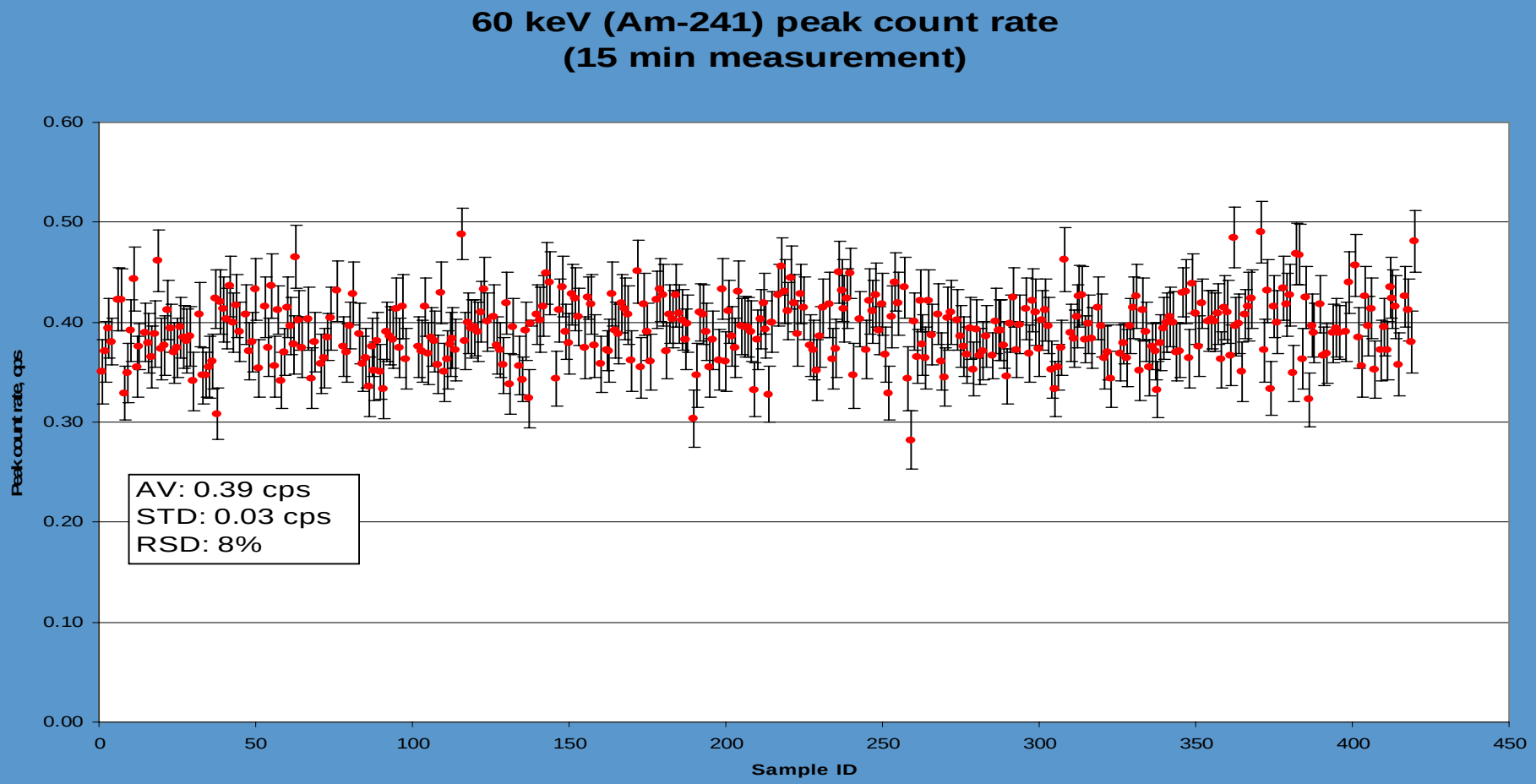
Quality control of spiked material



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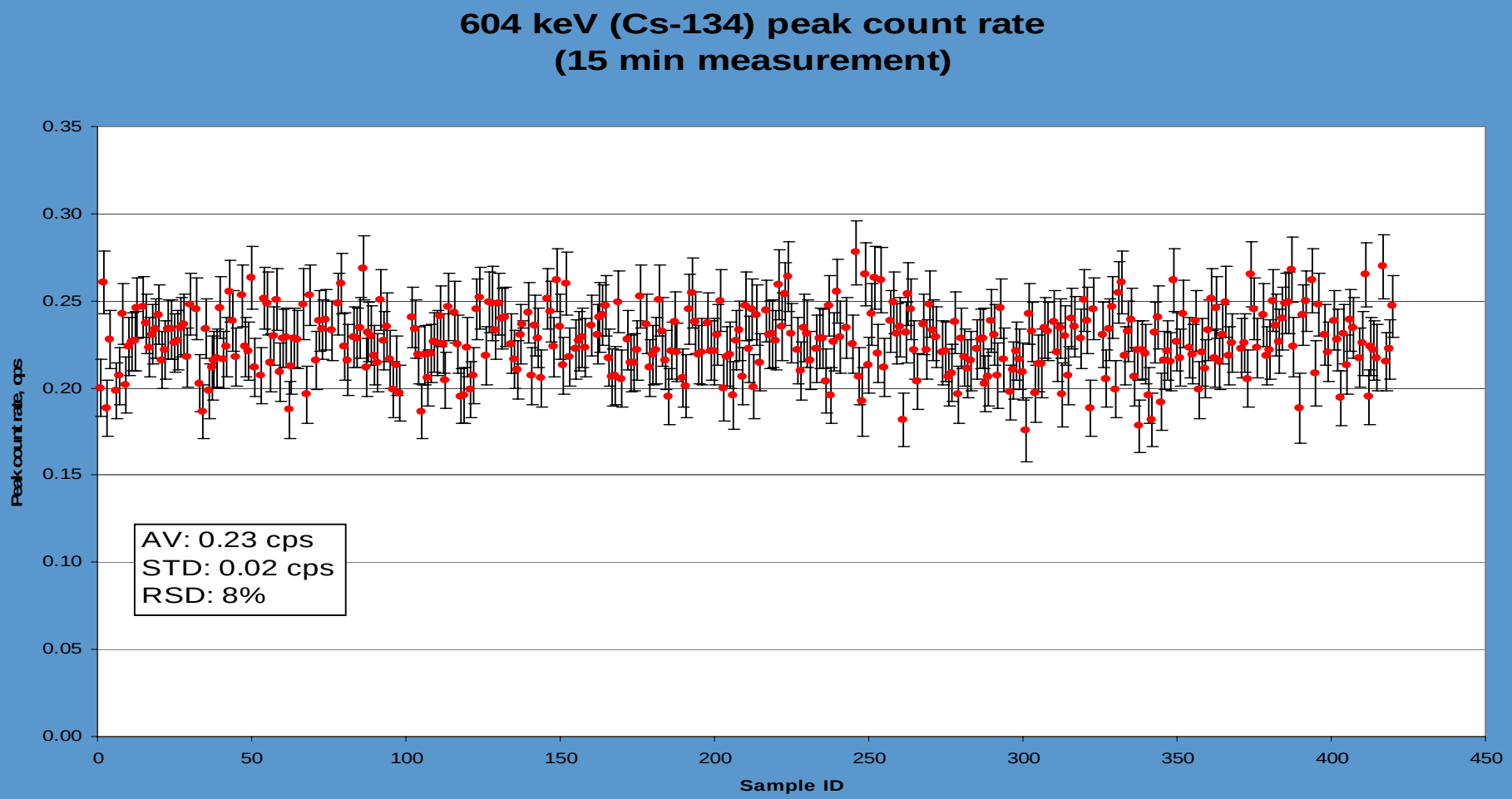

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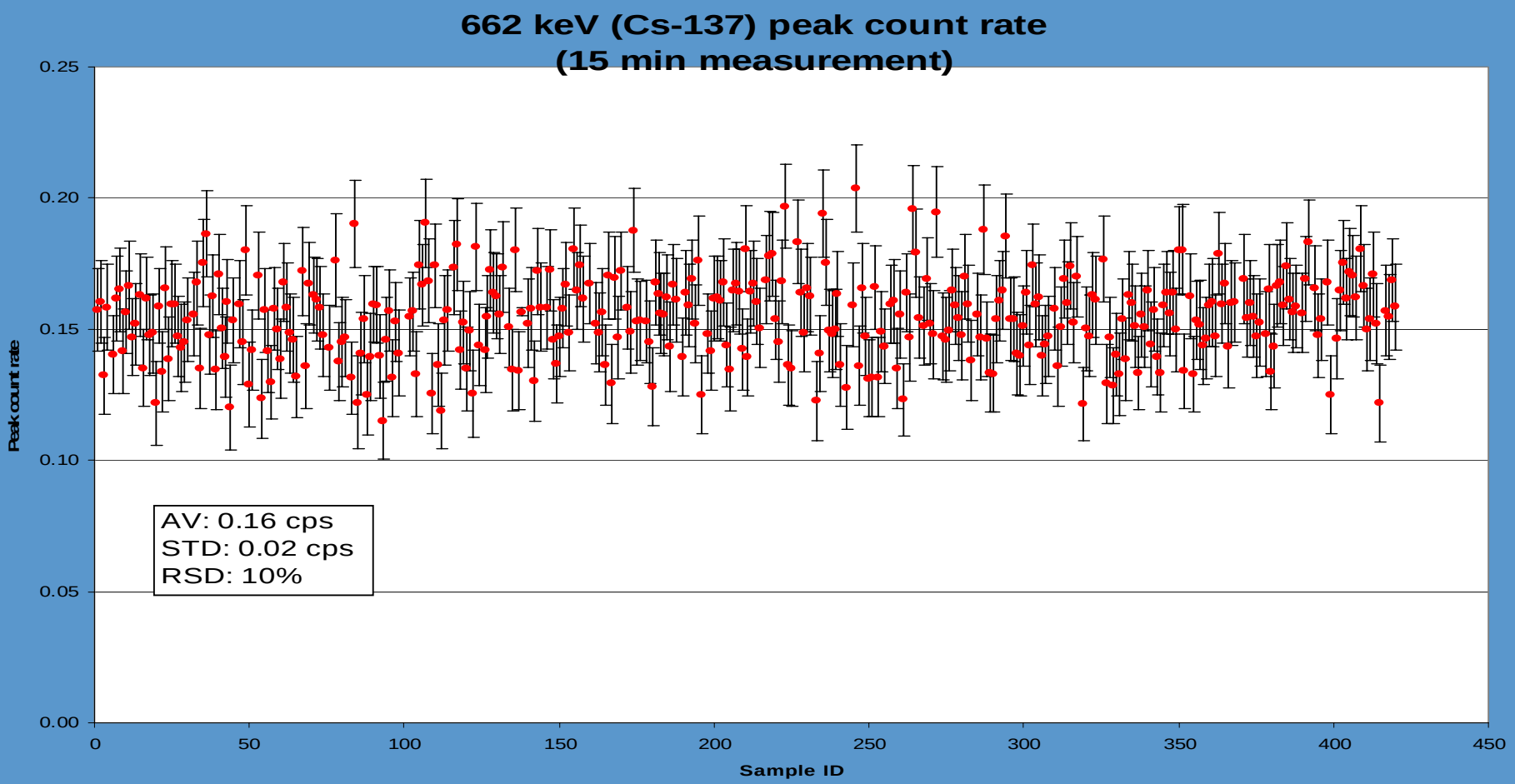

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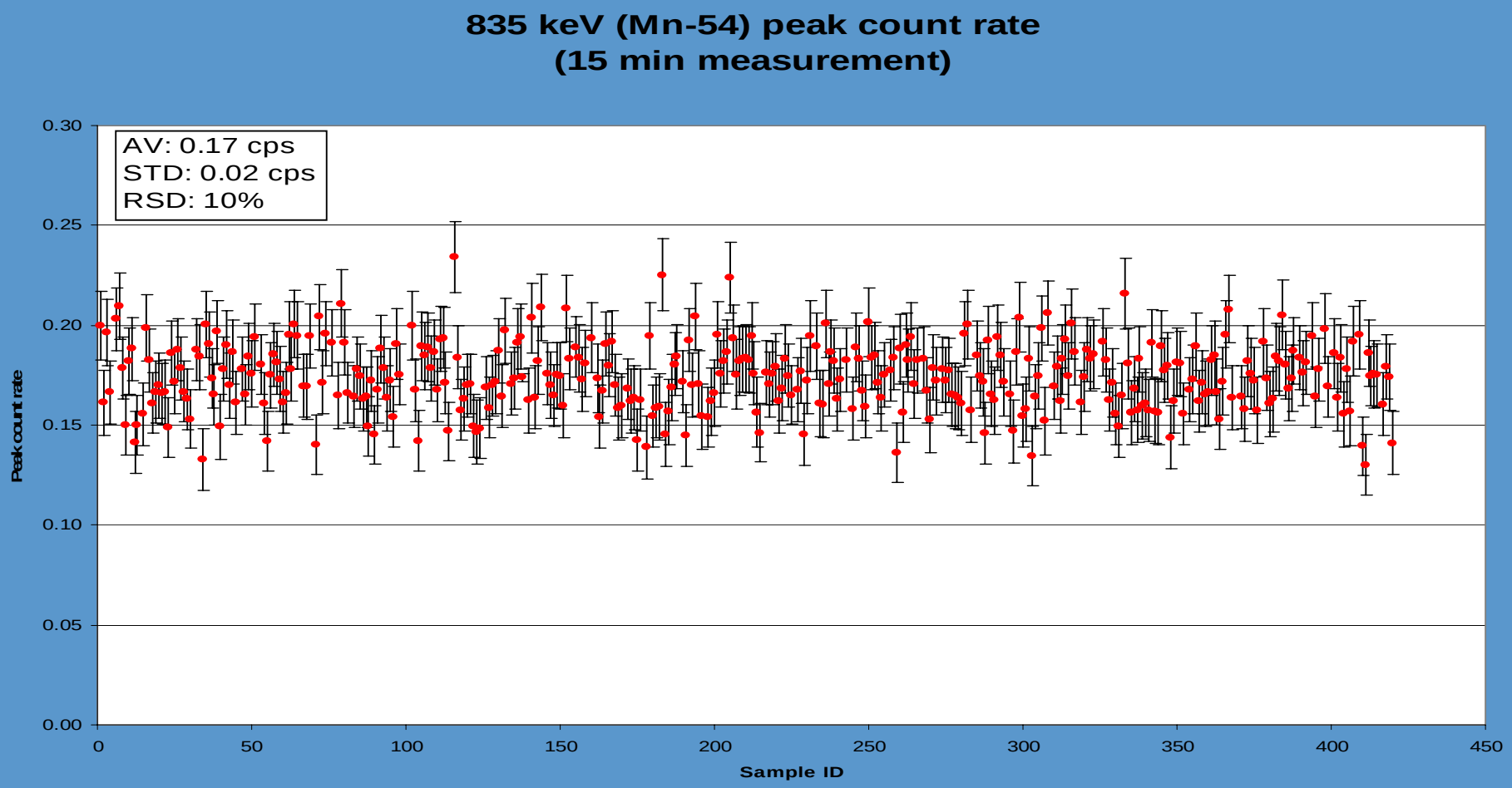

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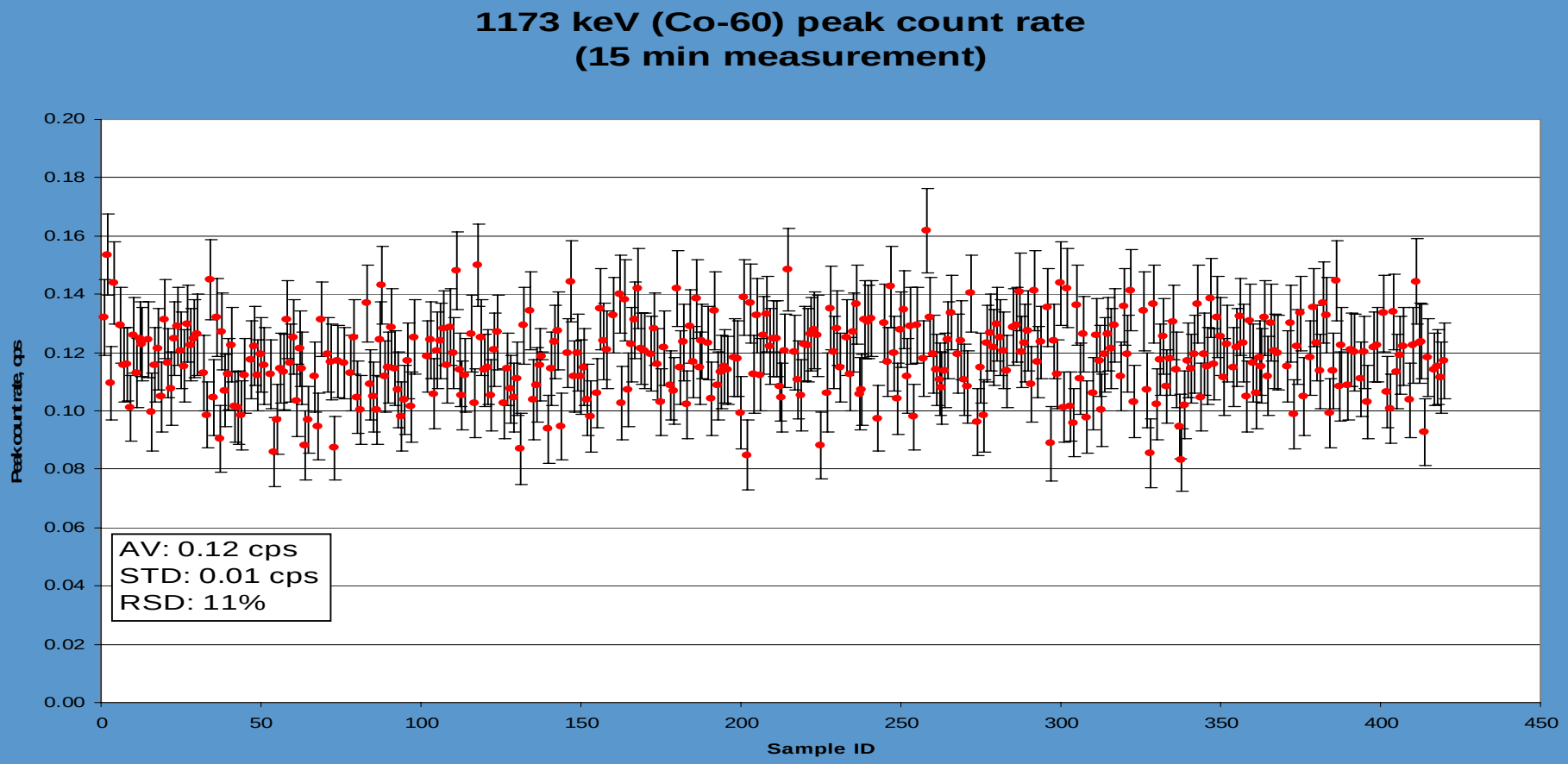

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Property values and associated uncertainties

The total combined uncertainty was estimated and included four major components:

- uncertainty of standard solution,
- uncertainty of the gravimetrical dilution,
- uncertainty originated from between bottle heterogeneity
- uncertainty of moisture content determination of the soil.

The two latter sources are the largest contributors to the overall uncertainties.

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IAEA-CU-2006-04 ALMERA PT: Materials

- In the ALMERA 2006 Proficiency Test **195 PT samples (soil, grass, water) were distributed to 65 labs in June 2006;**

- **The following proficiency test design was applied:**
  - **one spiked soil sample (200g)**
  - **one natural grass sample (100 g)**
  - **one spiked water sample (500 ml)**

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IAEA-CU-2006-04 ALMERA PT: Materials

Radionuclide	Soil sample 01		Grass sample 02		Water sample 03	
	Target value	standard uncertainty	Target value	standard uncertainty	Target value	standard uncertainty
	Bq kg^{-1} (dry mass)				Bq kg^{-1}	
^{40}K	-	-	1059	28	-	-
^{54}Mn	48.0	0.98	-	-	4.89	0.017
^{60}Co	56.1	1.37	-	-	5.80	0.04
^{65}Zn	77.6	2.54	-	-	7.27	0.075
^{109}Cd	177.6	8.40	-	-	19.62	0.10
^{134}Cs	64.2	1.87	-	-	13.03	0.10
^{137}Cs	52.6	1.08	11320	185	16.72	0.08
^{210}Pb	259.5	12.53	-	-	9.55	0.15
^{241}Am	96.6	2.78			3.66	0.023

IAEA-CU-2006-04 ALMERA PT: Participants

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Atoms for Peace: The First Half Century
1957–2007

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Department of Nuclear Sciences and Applications
Physics, Chemistry and Instrumentation Laboratory
Chemistry Unit

REPORT ON THE IAEA-CU-2006-04 ALMERA PROFICIENCY TEST ON THE DETERMINATION OF GAMMA EMITTING RADIONUCLIDES

A. Shakhashiro, U. Sansone, A. Trinkl, M. Makarewicz,
C. Yonezawa,C.K. Kim, G. Kis-Benedek, T. Benesch, R. Schorn

With measurement contributions from 39 laboratories

Seibersdorf, February 2007

Page i

In the ALMERA 2006 Proficiency Test **65 laboratories** from **43 countries registered and received PT materials,**

only 39 Laboratories from 28 countries reported their results

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II- performance indicators

Bias evaluation

Relative bias

Ratio

z-Score

Bias and precision evaluation

u-Score

IAEA-CU approach

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IAEA-CU-2006-04 ALMERA PT: Evaluation

Acceptance criteria: Trueness criterion

(I) Trueness: the result passes if (4)

$$A1 = \left| Value_{IAEA} - Value_{Laboratory} \right|$$

$$A2 = 2.58 \times \sqrt{Unc^2_{IAEA} + Unc^2_{Laboratory}}$$

A1< A2

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IAEA-CU-2006-04 ALMERA PT: Evaluation

Acceptance criteria: Precision criterion

(II) Precision (5):

$$P = \sqrt{\left(\frac{Unc_{IAEA}}{Value_{IAEA}}\right)^2 + \left(\frac{Unc_{Lab}}{Value_{Lab.}}\right)^2} \; X100\%$$

the result passes precision criteria if

$$P \leq LAP_{max}(\%)$$

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IAEA-CU-2006-04 ALMERA PT: Evaluation

The acceptable limits for LAP and MAB used for the evaluation in the proficiency test

Radionuclide	LAP (%)			MAB (%)		
	Soil sample 01	Grass Sample 02	Water Sample 03	Soil sample 01	Grass Sample 02	Water Sample 03
^{40}K	-	20	-	-	20	-
^{54}Mn	20	-	15	20	-	15
^{60}Co	20	-	15	20	-	15
^{65}Zn	20	-	15	20	-	15
^{109}Cd	25	-	20	25	-	20
^{134}Cs	20	-	15	20	-	15
^{137}Cs	20	20	15	20	20	15
^{210}Pb	30	-	30	30	-	30
^{241}Am	25	-	25	25	-	20

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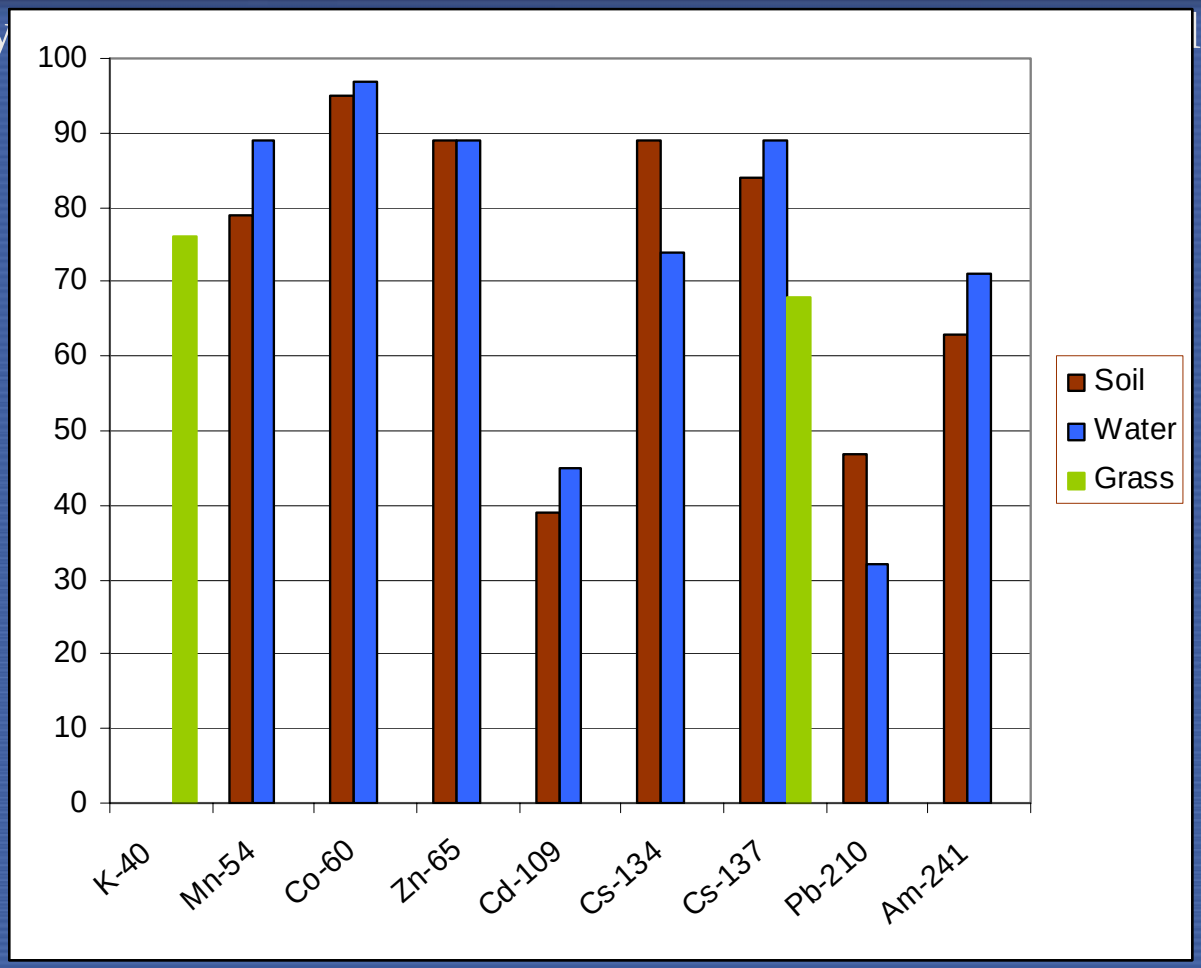
IAEA-CU-2006-04 ALMERA PT: Evaluation

Summary … lts



Percentage of Acceptable scores per analyte sorted by matrix

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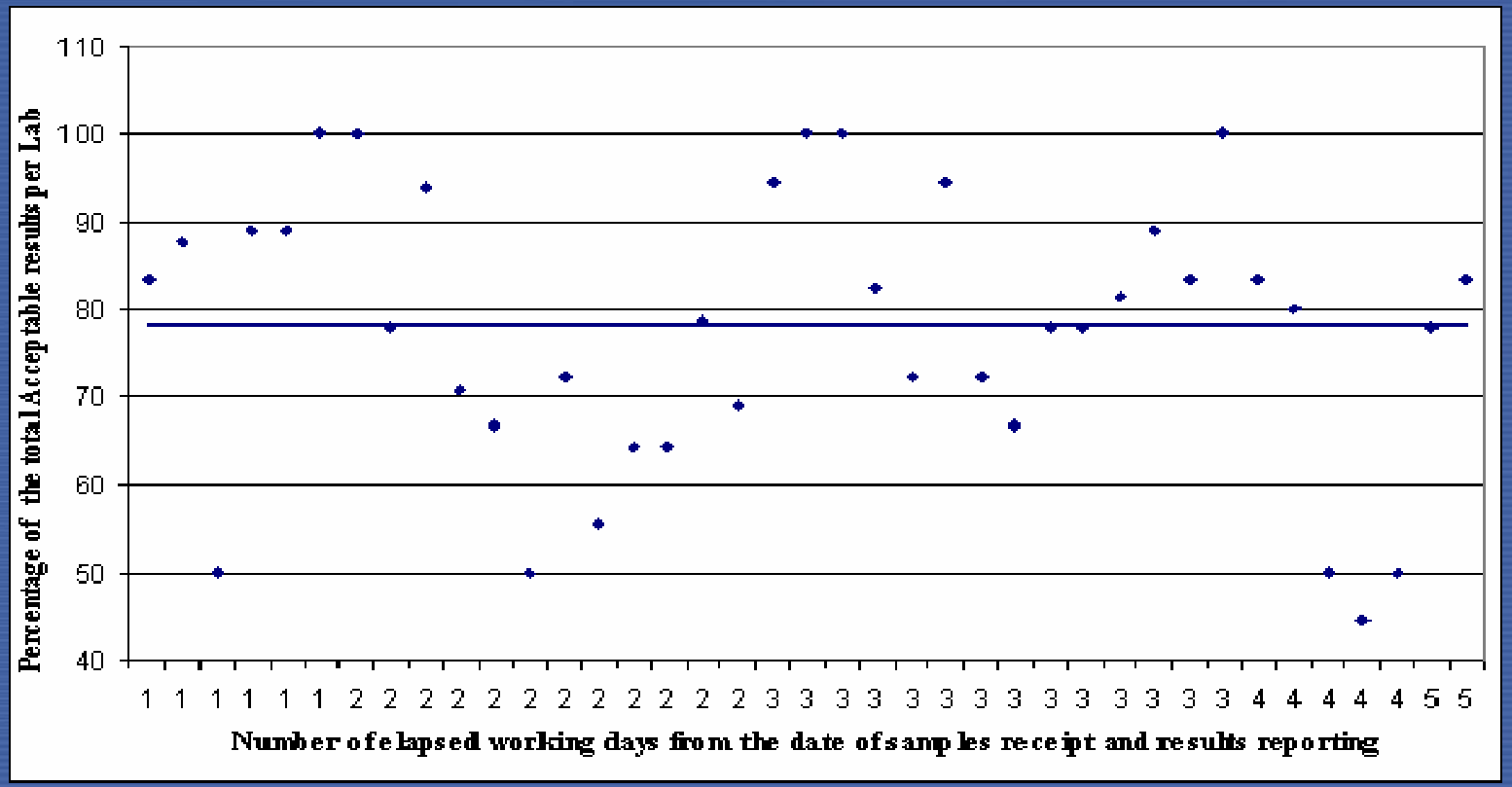
IAEA-CU-2006-04 ALMERA PT: Discussion

Analytical performance level vs. number of elapsed working days from the date of samples receipt and results reporting.



The line represents the percentage of the total acceptable results

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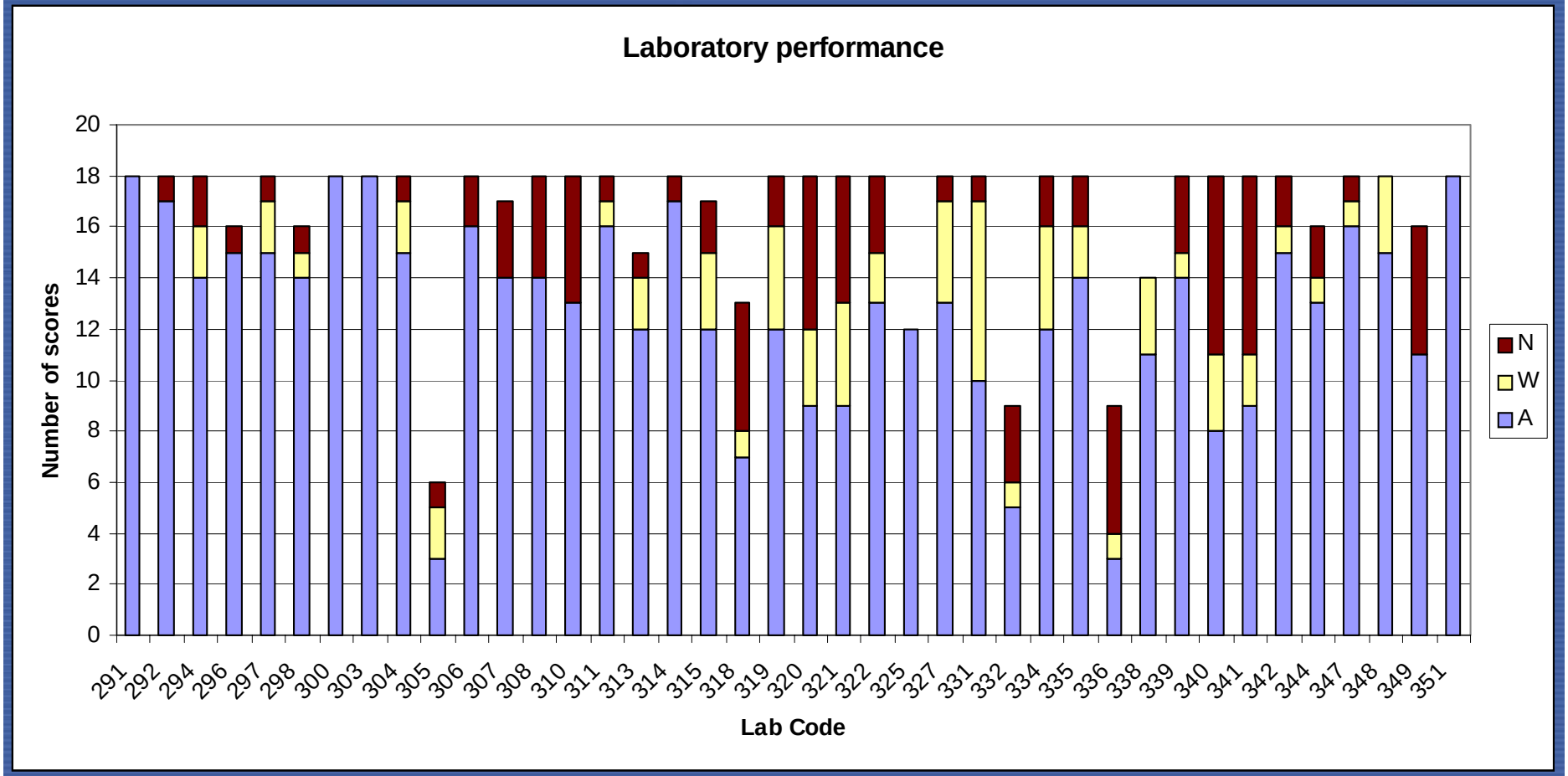
IAEA-CU-2006-04 ALMERA PT: Discussion



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IAEA-CU-2006-04 ALMERA PT: Discussion

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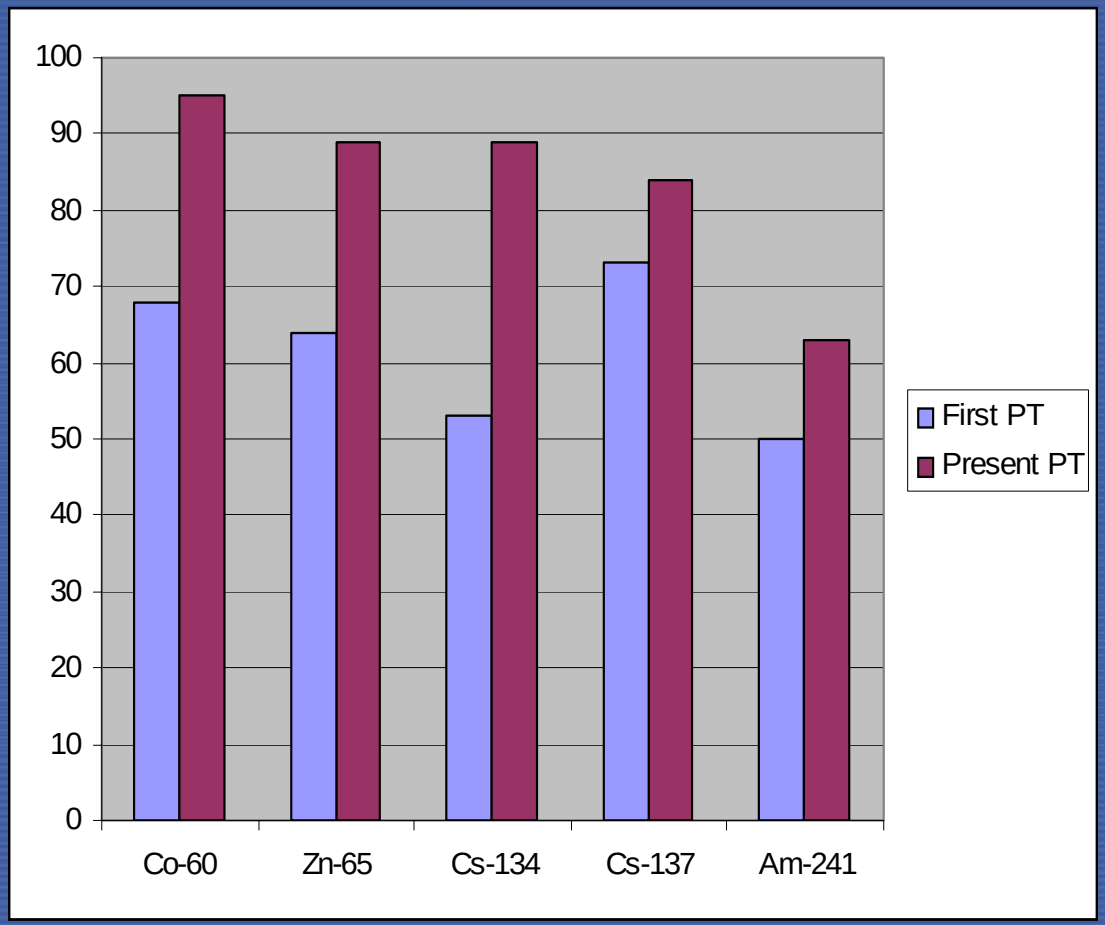

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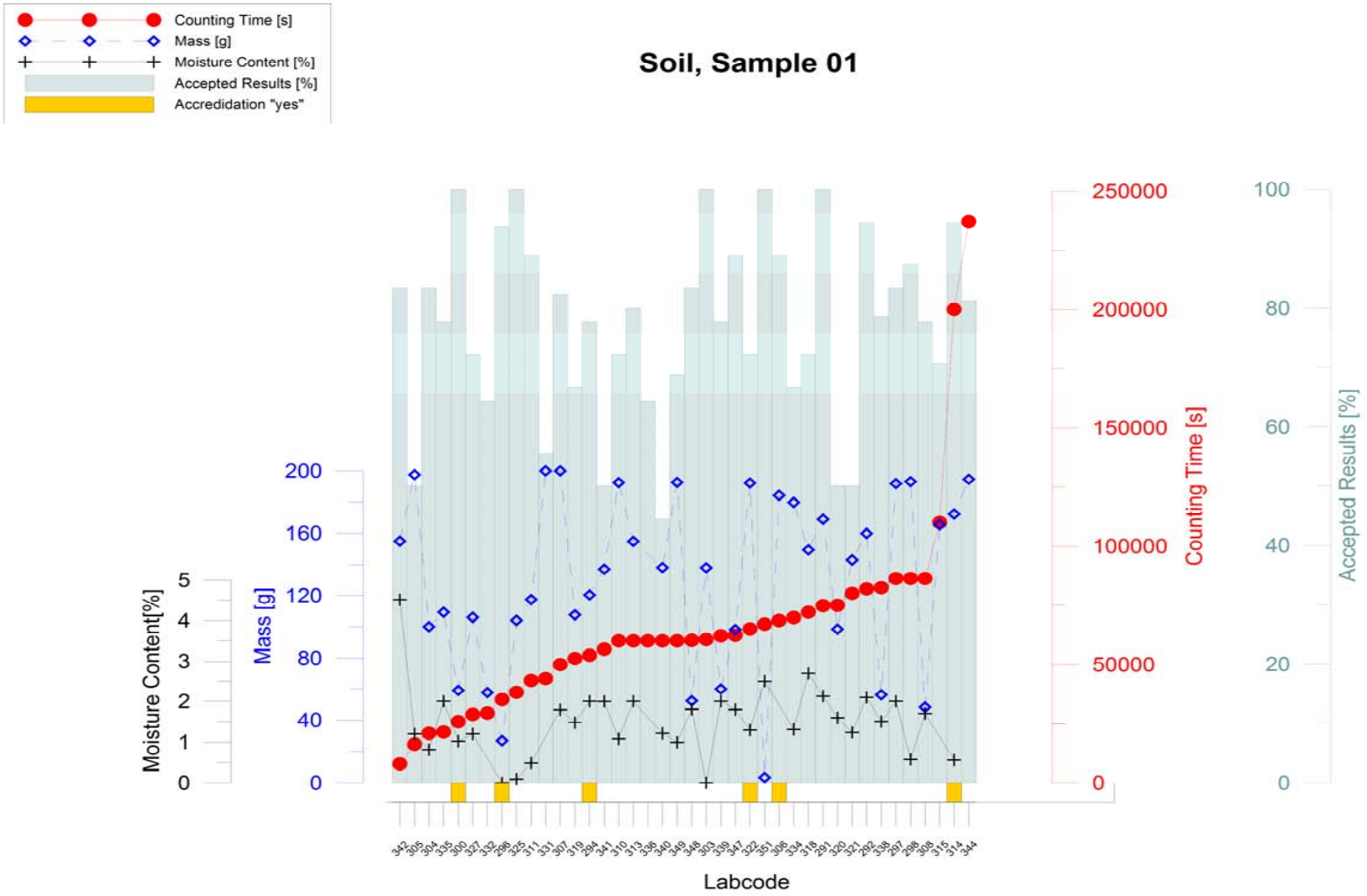

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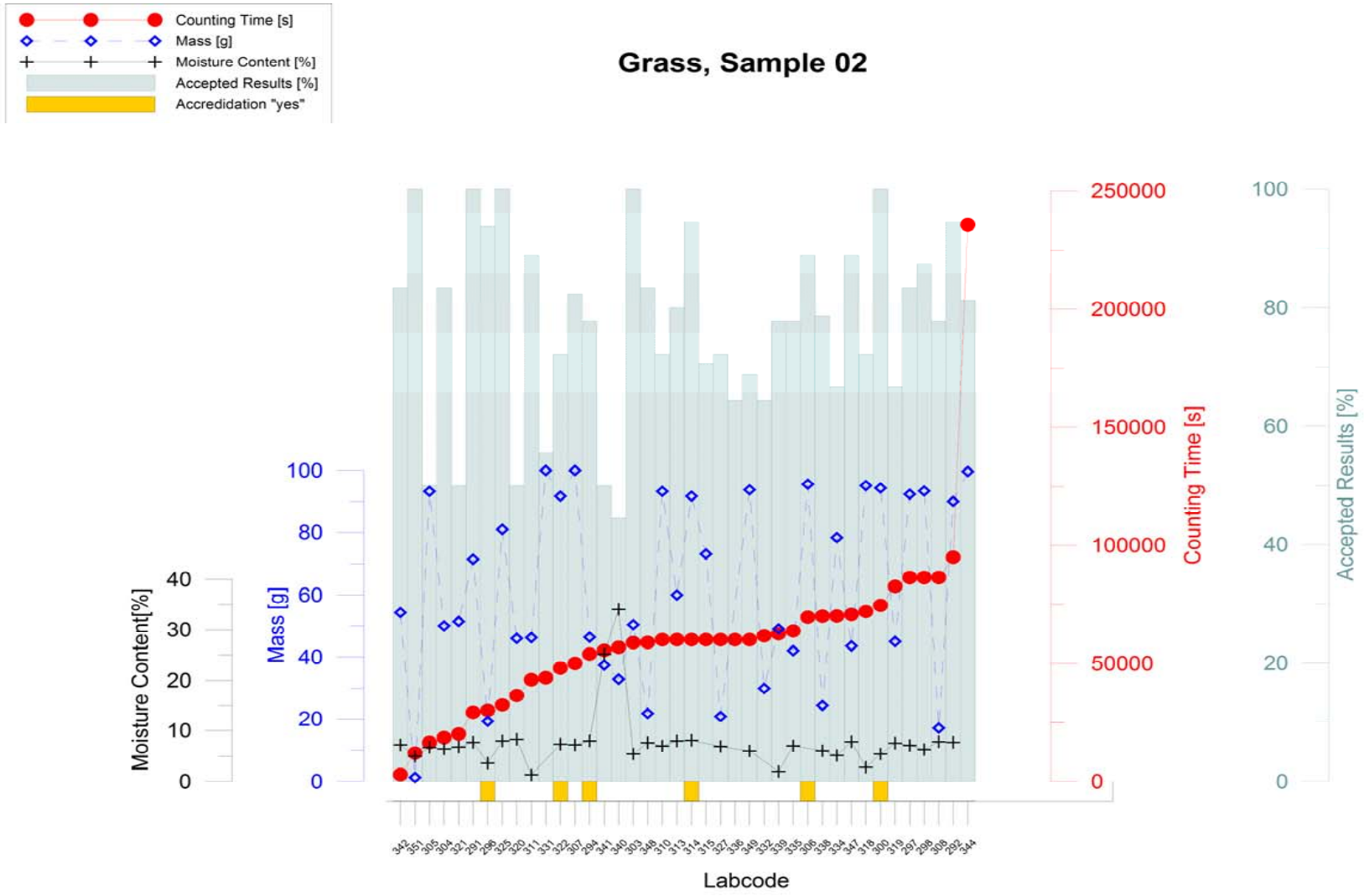

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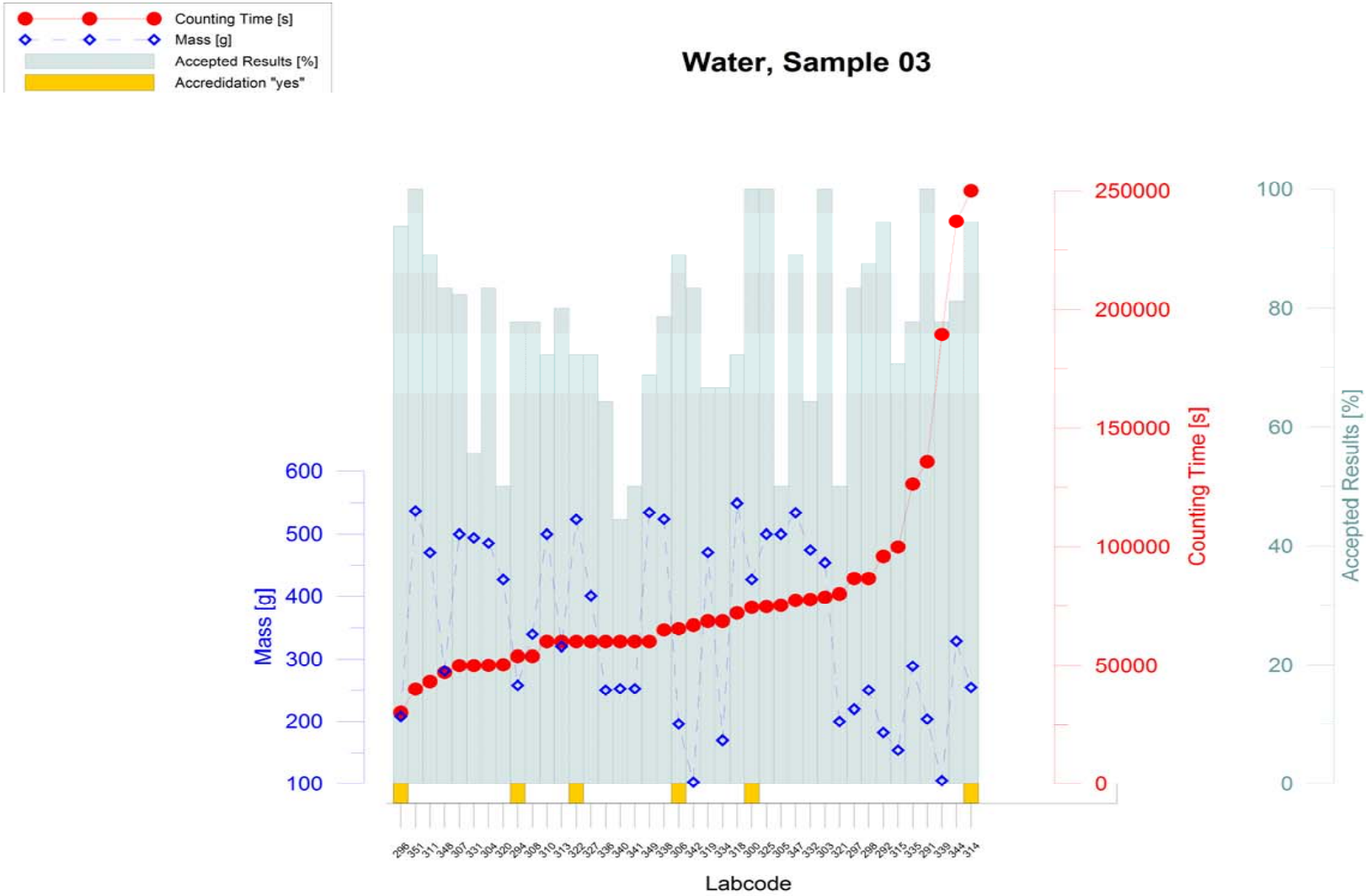
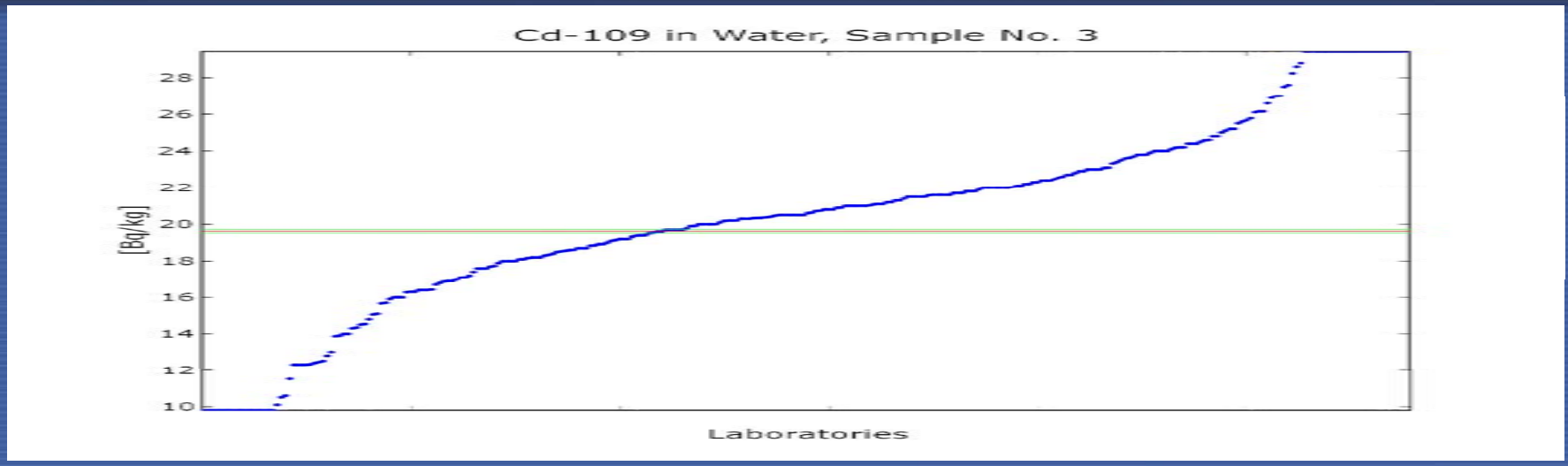
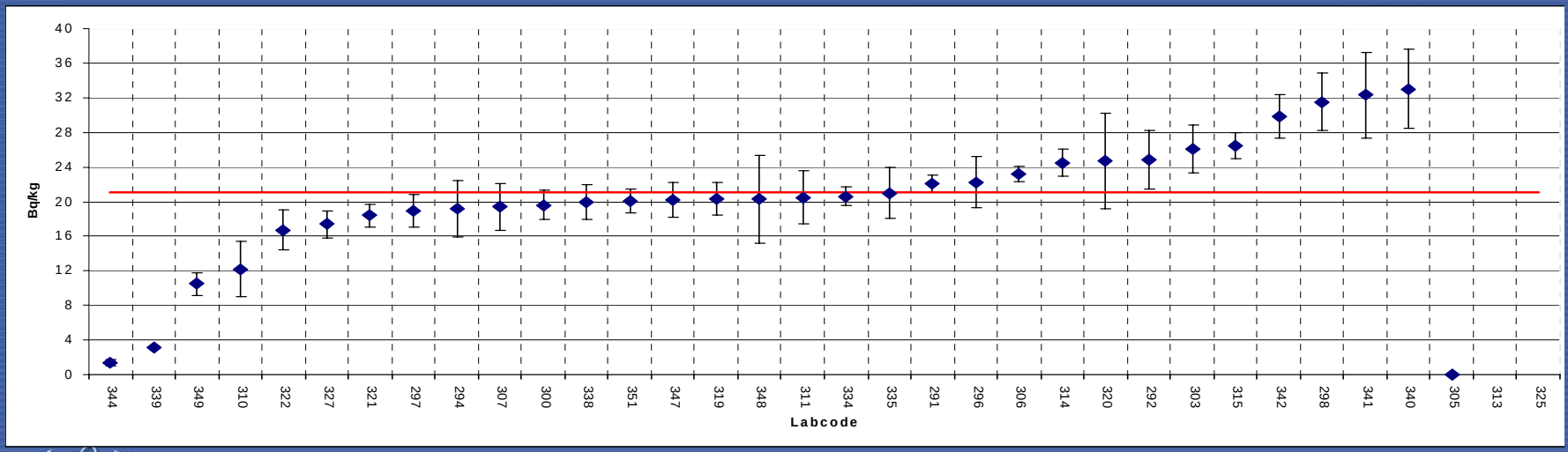


ALMERA comparing to WWOPT





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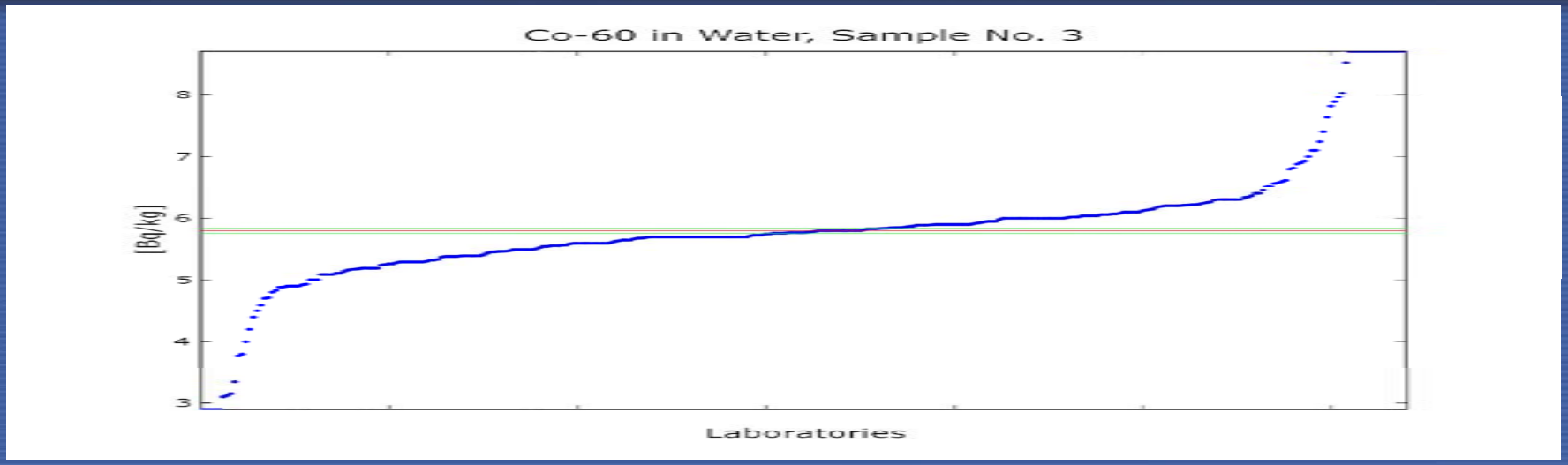

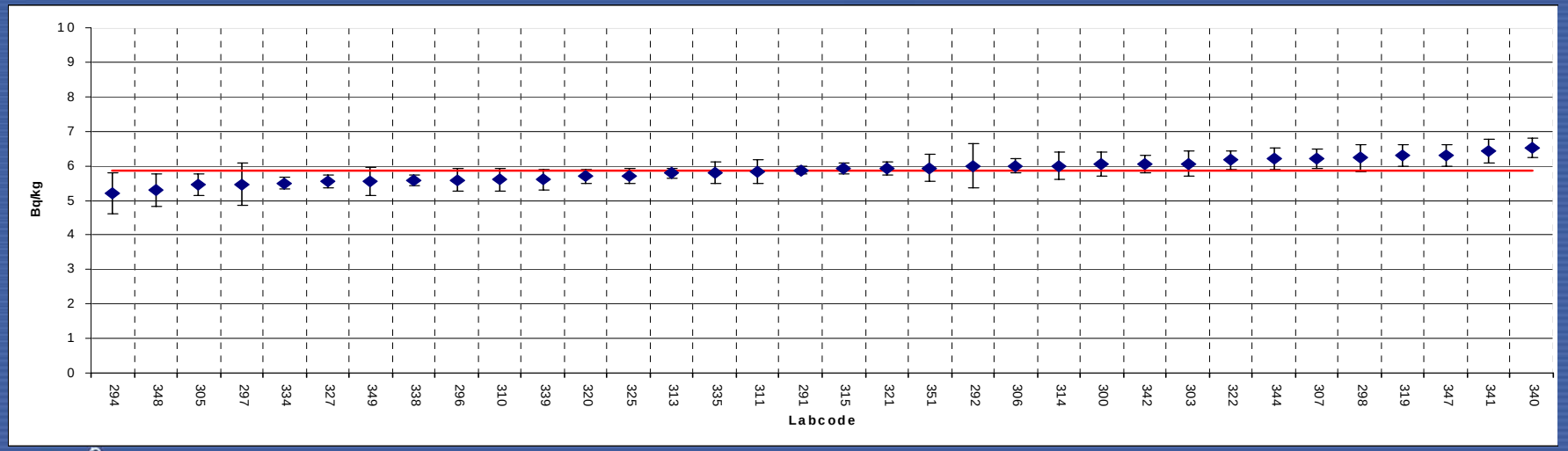

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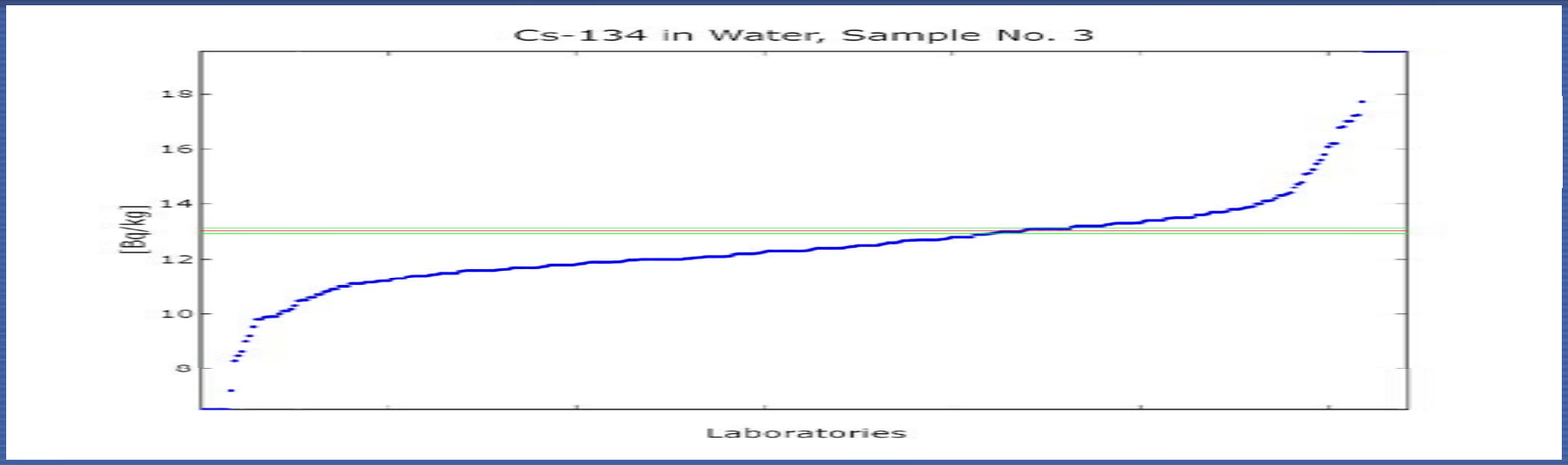

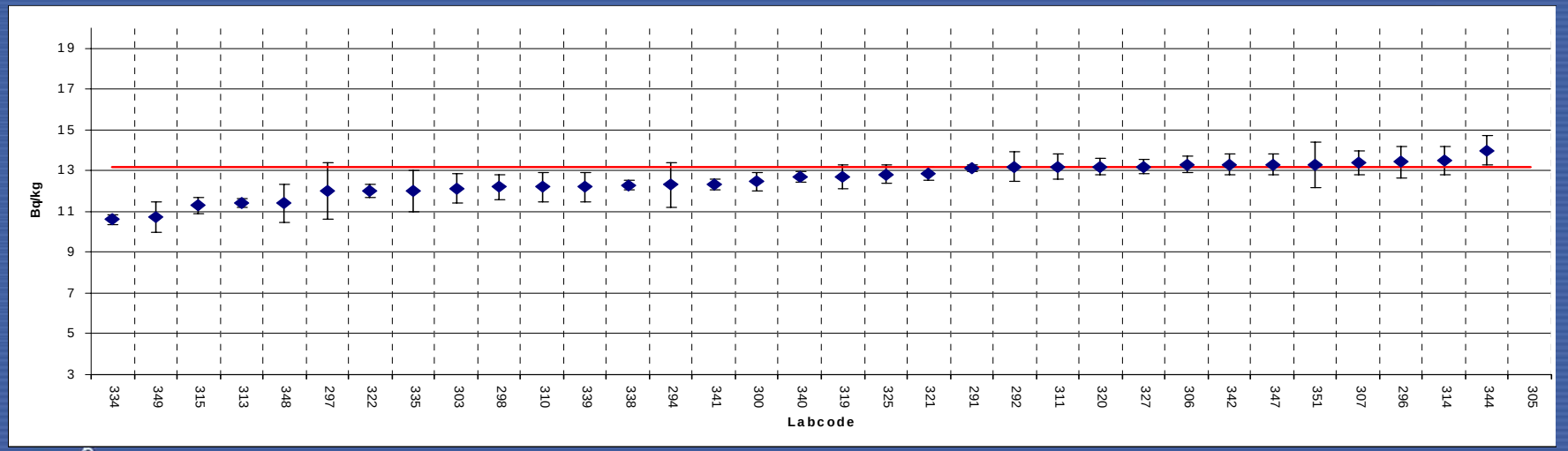

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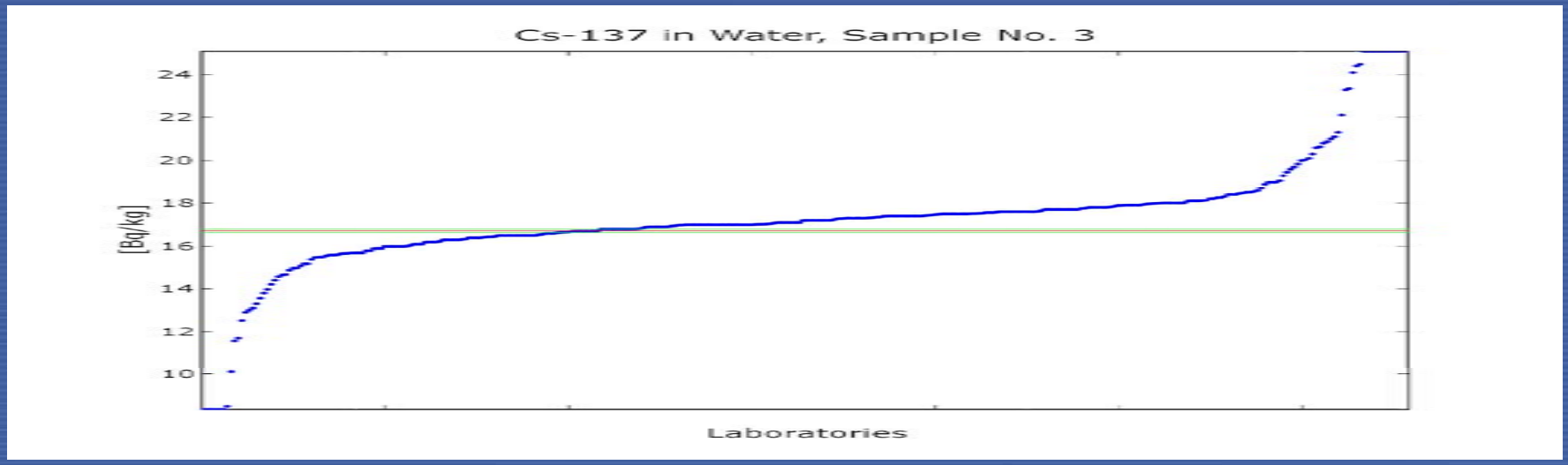

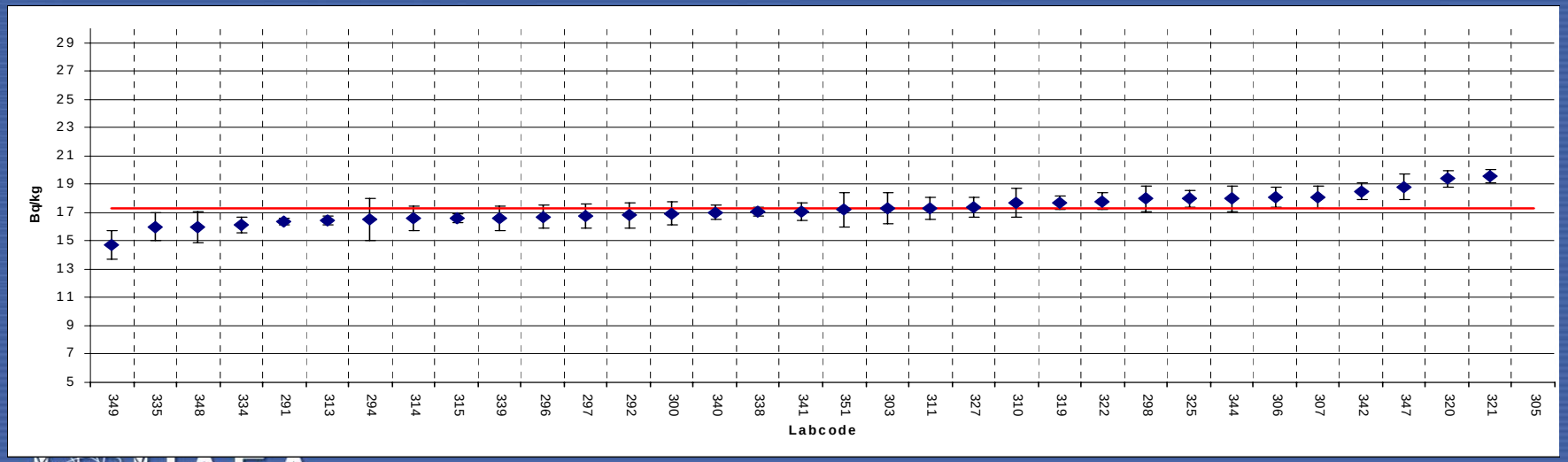

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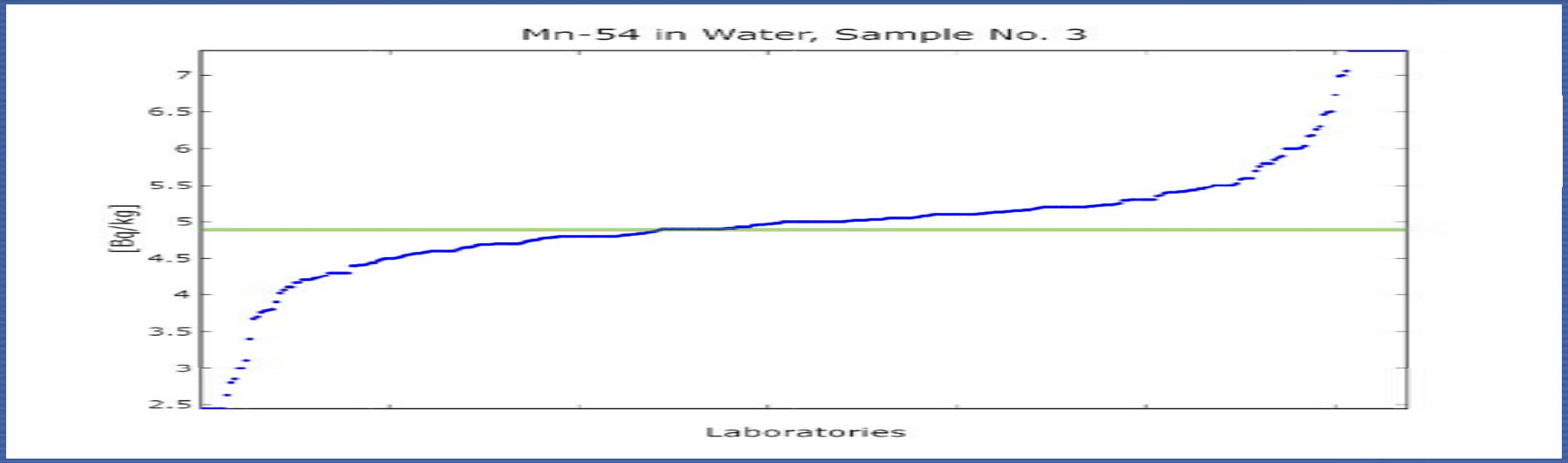

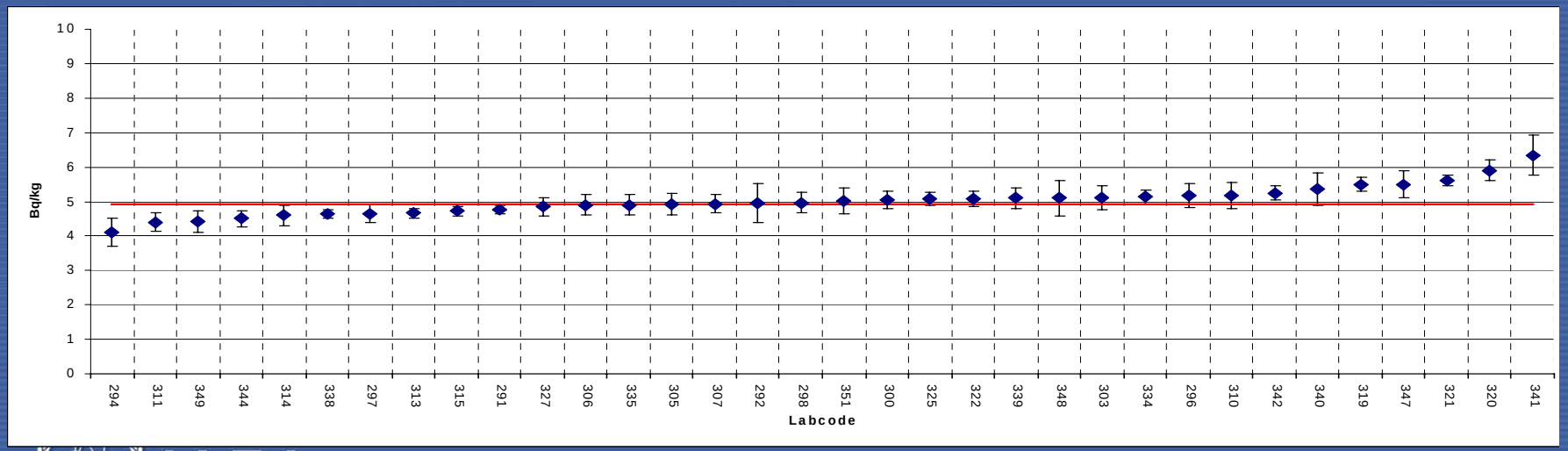

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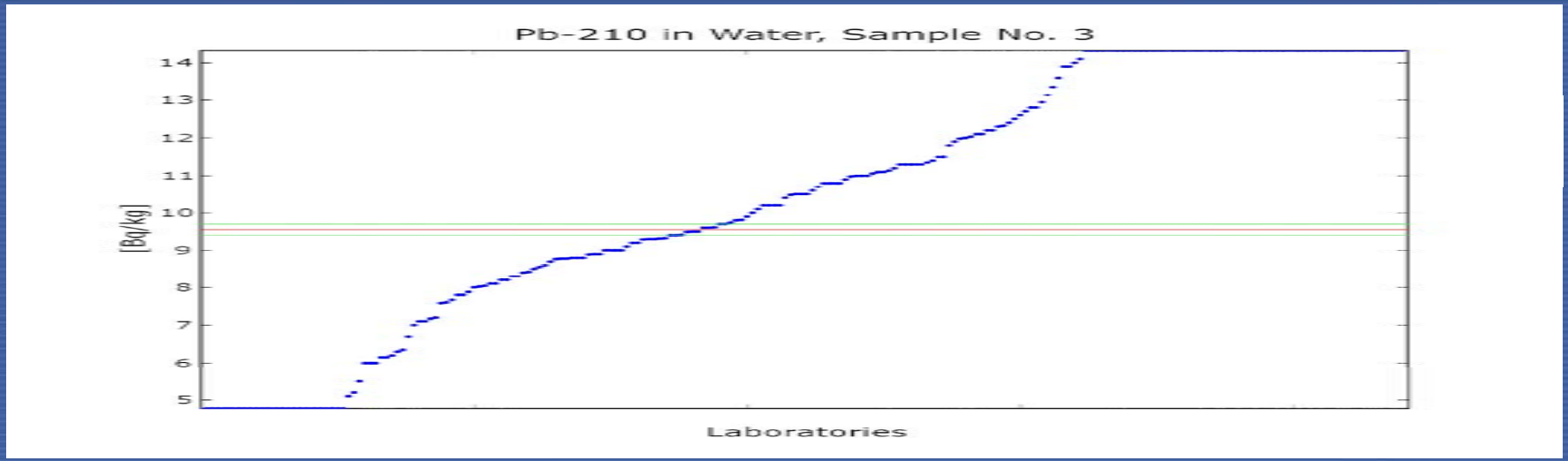

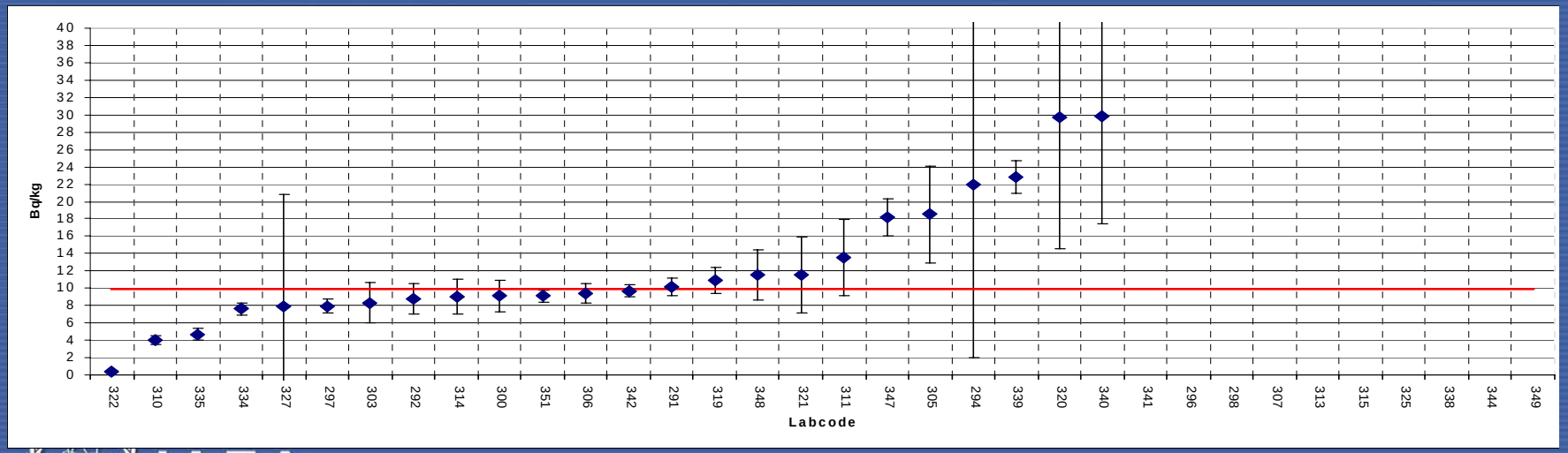

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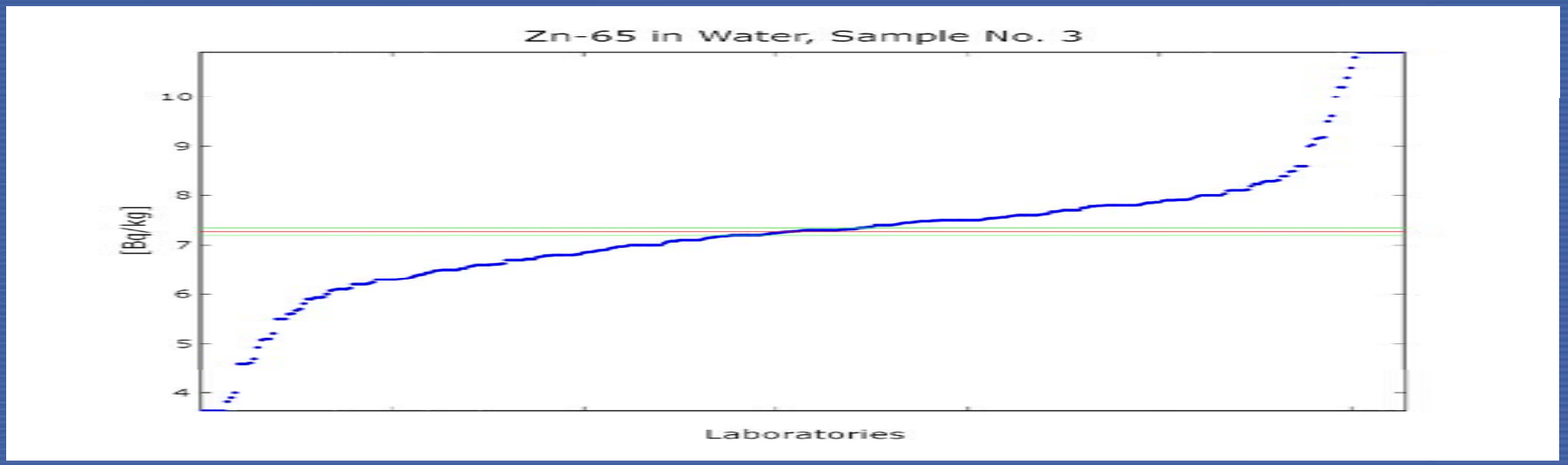

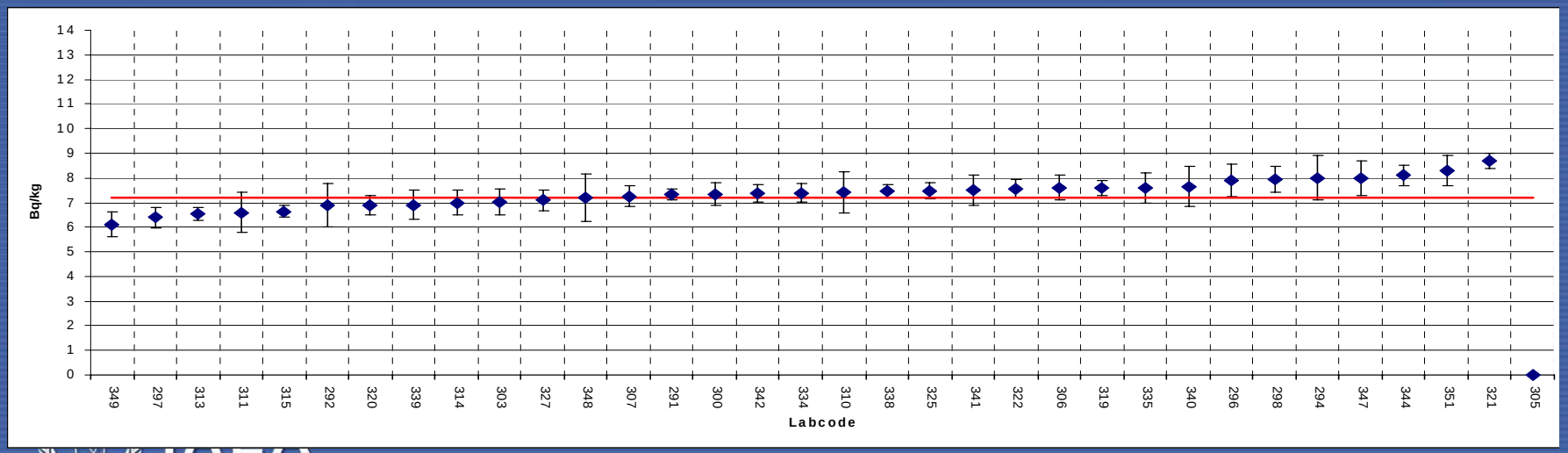

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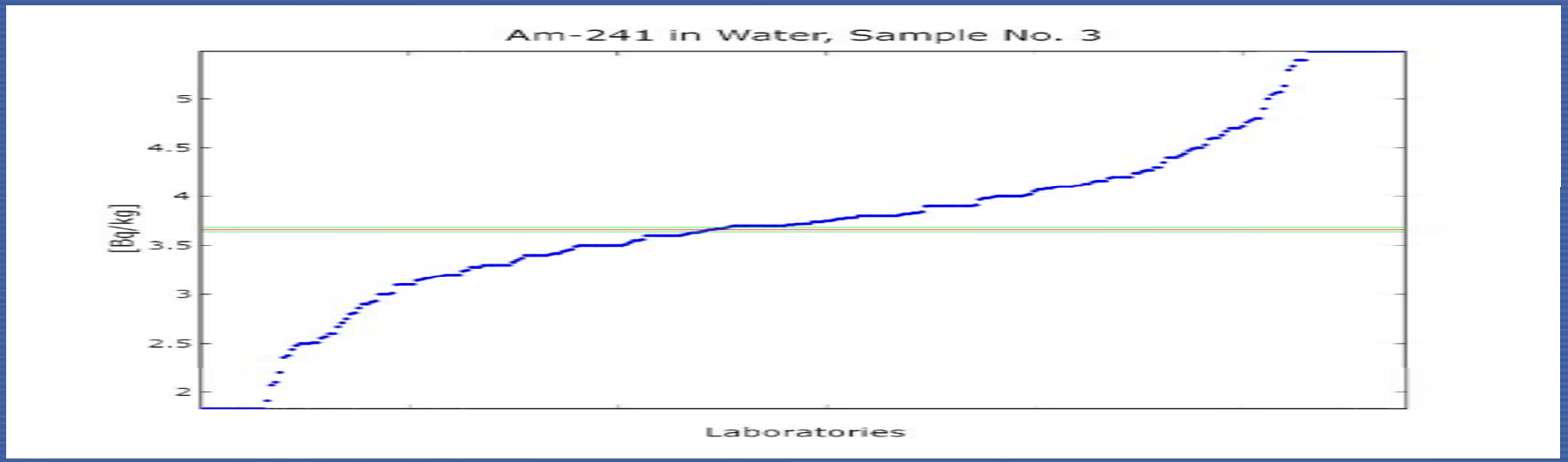

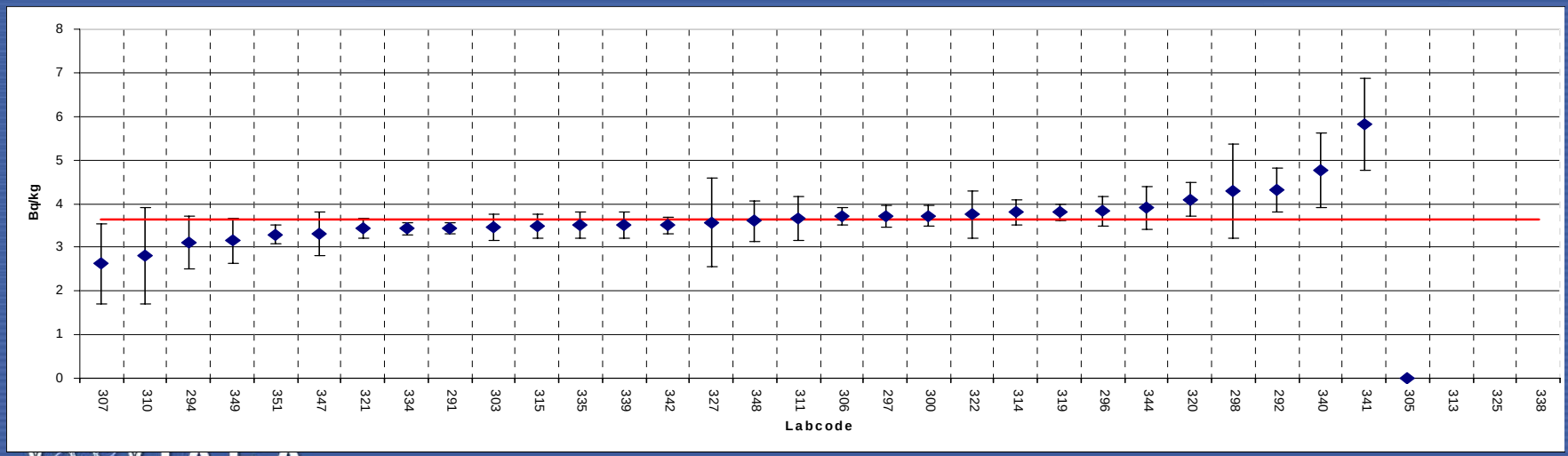

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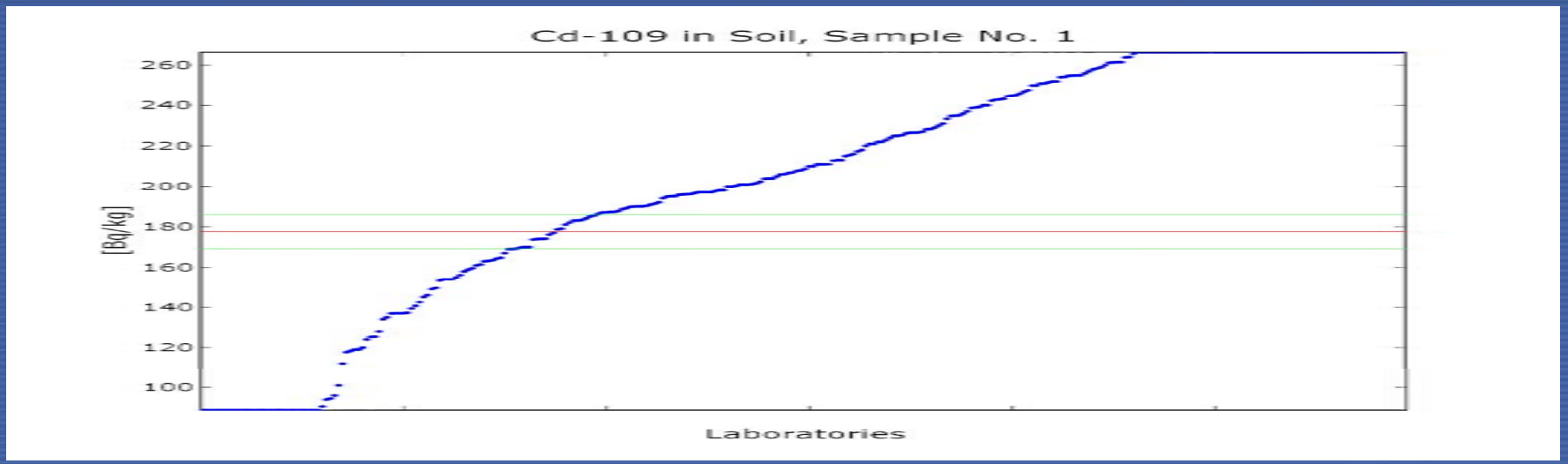

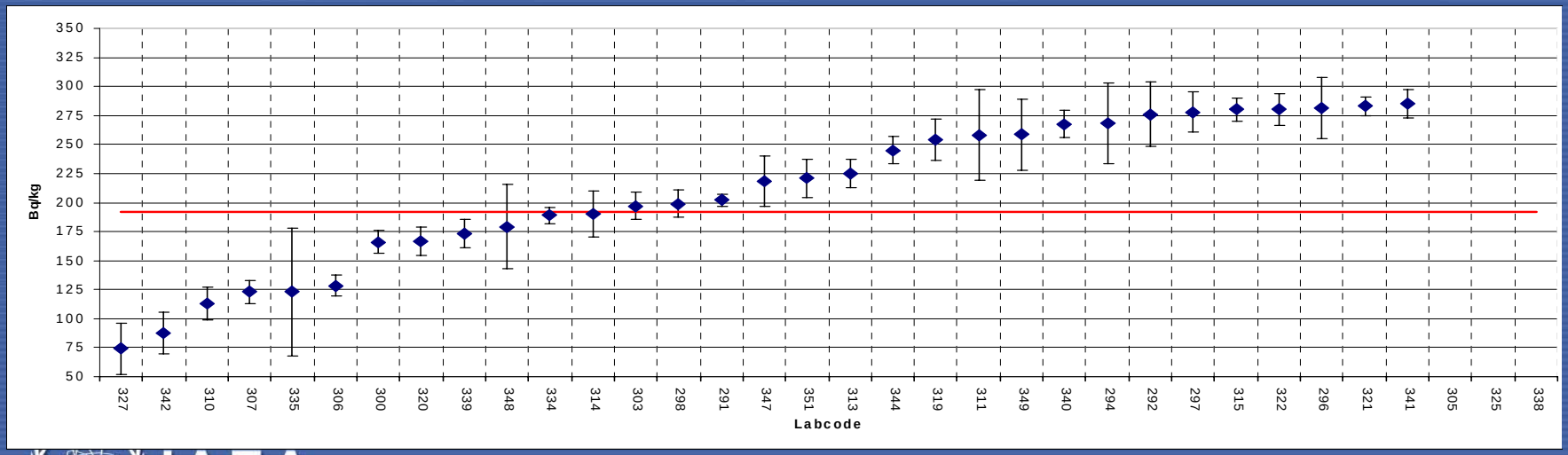

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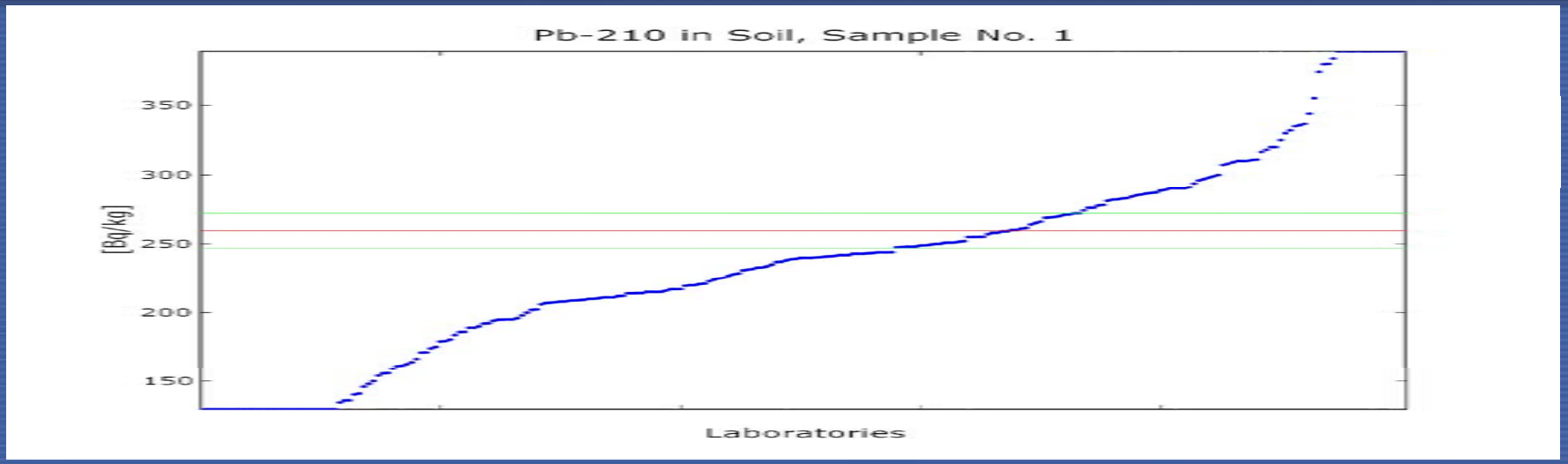
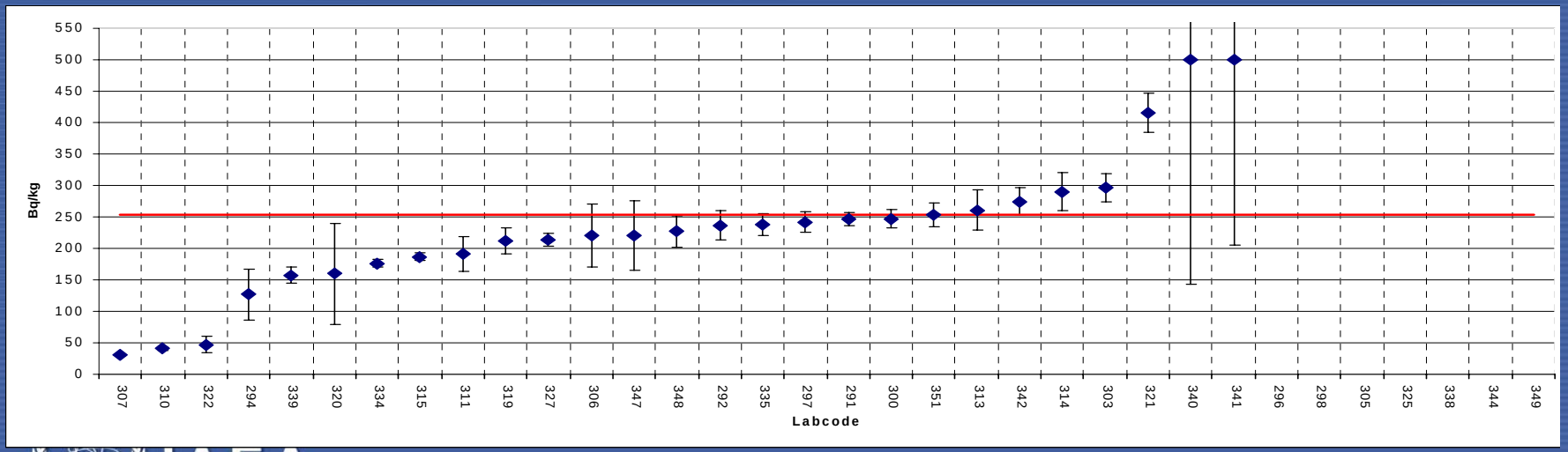
ALMERA comparing to WWOPT





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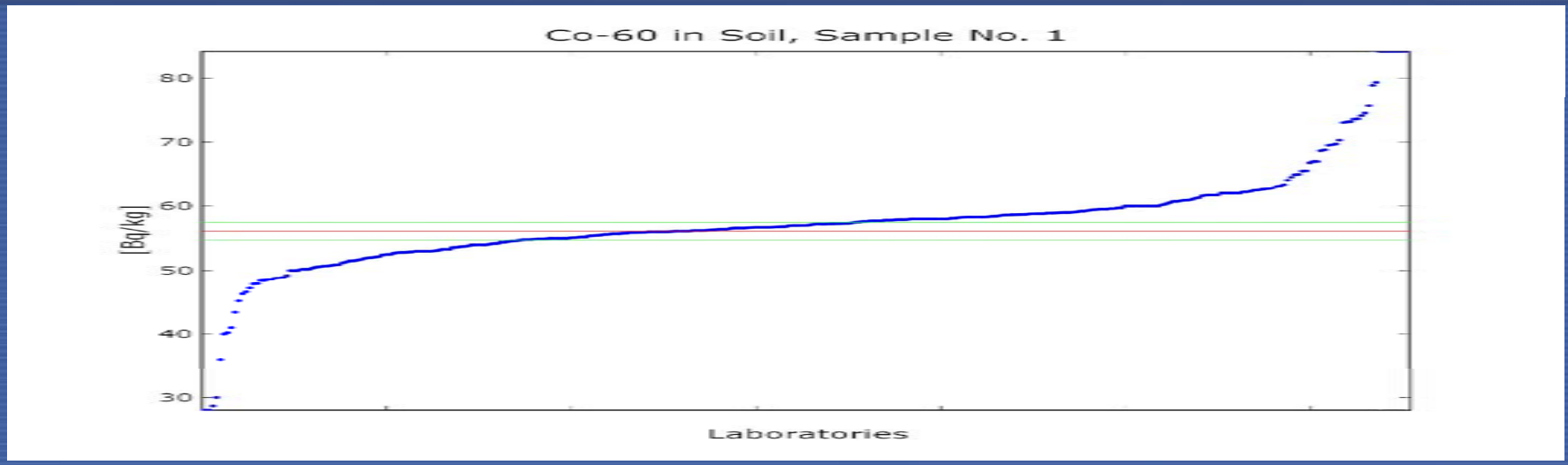
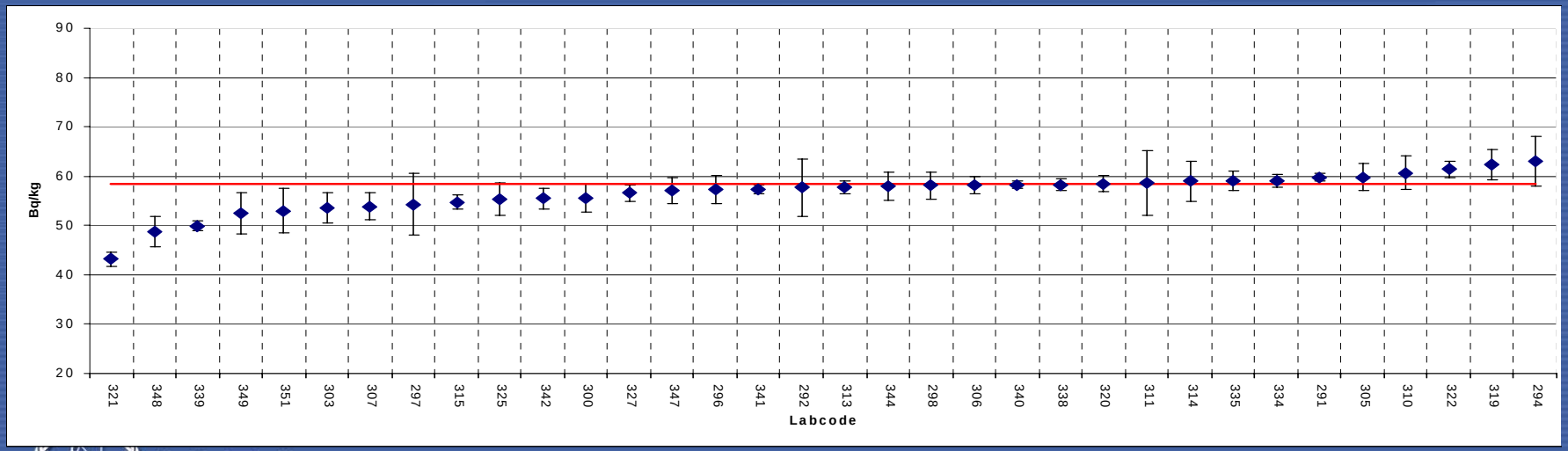
ALMERA comparing to WWOPT





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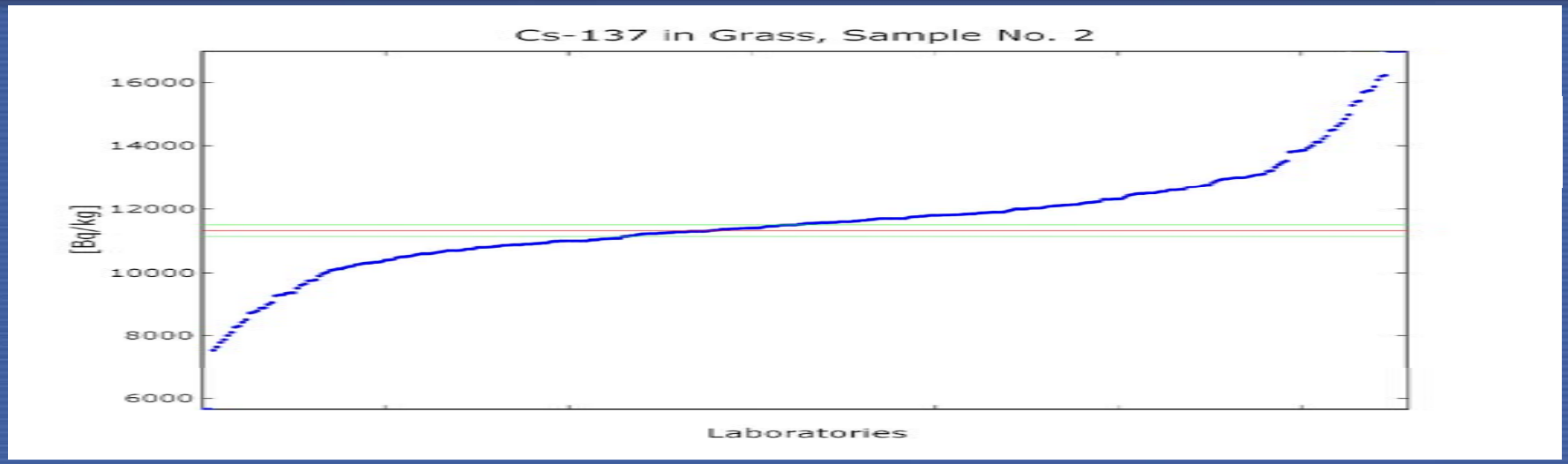
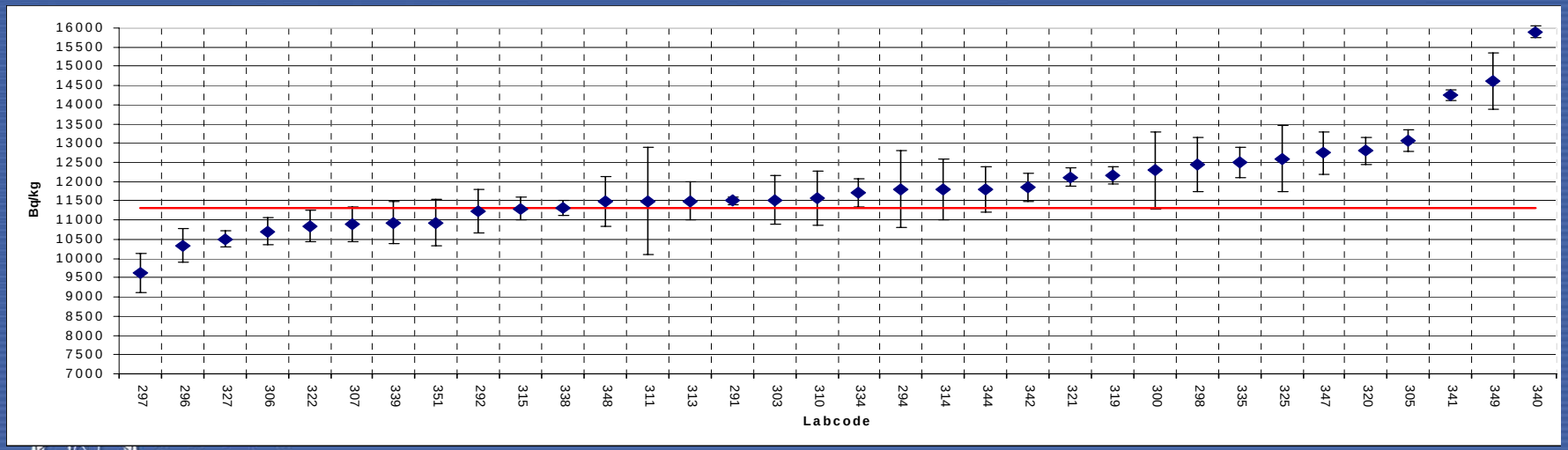
ALMERA comparing to WWOPT





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IAEA-CU-2006-04 ALMERA PT: Conclusions

- This proficiency test exercise was successfully completed.
- 677 results were reported to the IAEA from 38 ALMERA laboratories in 29 countries.
- 30 laboratories reported within the agreed deadline for the rapid reporting measurement (three working days).
- The overall evaluation showed that 78 % of all reported results fulfilled the PT criteria.
- Comparability of measurement results of K-40, Mn-54, Co-60, Zn-65, Cs-134, Cs-137 and Am-241was tested.

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IAEA-CU-2006-04 ALMERA PT: Conclusions

- ALMERA Summary performance is higher than the WWOPT.
- Dispersion of the results of ALMERA is smaller than in the WWOPT.
- More efforts should be done to improve the comparability of Cd-109 and Pb-210.

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IAEA-CU-2006-04 ALMERA PT: Recommendations

• Proposal to form a working group to study in cooperation with Seibersdorf laboratories) the ways to improves the analytical performance of the network in Cd-109 and Pb-210.

• Proposal to form a working group to work out a harmonised QC protocol for each analytical method to be called" ALMERA recommended QC protocol".

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IAEA-CU-2006-04 ALMERA PT: Acknowledgment

• The participating Laboratories' contributions with their measurements and timely response are highly appreciated,

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Thank you for your attention