



**The Abdus Salam
International Centre for Theoretical Physics**



1833-4

**Workshop on Understanding and Evaluating Radioanalytical
Measurement Uncertainty**

5 - 16 November 2007

ALMERA 2006 Proficiency Test on the determination of ^{210}Po in water

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**“IAEA-CU-2007-09 ALMERA Proficiency Test ”
on the determination of ^{210}Po in water**

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**International Atomic Energy Agency,
Agency’s Laboratories Seibersdorf,**



IAEA

International Atomic Energy Agency

Introduction

- Po-210 poisoning case,
- CU was requested to evaluate the preparedness of ALMERA labs to respond to emergency analysis of Po-210 contamination.
- Survey of interest for participation



Objectives

- To gather information on the current state of practice for Po-210 measurements at different activity levels in liquid samples
- To check false positive reporting
- To explore options for method development.



*IAEA-CU-2007-09 Po-210 PT: **Participants***

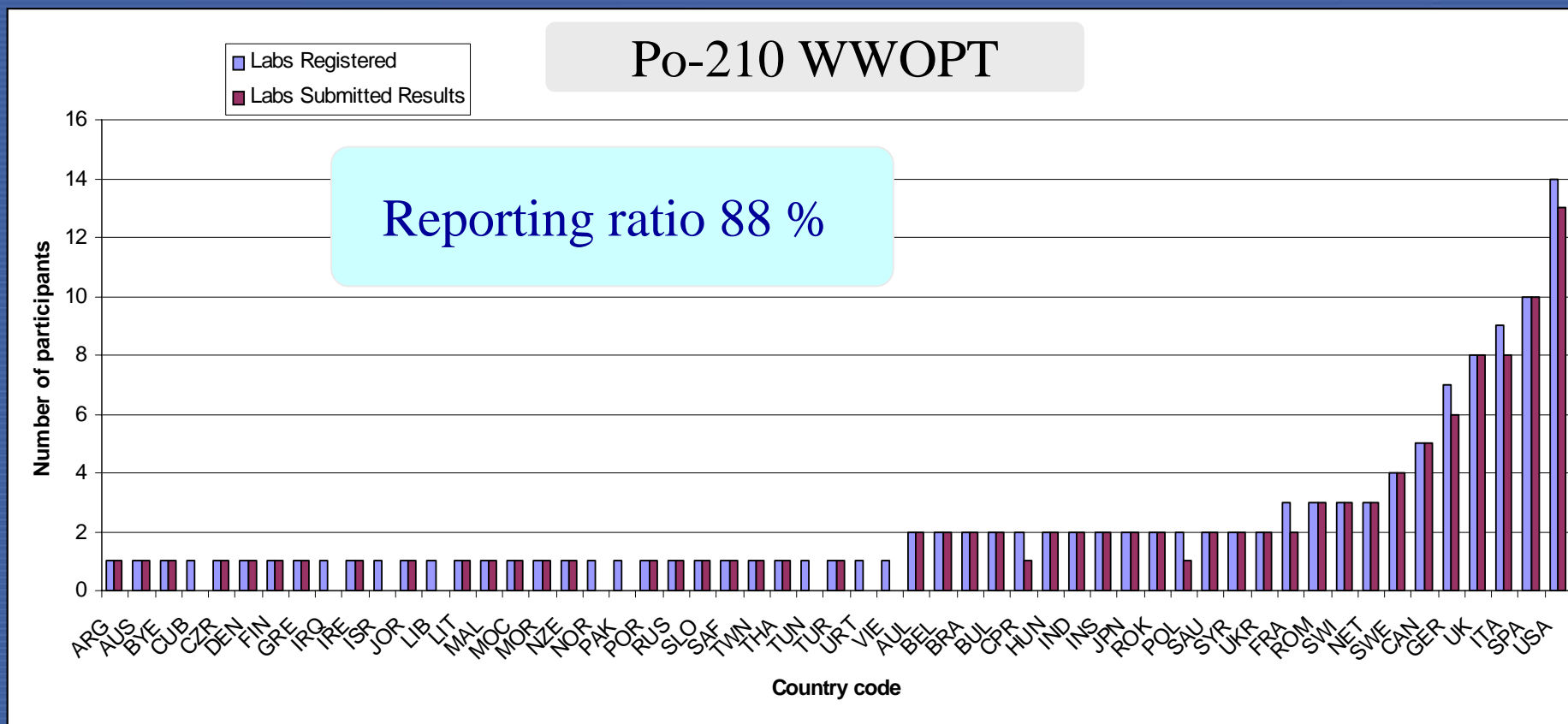


In the WWO PT for Po-210
127 laboratories from **56**
countries registered and
received PT materials,

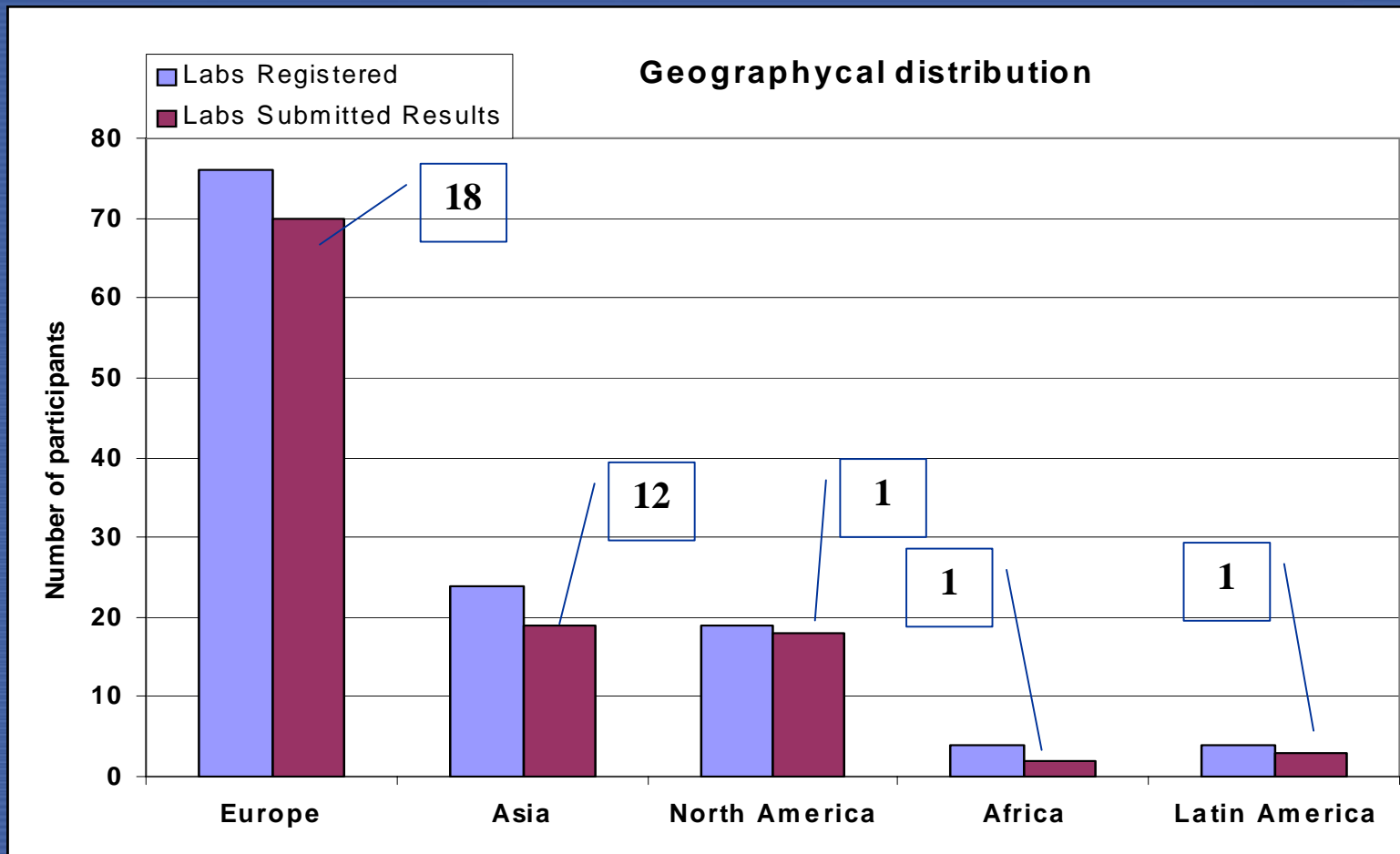
Results reported by 112
labs from **46 countries.**



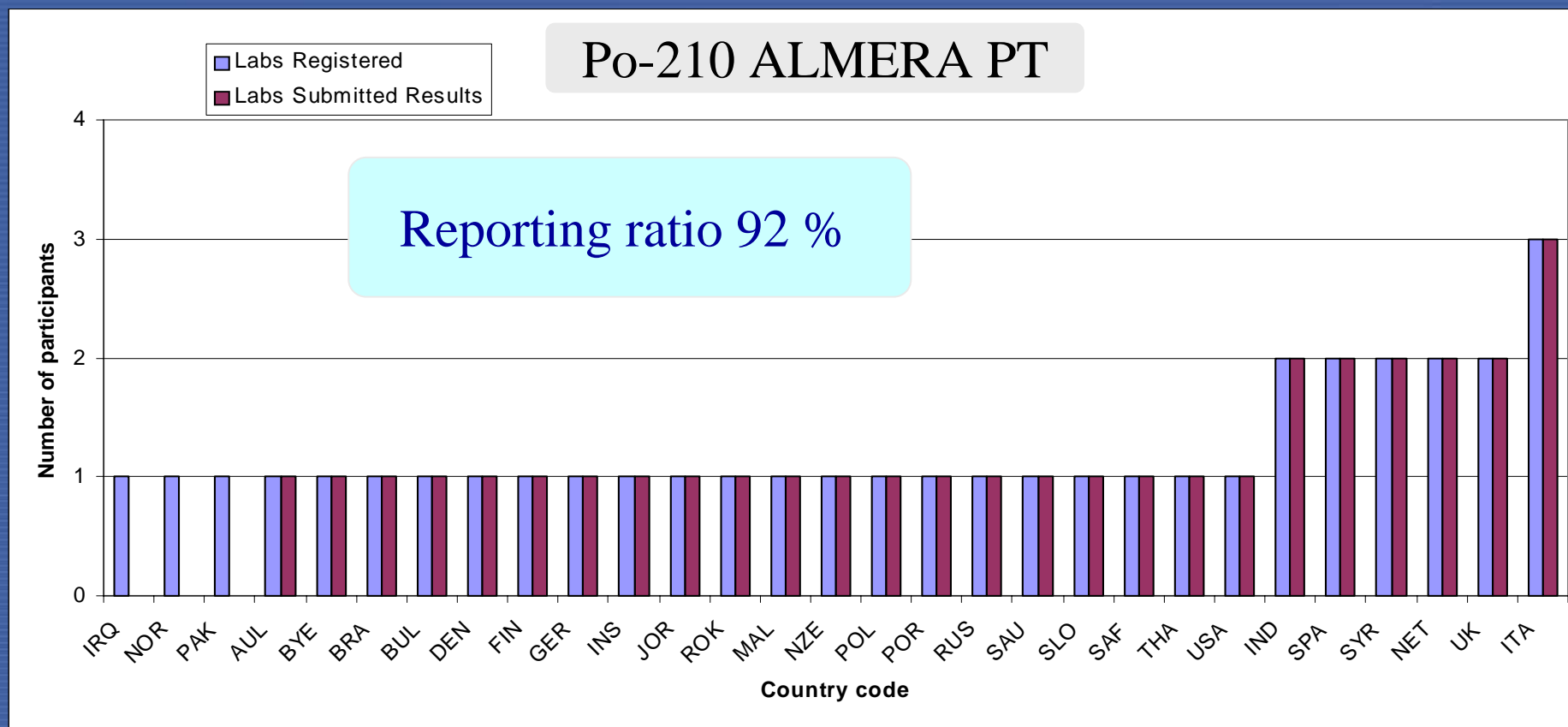
IAEA-CU-2007-09 Po-210 PT: *Participants*



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Methods and materials

Samples preparation:

- Acidified demineralised water from Seibersdorf,
- Gravimetrically spiked in one batch for samples 01-03 and 02-04,
- Mixed with a pump.
- Homogeneity test,
- Stability test



IAEA-CU-2007-09 ALMERA PT: *Materials*

- The following proficiency test design was applied:
 - two spiked water samples, 50 g each containing ~10 Bq Po-210,
 - two spiked water samples, 50 g each containing ~5 Bq Po-210,
 - one blank water sample.



IAEA-CU-2007-09 ALMERA PT: *Materials*

DEUTSCHER KALIBRIERDIENST DKD
 Kalibrierlaboratorium für Radioaktivität
Calibration laboratory for activity, specific activity, photon flux and particle flux
 Akkreditiert durch die / accredited by the
 Akkreditierungsstelle des DKD bei der
 PHYSIKALISCH-TECHNISCHEN BUNDESANSTALT (PTB)

Eckert & Ziegler Isotope Products
DBA Isotope Products Laboratories
 24937 Avenue Tibbitts
 Valencia, CA 91355

000444
 DKD-K-36901
 07-04

Kalibrierschein
Calibration Certificate

Gegenstand <i>Object</i>	Po-210 alpha standard solution	Dieser Kalibrierschein dokumentiert die Rückführung auf nationale Normale zur Demimmung der Einheiten in Übereinstimmung mit dem Internationalen Einheitensystem (SI). Der DKD ist Unterzeichner der multilateralen Übereinkommen der Europäischen Organisation für Akkreditation (EA) und der International Laboratory Accreditation Cooperation (ILAC) zur gegenseitigen Anerkennung der Kalibrierscheine. Für die Einhaltung dieser gegenseitigen Frist zur Wiederholung der Kalibrierung ist der Benutzer verantwortlich. This calibration certificate documents the traceability to national standards, which realize the units of measurement according to the International System of Units (SI). The DKD is signatory to the multilateral agreements of the European organization for Accreditation (EA) and of the International Laboratory Accreditation Cooperation (ILAC) for the mutual recognition of calibration certificates. The user is obliged to have the object recalibrated at appropriate intervals.
Hersteller <i>Manufacturer</i>	Eckert & Ziegler Isotope Products	
Typ <i>Type</i>	10 mL V-vial, catalog number 7310	
Fabrikations-Nr. <i>Serial number</i>	1233-16-1	
Auftraggeber <i>Customer</i>	Eckert & Ziegler/Isotope Prod. Europe Robert-Rossie-Str. 10 Berlin, 13125 Germany	
Auftragsnummer <i>Order No.</i>	111215	
Anzahl der Seiten des Kalibrierscheines <i>Number of pages of the certificate</i>	3	
Datum der Kalibrierung <i>Date of calibration</i>	1 Apr 07	

Dieser Kalibrierschein darf nur vollständig und unverändert weiterverabreitet werden. Auszüge oder Änderungen bedürfen der Genehmigung sowohl der Akkreditierungsstelle des DKD als auch des ausstellenden Kalibrierlaboratoriums. Kalibrierscheine ohne Unterschrift und Stempel haben keine Gültigkeit.
 This calibration certificate may not be reproduced or further used except with the permission of both the Accreditation Body of the DKD and the issuing laboratory. Calibration certificates without signature and seal are not valid.

Stempel <i>Seal</i>	Datum <i>Date</i>	Leiter des Kalibrierlaboratoriums <i>Head of the calibration laboratory</i>	Stellvertreter <i>Deputy</i>	Betreiber <i>Person in charge</i>
	1 Feb 07	 Dr. van Dalsem		 J. Milford
24937 Avenue Tibbitts Valencia, CA 91355	Tel: +1-661-359-1010 Fax: +1-661-257-8303 www.setecprod.usa.com			1800 North Keystone Street Burbank, CA 91504

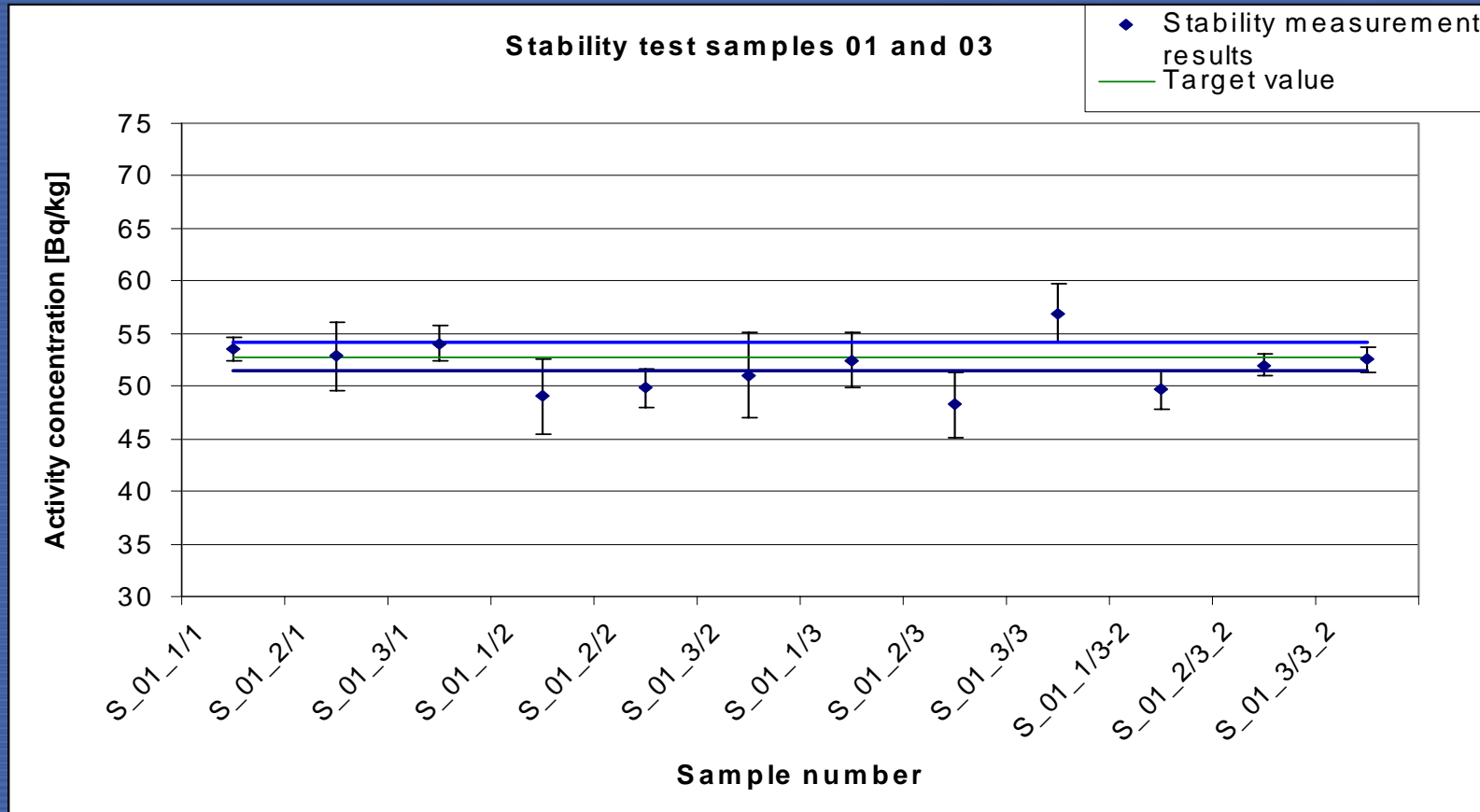


Activity concentration of the Standard solution:

$$377 \pm 10 \text{ Bq kg}^{-1}$$

IAEA-CU-2007-09 ALMERA PT: *Materials*

Stability test: from 19 March to 7 May 2007

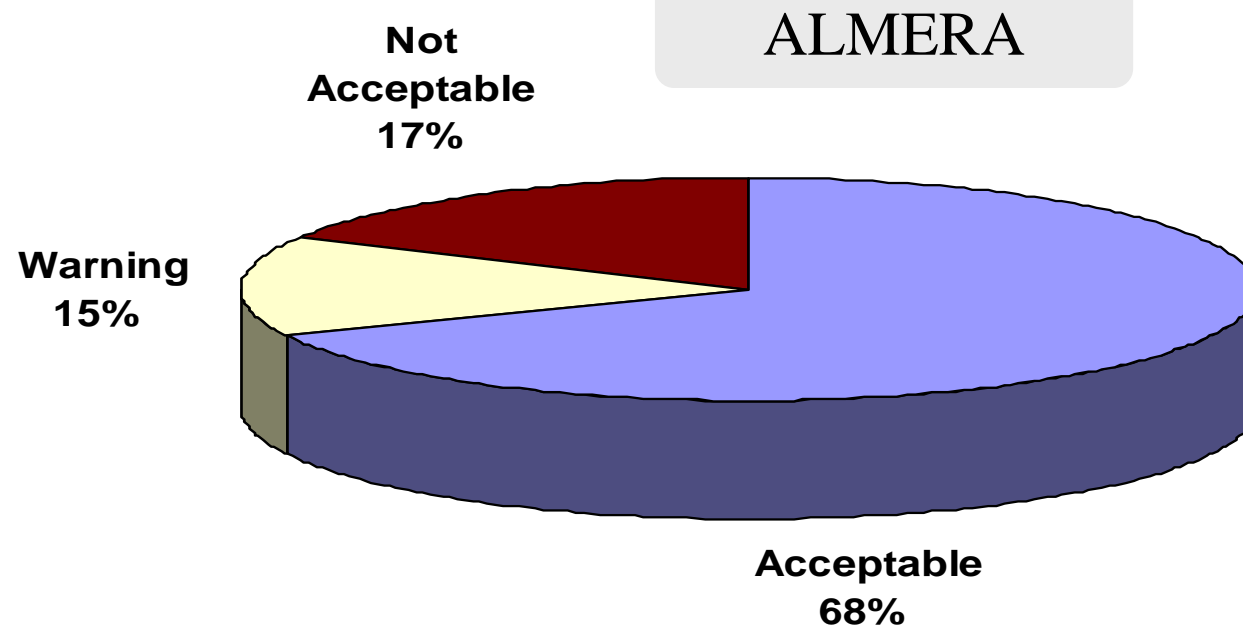


IAEA-CU-2007-09 ALMERA PT: Evaluation

Target values and associated standard uncertainties

Sample code	Sample 01	Sample 02	Sample 03	Sample 04	Sample 05
Activity [Bq.kg⁻¹]	52.8 ± 1.4	101.6±2.8	52.8 ± 1.4	101.6±2.8	<0.1
LAP [%]	15	15	15	15	-
MAB [%]	20	20	20	20	-

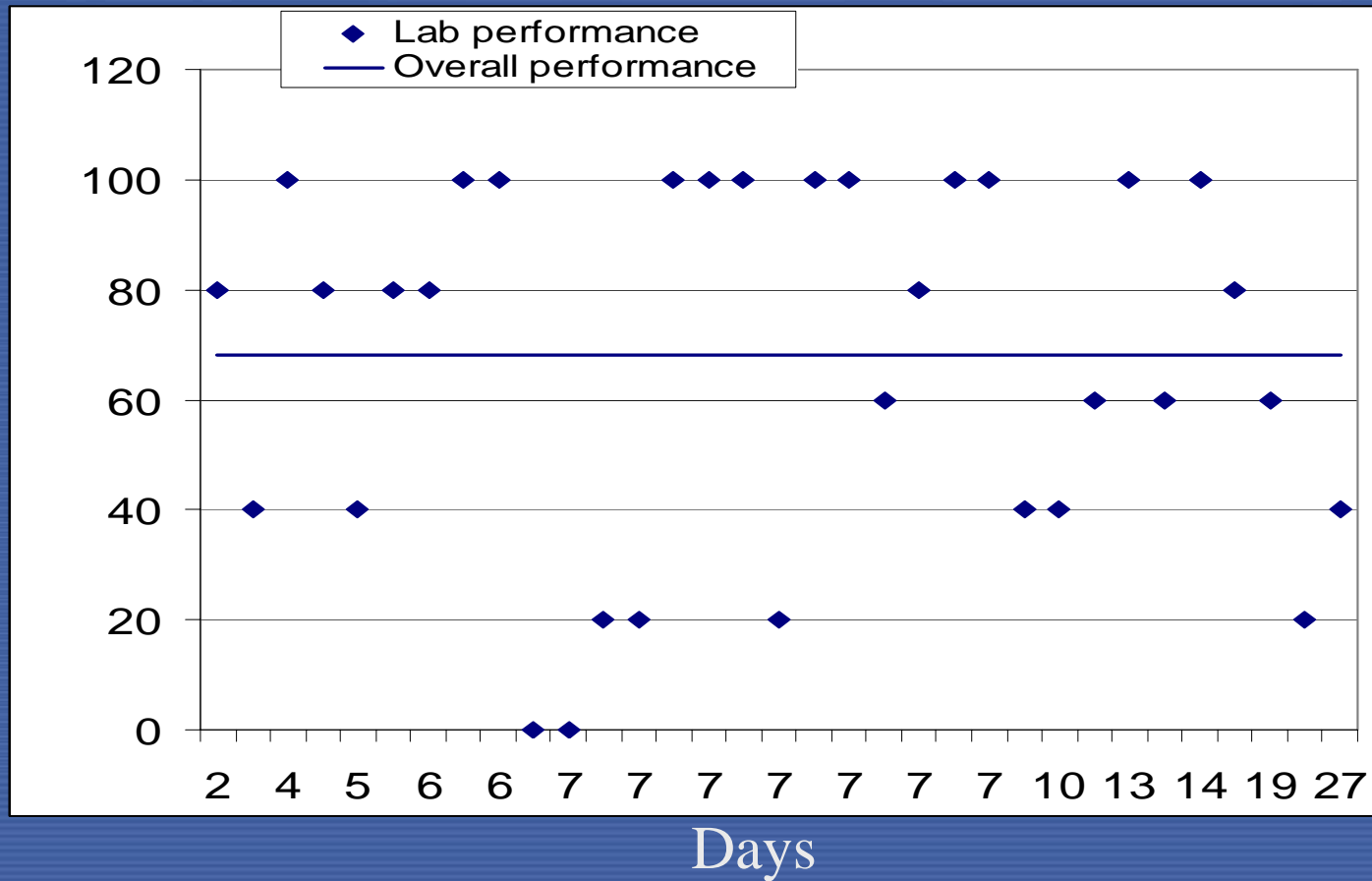
IAEA-CU-2007-09 ALMERA PT: *Evaluation*



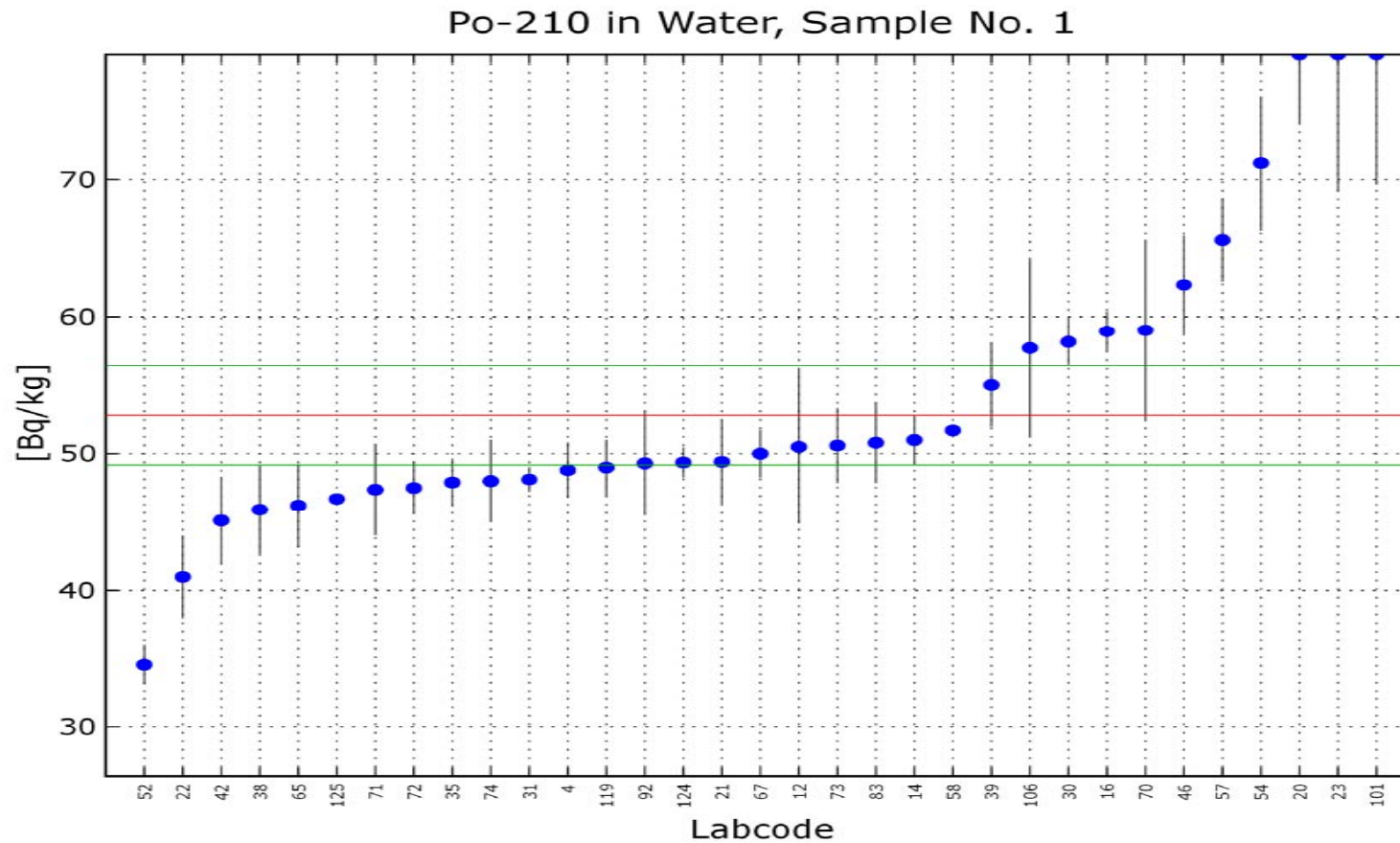
IAEA-CU-2007-09 ALMERA PT: *Evaluation*

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

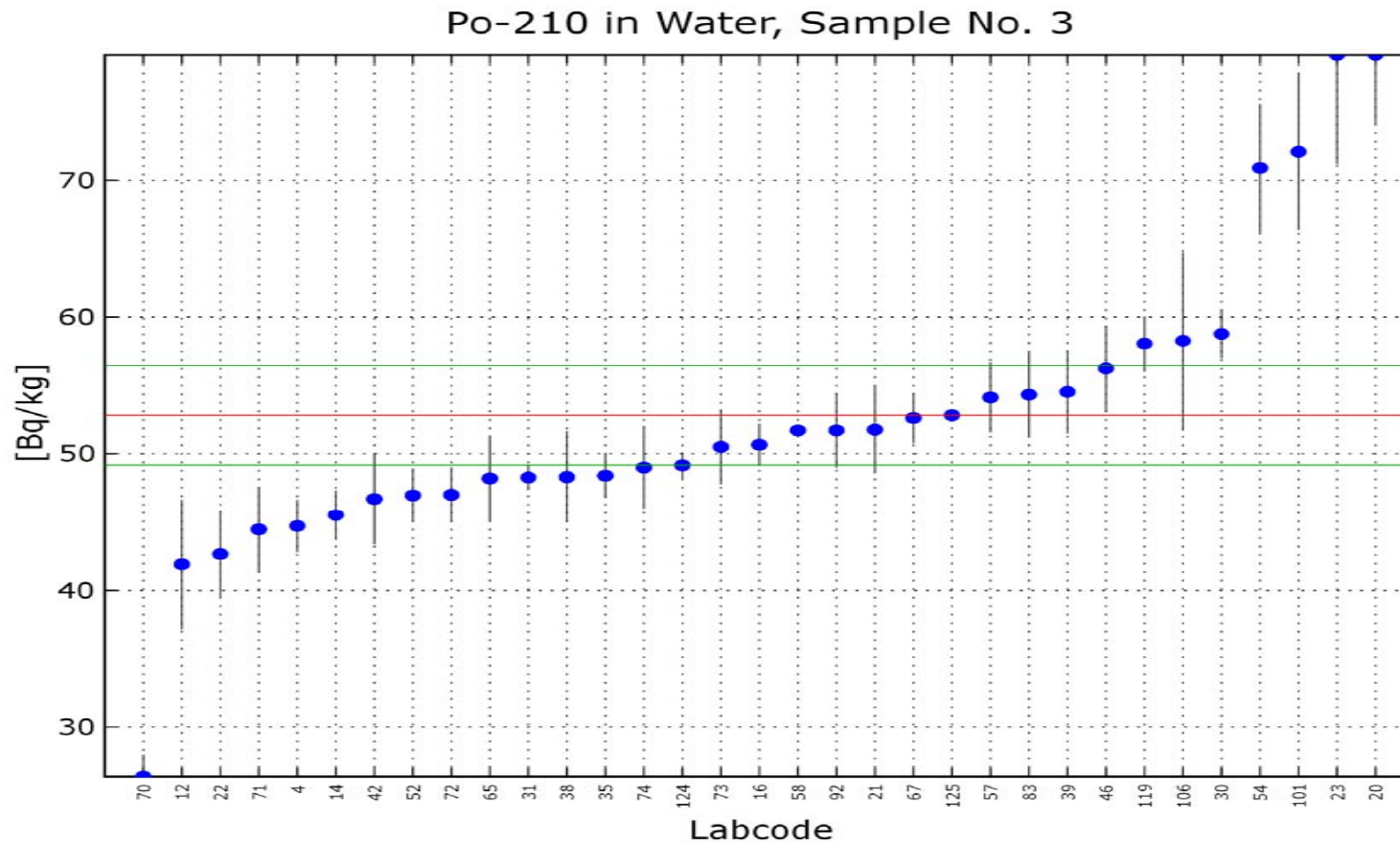
percentage of the total acceptable results



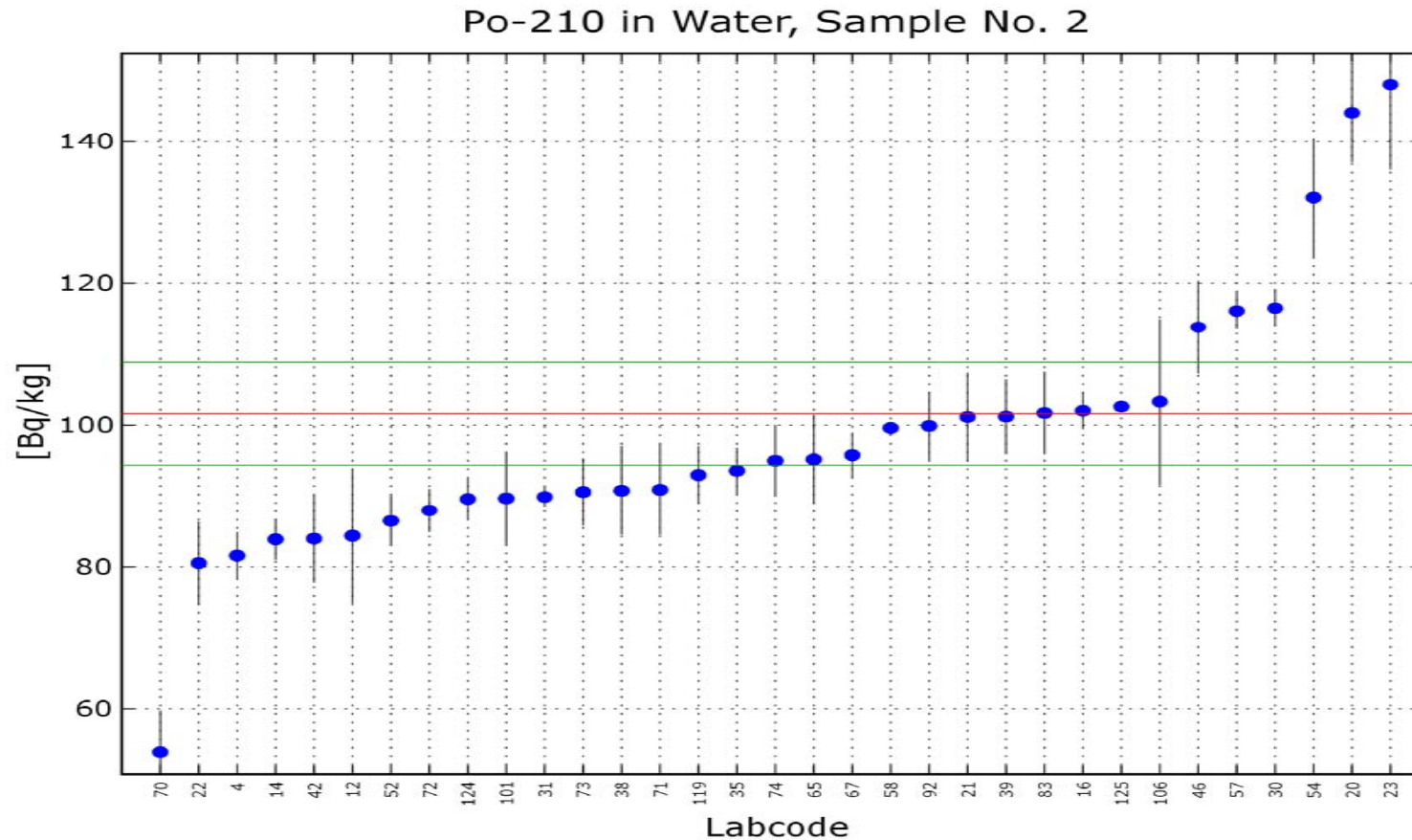
IAEA-CU-2007-09 ALMERA PT: *Discussion*



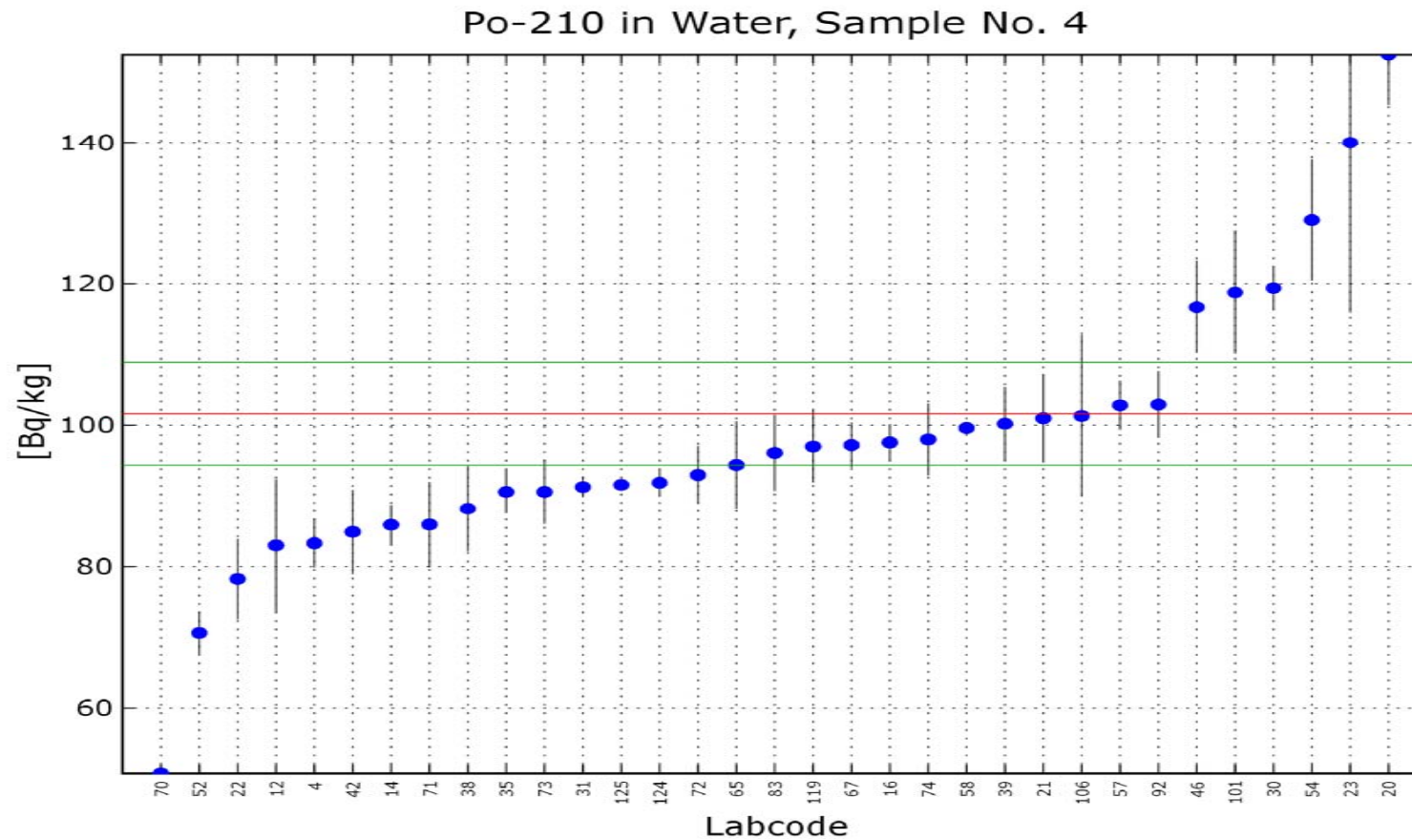
IAEA-CU-2007-09 ALMERA PT: *Discussion*



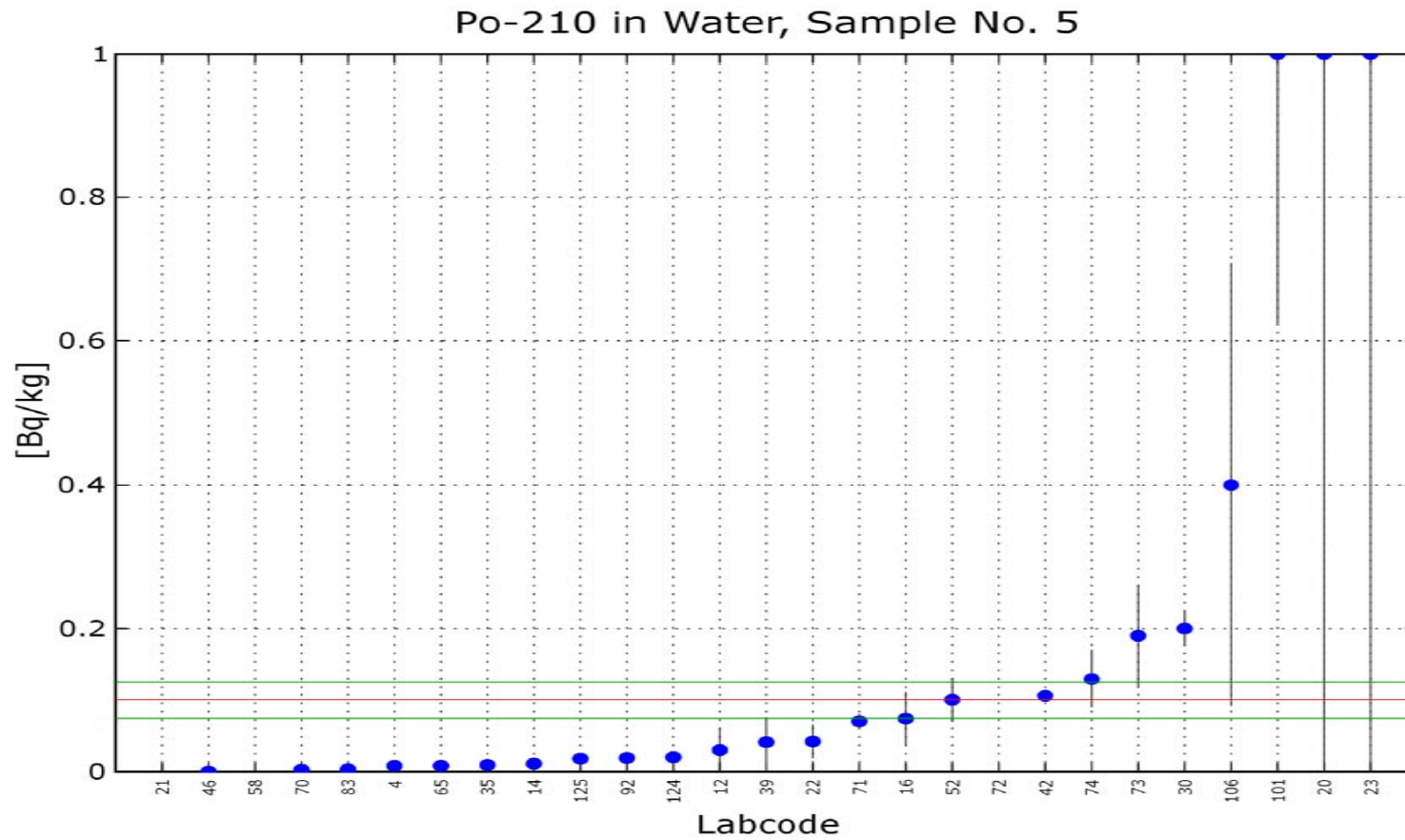
IAEA-CU-2007-09 ALMERA PT: Discussion



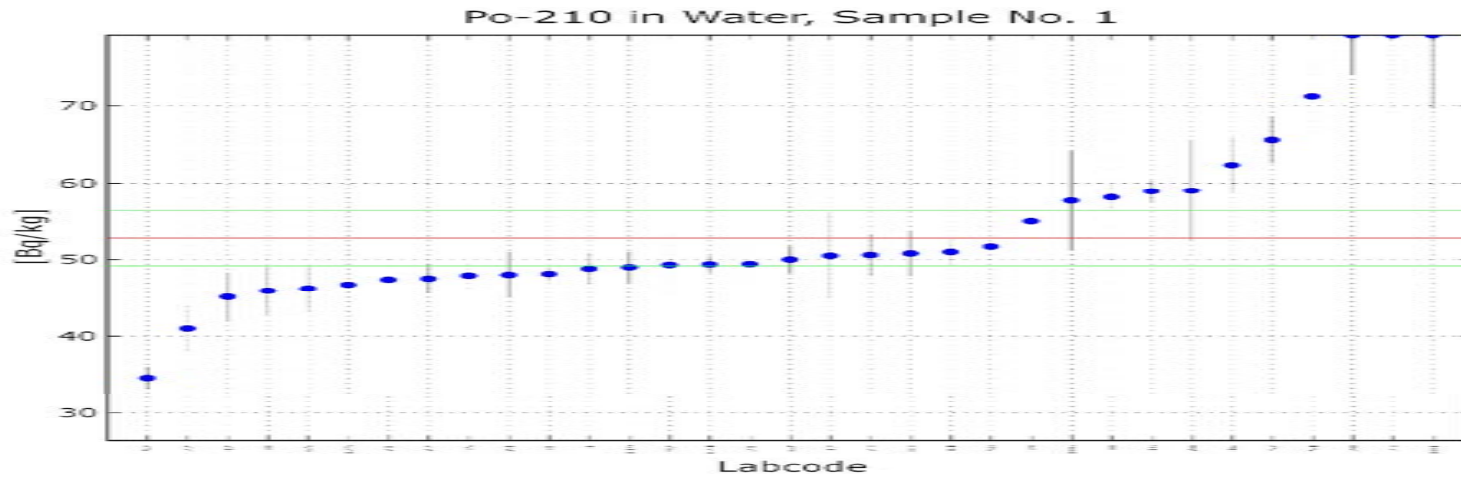
IAEA-CU-2007-09 ALMERA PT: Discussion



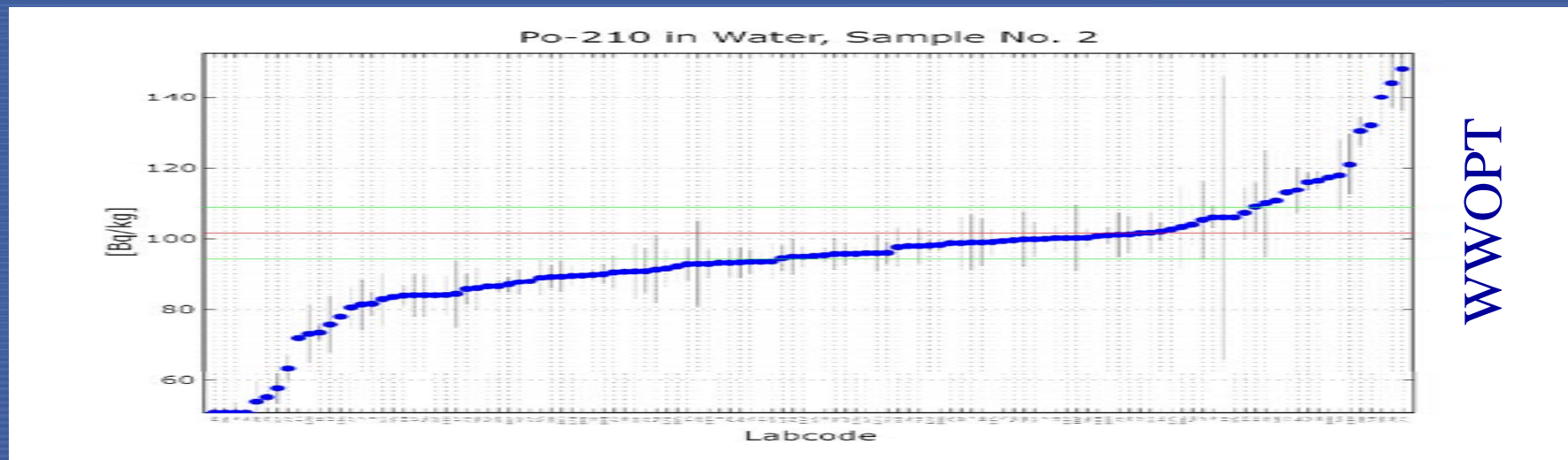
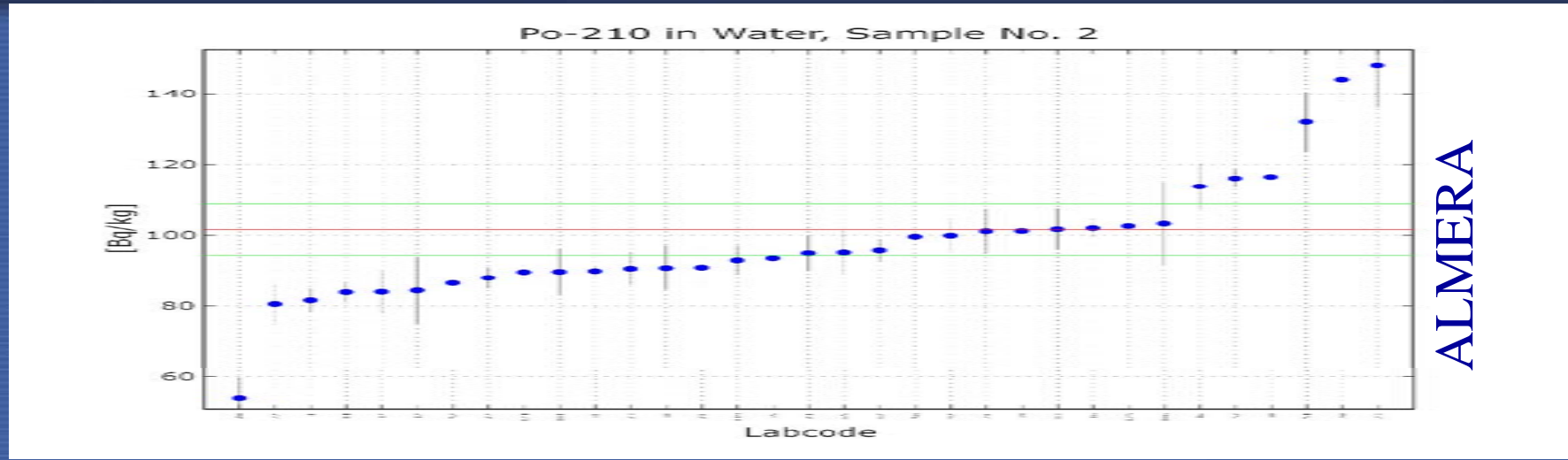
IAEA-CU-2007-09 ALMERA PT: *Discussion*



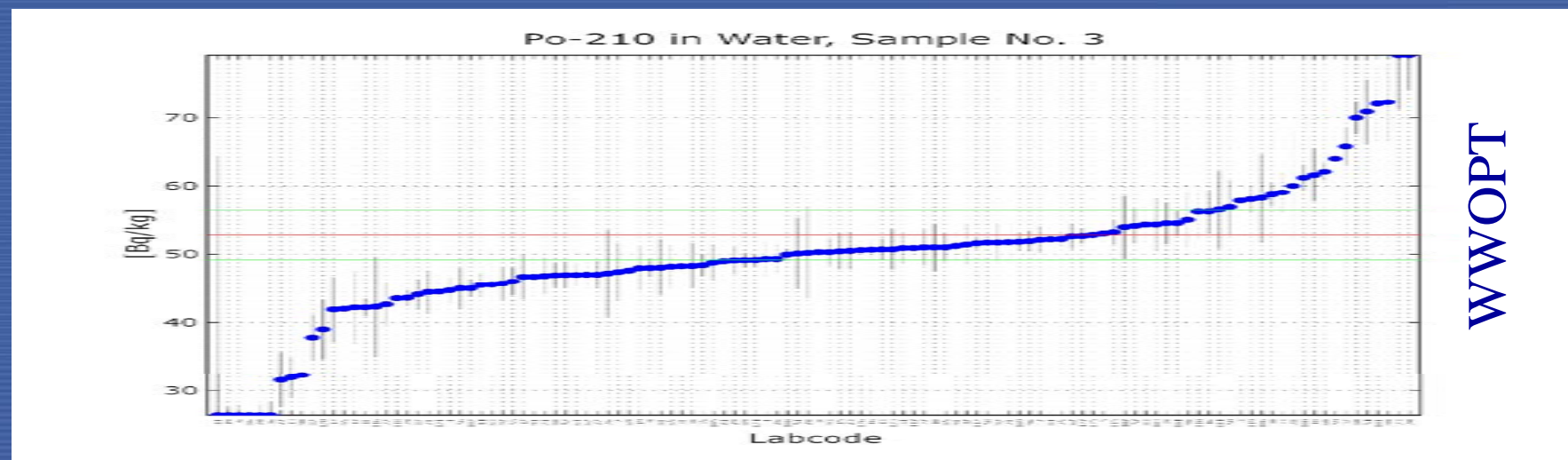
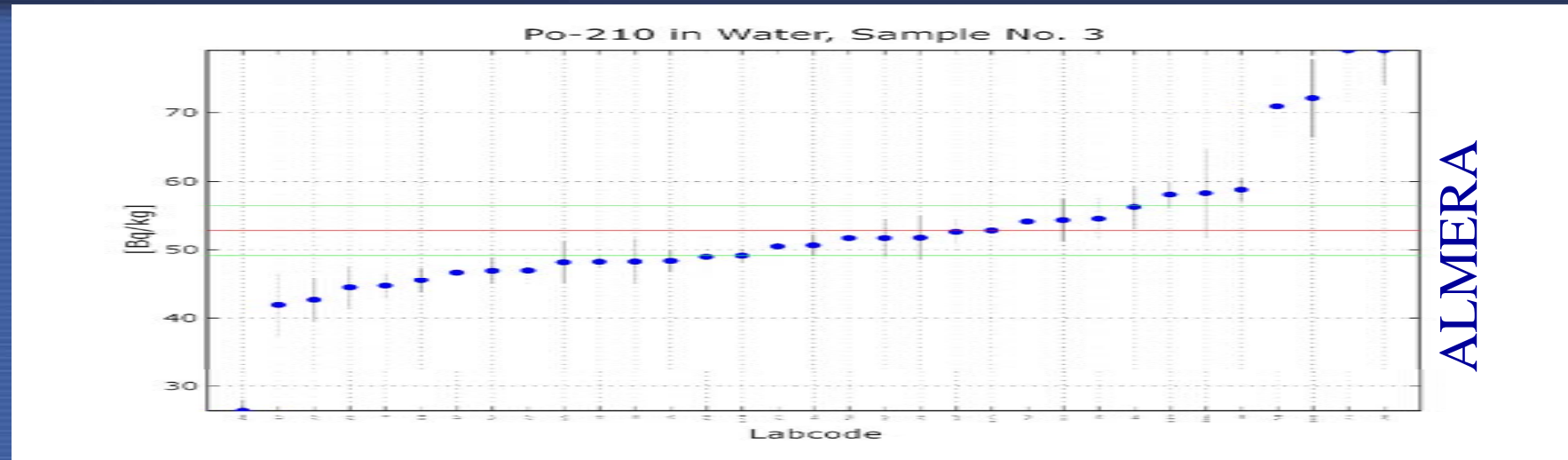
IAEA-CU-2007-09 ALMERA PT: Discussion



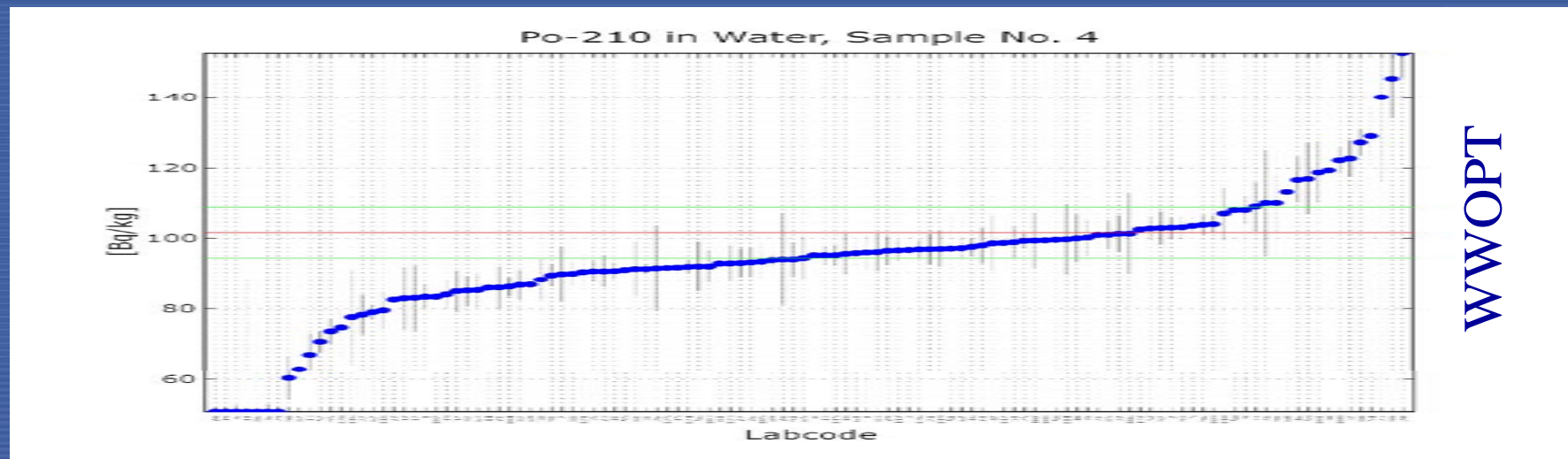
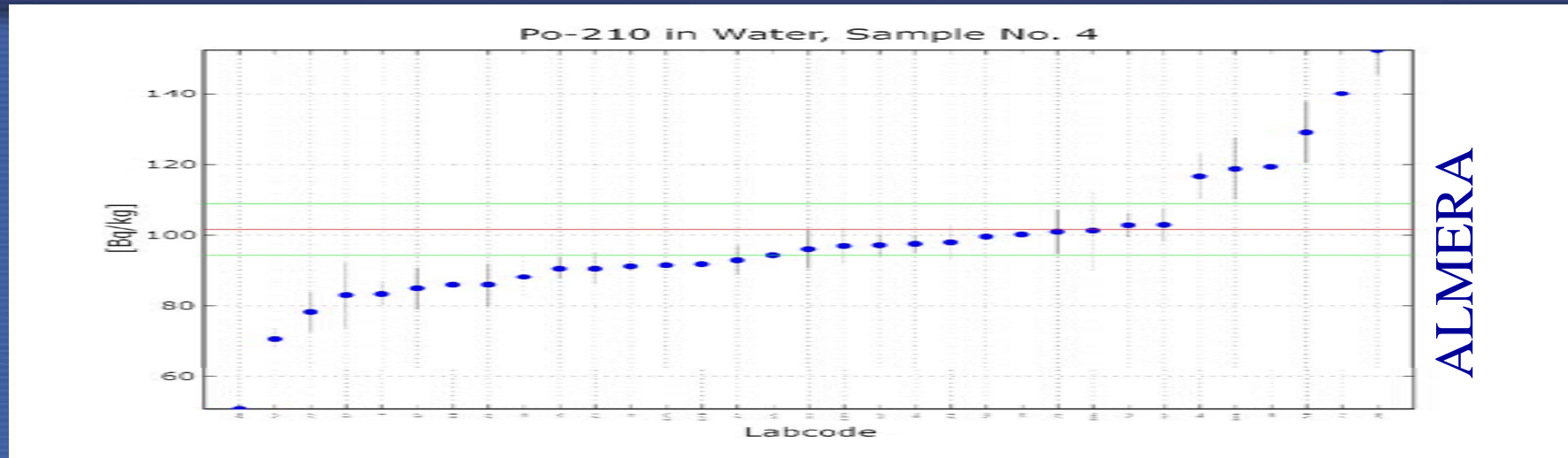
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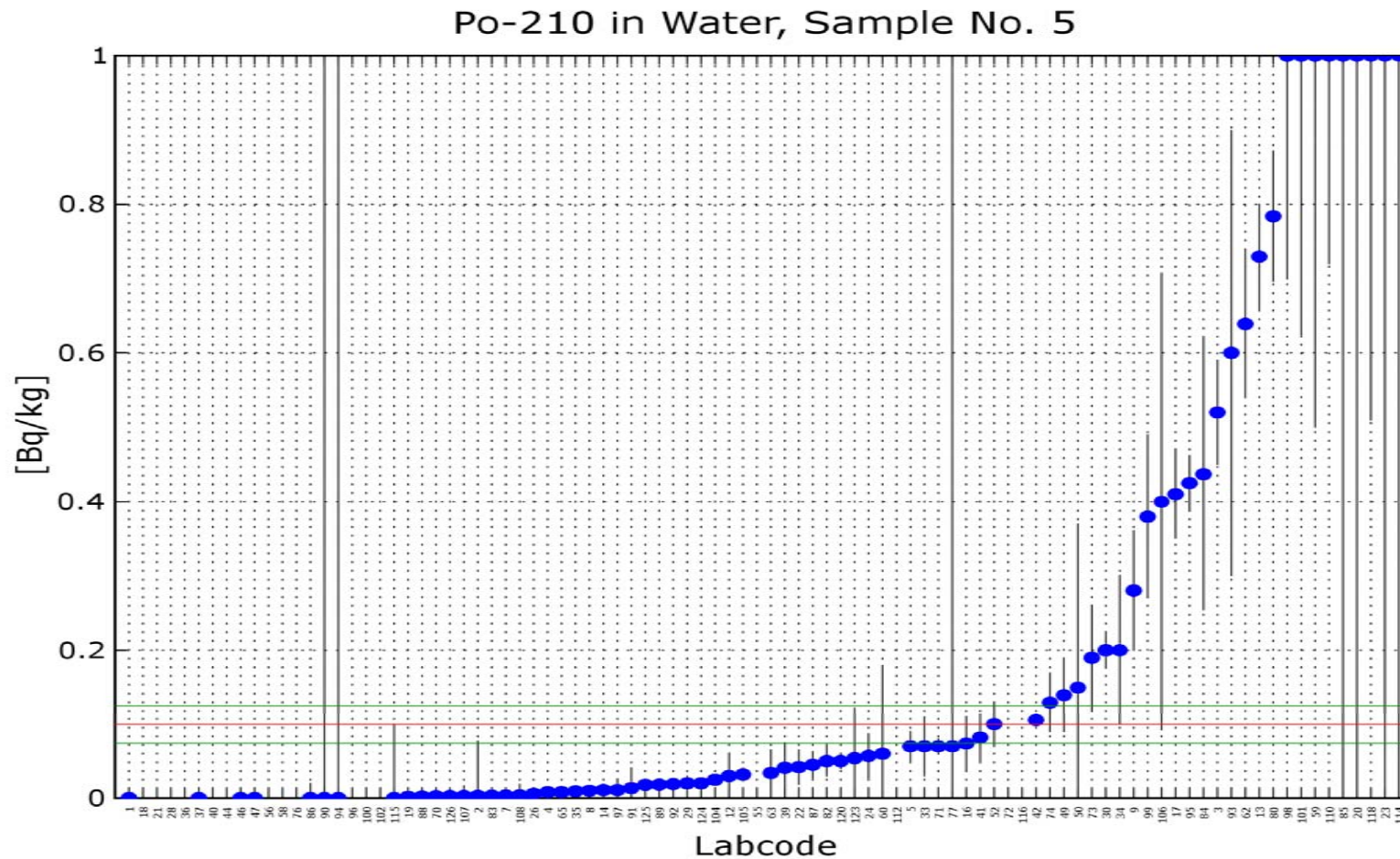
IAEA-CU-2007-09 ALMERA PT: Discussion



IAEA-CU-2007-09 ALMERA PT: Discussion

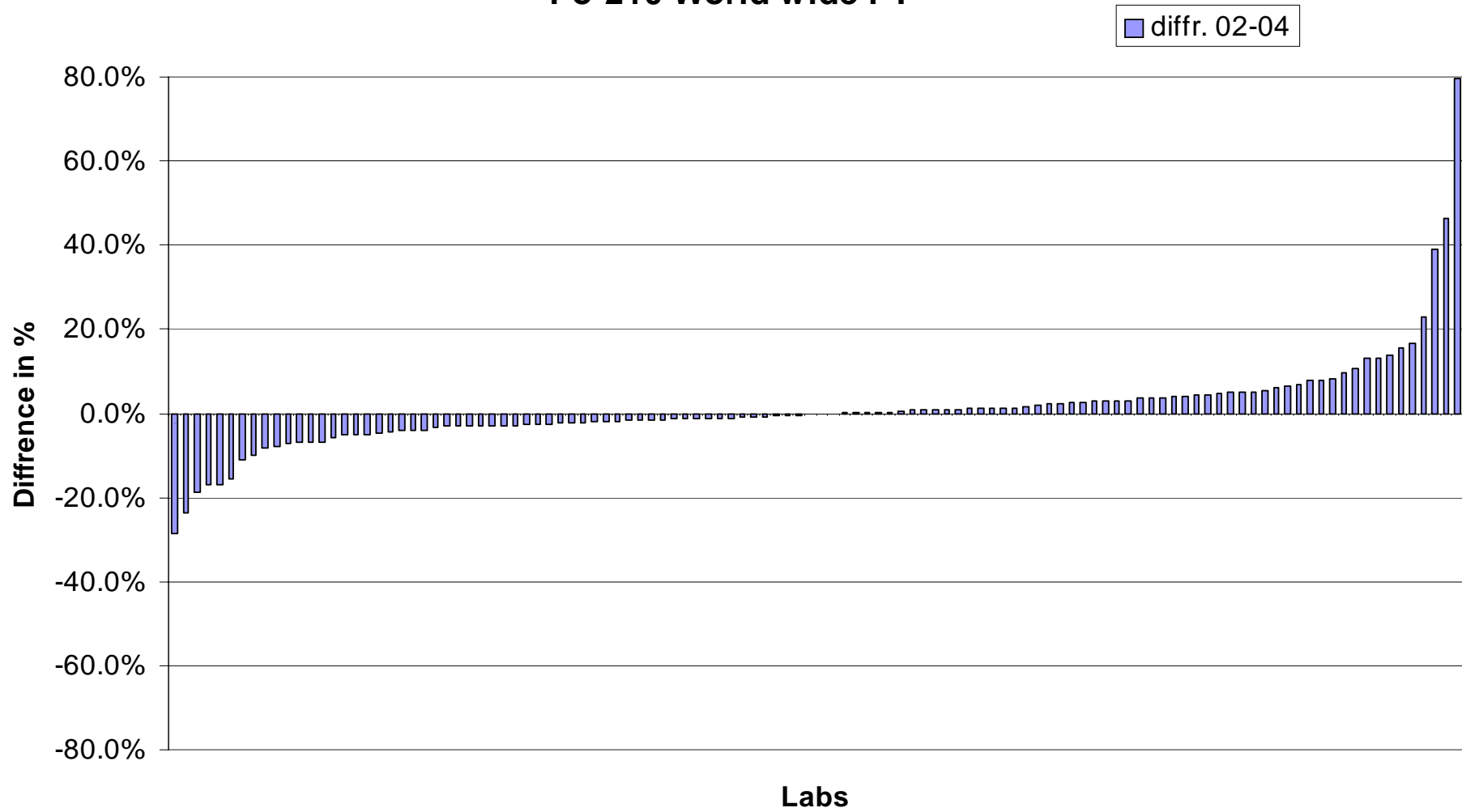


IAEA-CU-2007-09 ALMERA PT: Discussion

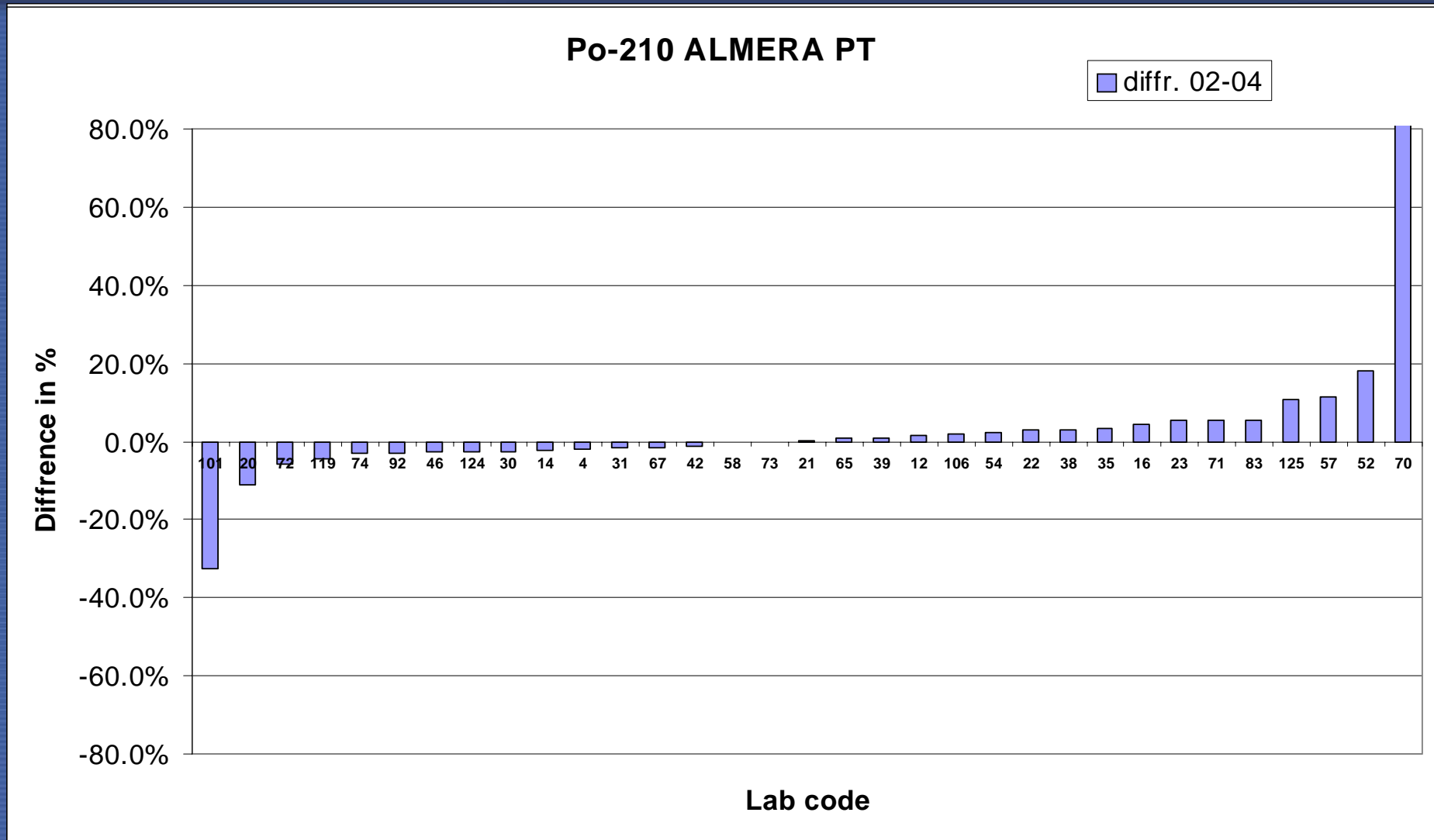


IAEA-CU-2007-09 ALMERA PT: Discussion

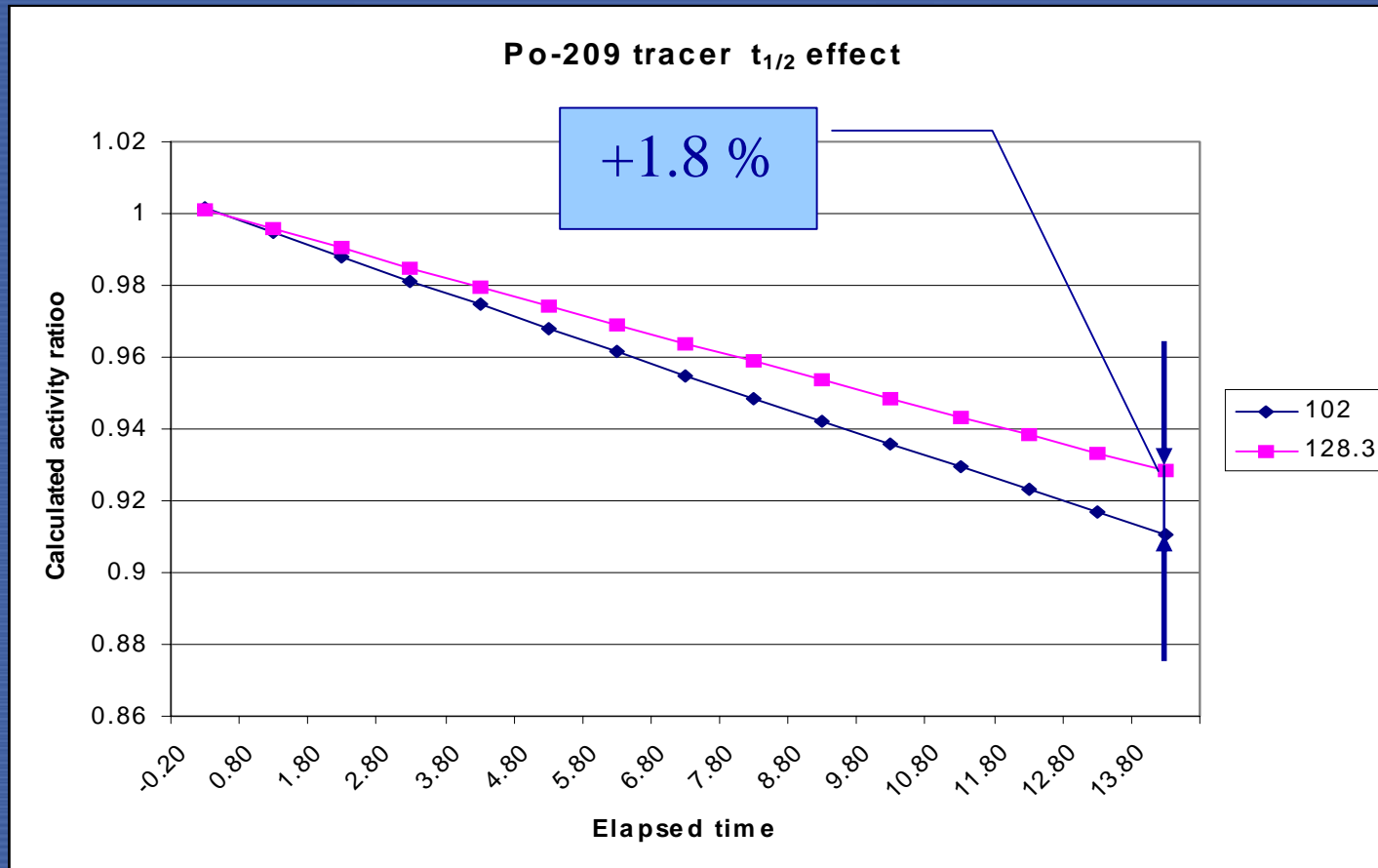
Po-210 World wide PT



IAEA-CU-2007-09 ALMERA PT: Discussion



IAEA-CU-2007-09 ALMERA PT: *Discussion*



IAEA-CU-2007-09 ALMERA PT: *Discussion*

Lab Code	Method validation comments	Claimed MDL	Reported MDL	Score S-05
4	Detection Limit calculated by ISO-11929 standard LID= 0.013 Bq/Kg (99%) (Confidence level)	0.013	0.008	A
12	All 5 samples analysed first based on 20 mL aliquots with DL's below 0.1 Bq/kg. Analyses of samples 1-4 repeated based on 2-3 mL aliquots to match spike amounts.	0.1	0.03	A
14	LLD: 0.04 Bq/kg (Po-210)	0.04	0.011	A
16	NA		0.0737	A
20			4	N
21	NIL		0	
22	a) Spectrometric system is checked by counting tracer(Pu-242) for MDL level concentration.b) Background count rate fro reproducibility		0.042	A
23	NULL		27	N
30			0.2	N
31	Minimum detection limit was calculated by L. A. Currie's equation. The MDL is 0.07 Bq/kg. Repeatability was not tested. Each sample was counted once by alpha spectrometer. Reproducibility was tested. The identical sample was measured three times. The RSD of results is less than 1.5%.	0.07	<0.07	A
35			0.0092	A

IAEA-CU-2007-09 ALMERA PT: Discussion

Lab Code	Method validation comments	Claimed MDL	Reported MDL	Score S-05
38	MDL is dependant on sample mass. For low klevel work where 100g of sample is taken the MDL is 0.005Bq/kg. For these IAEA samples where the activity was very high 4 g of sample was used to achieve an MDL around 0.1Bq/kg Repeatability at k=2 is 4.2% For this PT MDL=0.15Bq/kg	0.1	<0.0453	A
39	at Counting Time 25200s, sample Mass 10.4g, Counting Efficiency 37.2%, Recovery 96% (for low salinity waters)	0.15	0.041	A
42			0.1055	A
46	1-LLD=0.00481Bq/L 2-Triplicate samples analysed. 3-Above 95%.	0.005	0	
52			0.1	A
54	Method validation for polonium in solid, water and urine samples is in progress.		<0.2	A
57	Minimum Detection Limit for Sample Code 1 to 4 - 0.2 Bq/Kg(3 sigma) Repeatability - +/- 3% Reproducibility - +/- 4%	0.2	<0.15	A
58			0	
65	MDA=0.01 Bq/kg, repeatability = 6%	0.01	0.008	A
67	MDC 0.1 Bq/kg for 5g sample and 23 hour counting time.	0.1	<0.073	A
70			0.0026	A
71	* Genie 2000 softwares validated by CANBERRA * The metthod validation was performed by analysing IAEA-326 Soil and IAEA-315 Sediment. The obtained data were all in good agreement with the recommended values. The obtained precision (relative standard deviations) is < 10% and the accuracy (relative bias) is < 2%. The minimum detection limit for 5 kg of water sample is 0.016 mBq/kg and the corresponding value for 2.5 g of water 32 mBq/kg.	0.02	0.07	A

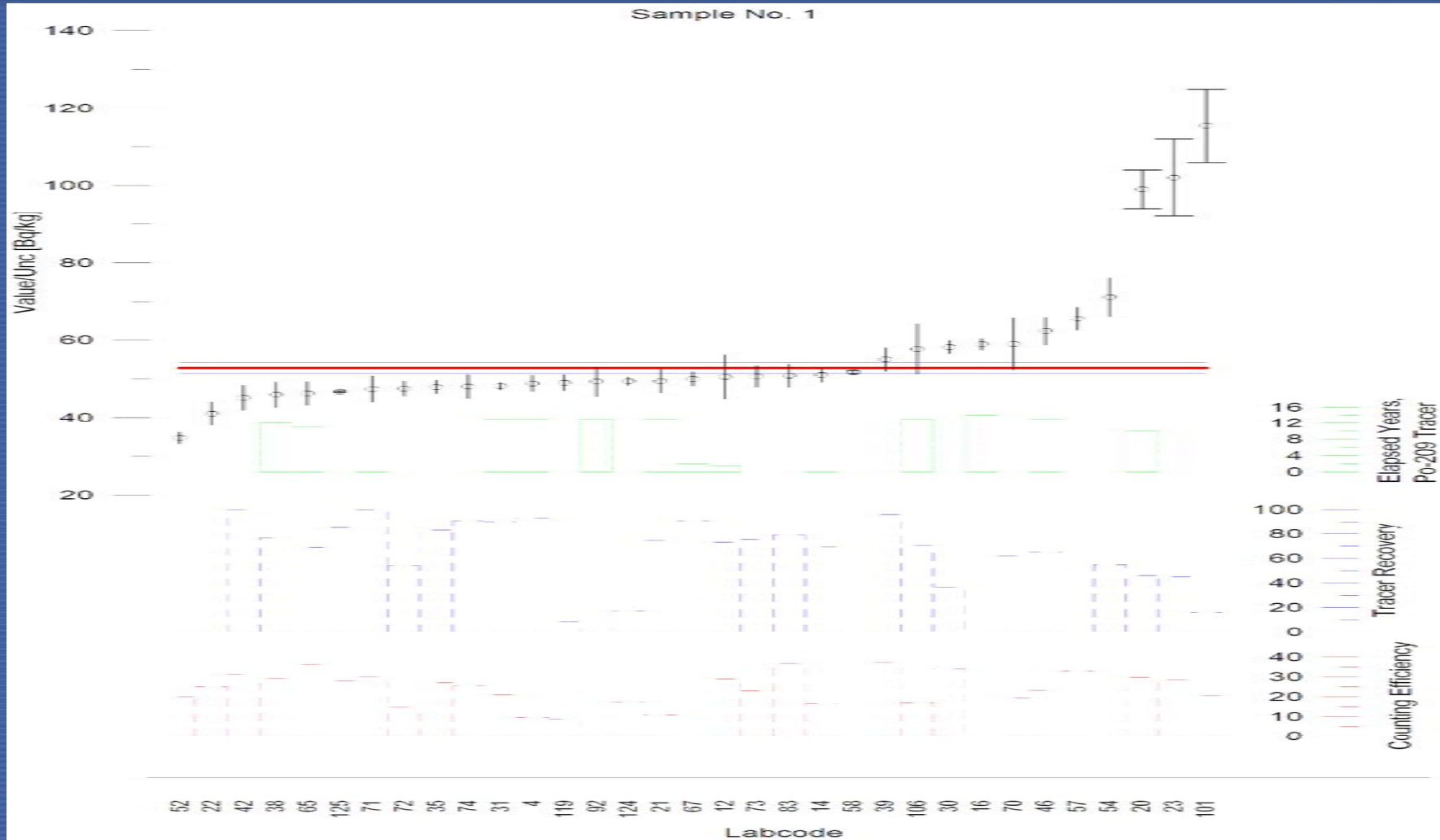


IAEA

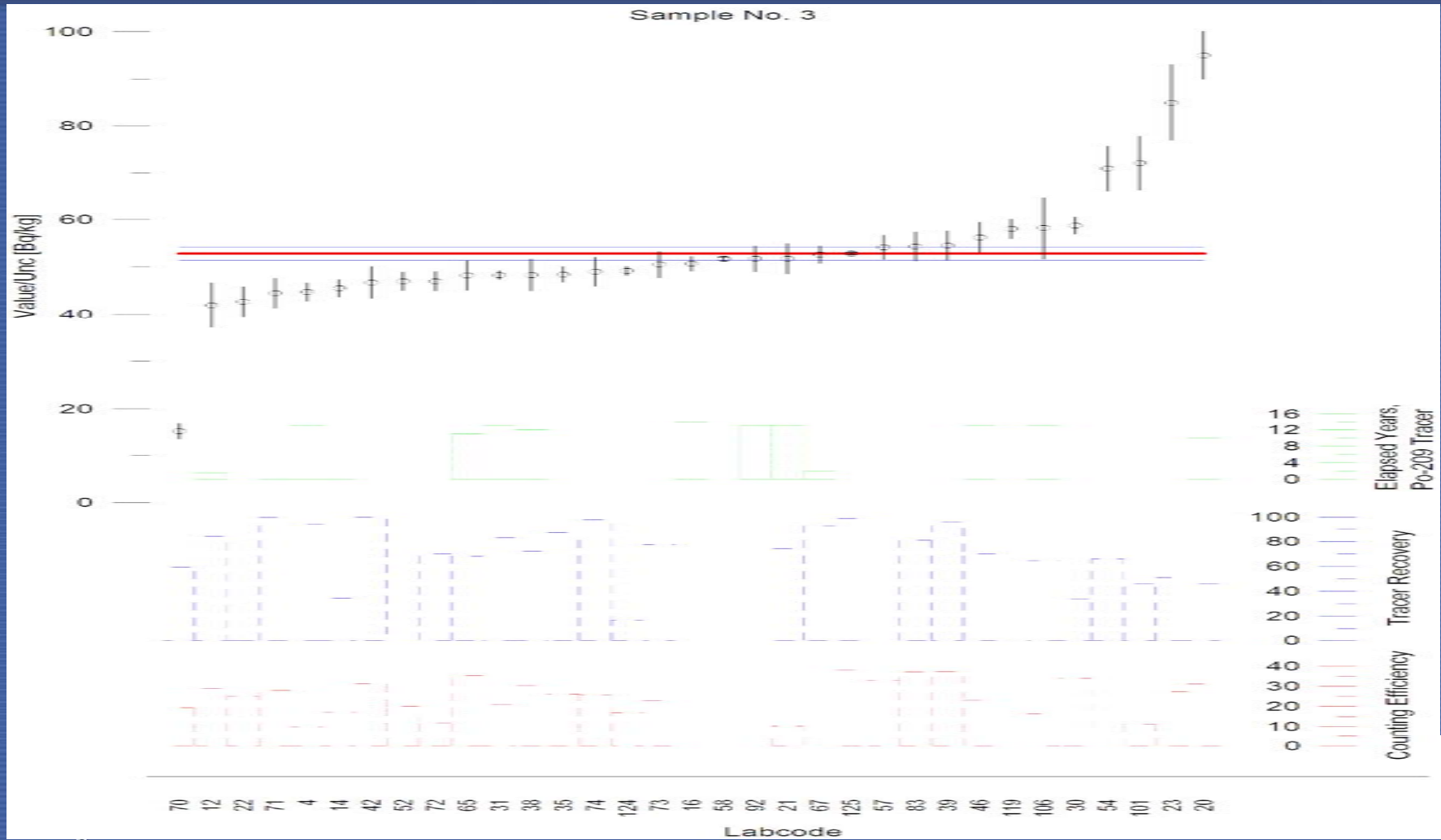
IAEA-CU-2007-09 ALMERA PT: Discussion

Lab Code	Method validation comments	Claimed MDL	Reported MDL	Score S-05
72	In 2004 and 2005 the Dutch norm NEN 5694 (Methods for radiochemical determination of Po-210 and Pb-210) was validated in various matrices; e.g. biological, silicium-containing and non-Si-containing samples. I could give the validation parameters for these matrices. But as they have nothing to do with Seibersdorf Demineralized water there is no sense in giving those data. Furthermore, the minimum detection limit highly depends on the processed sample volume. Again there is no sense in giving a detection limit as such. A water sample is much simpler than a silicium-containing sample with a strongly oxidizing chemical treatment.		0.1	A
73	The method validation was performed on urine samples of 500 ml. Considering a counting time of 200000s the validation parameters were: Minimum detection limit= 5 mBq/l Repeatability limit = 5% Reproducibility limit = 9%	0.005	0.19	N
74			0.13	A
83			0.0032	A
92			0.019	A
101			2.446	N
106	MDA=0.04 Bq/kg where efficiency=0.2; yield=0.6; sample mass=25g, counting time=86400s. Accuracy: 15% Precision: 10% (12 samples on day of analyses) Reproducibility: 13% (more than 50 test samples analysed over a year as test control samples)	0.04	0.4	A
119			<0.0045	A
124			0.02	A
125			0.018	A

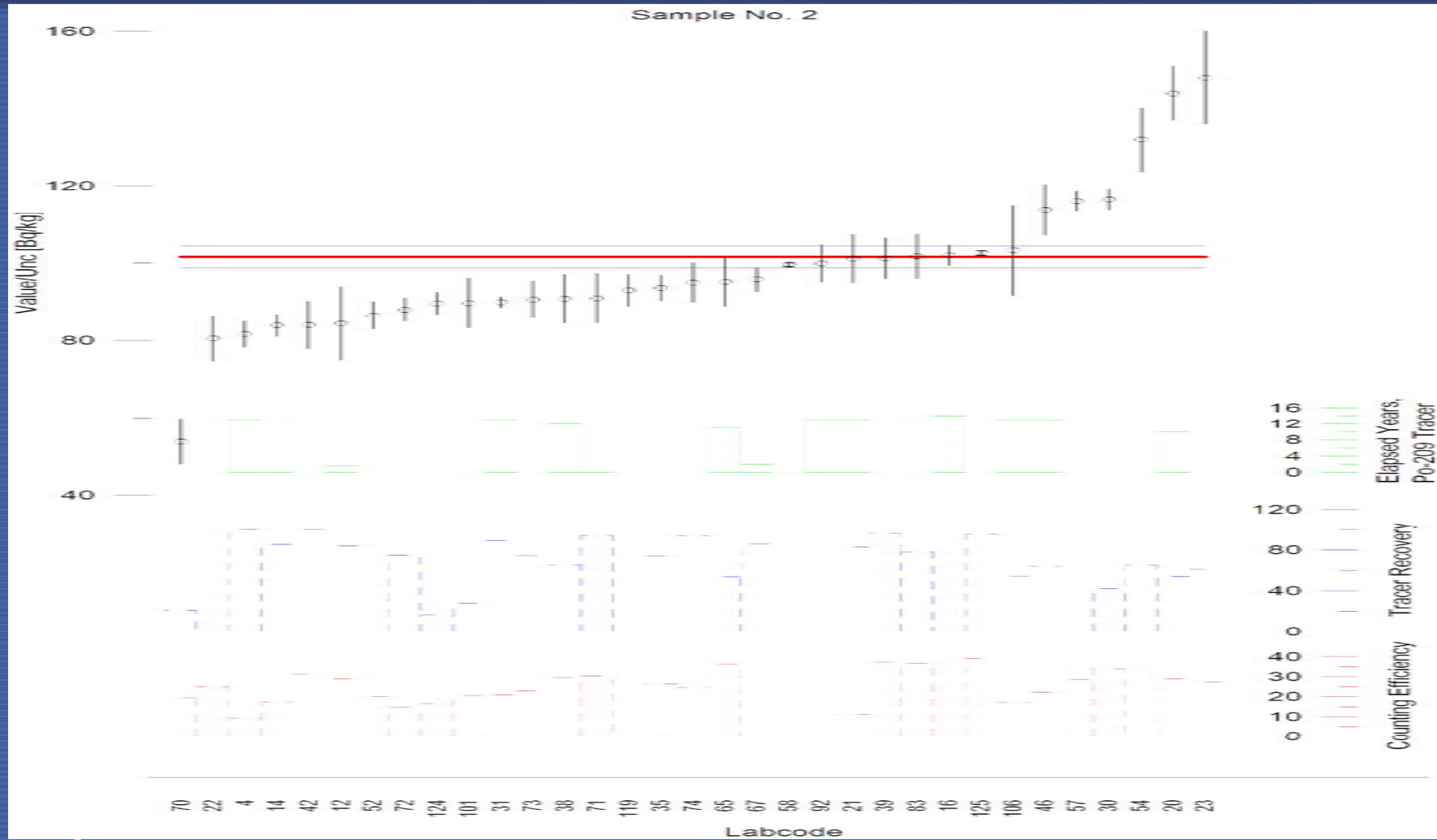
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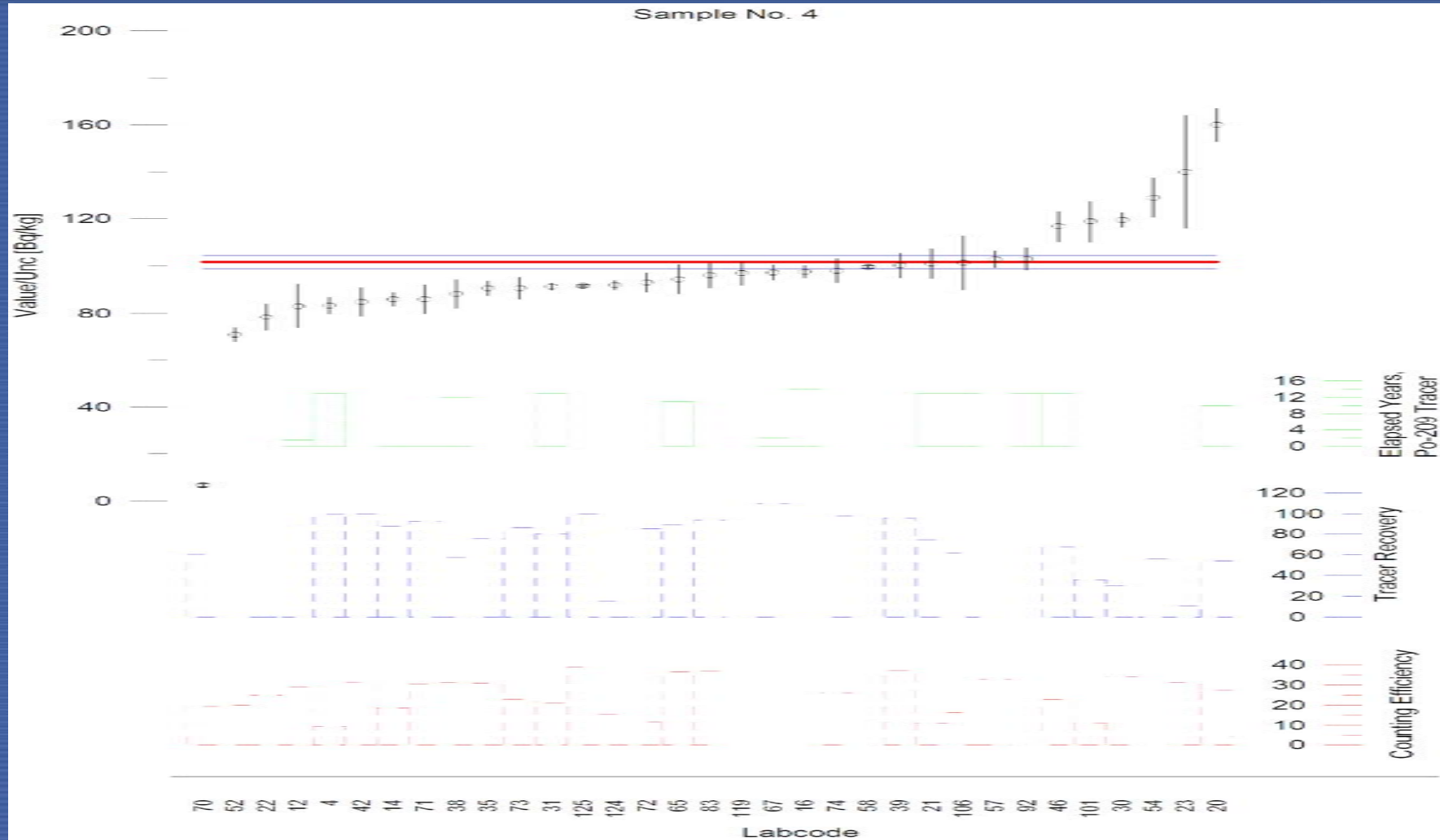
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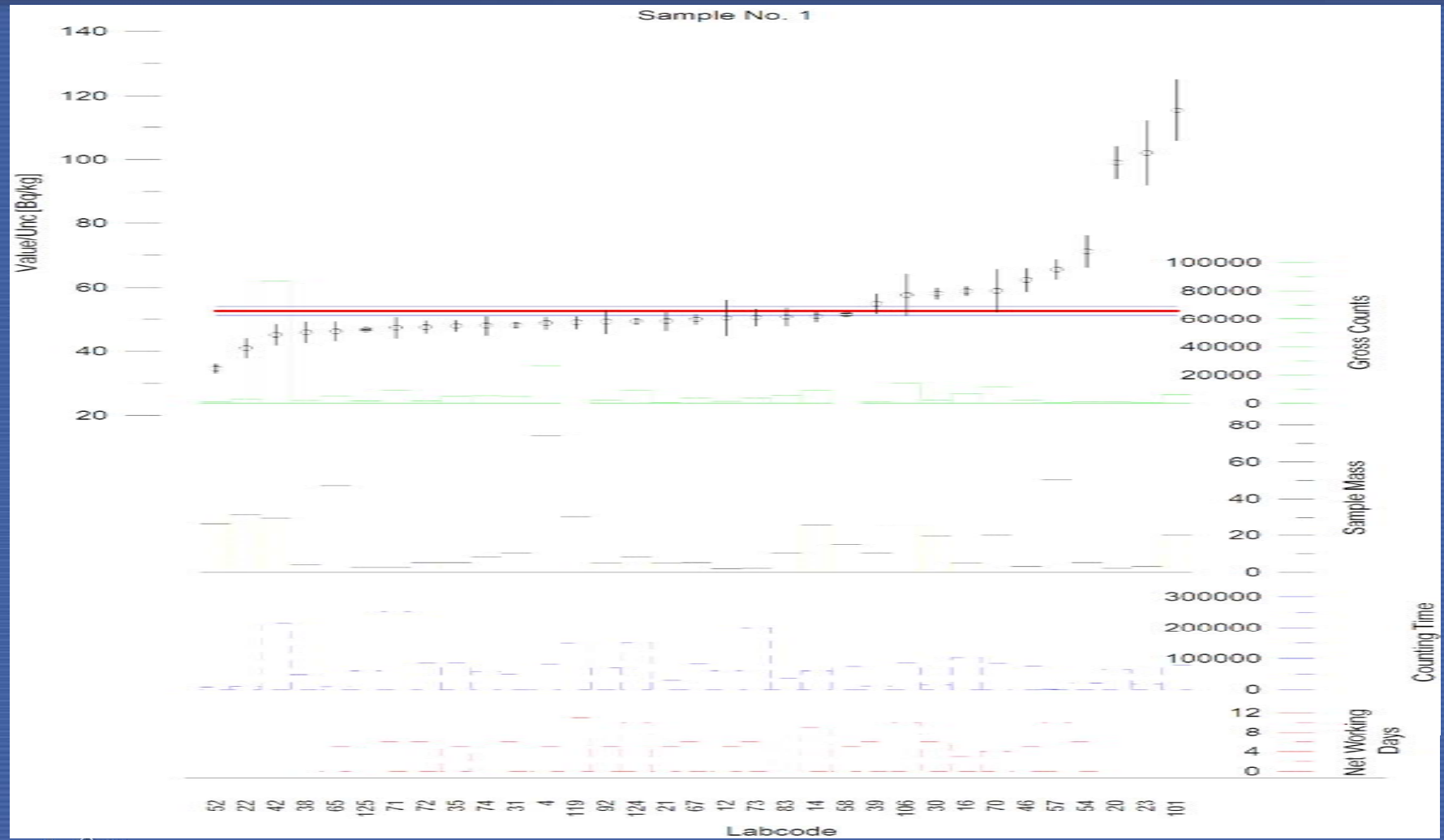
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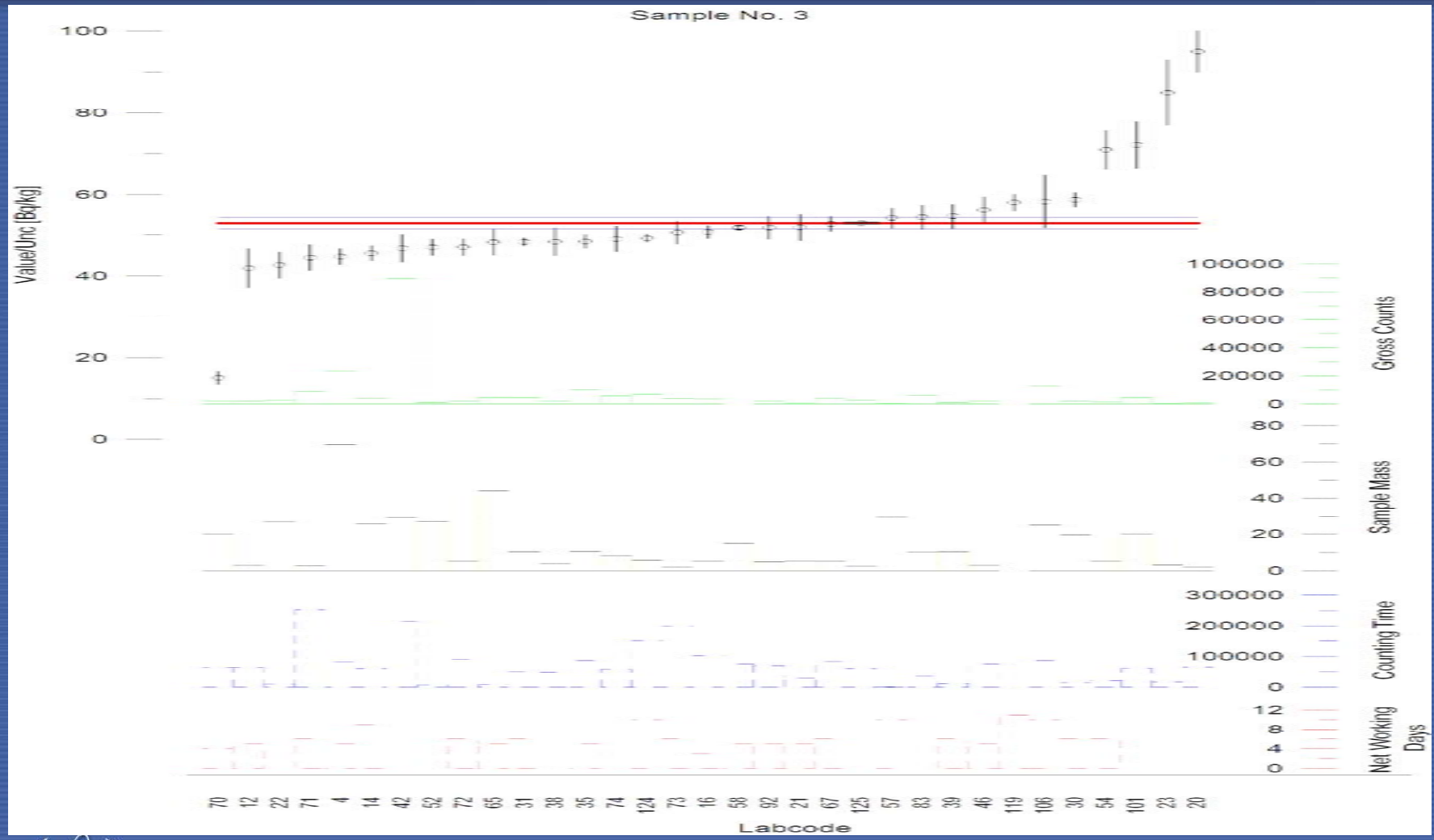
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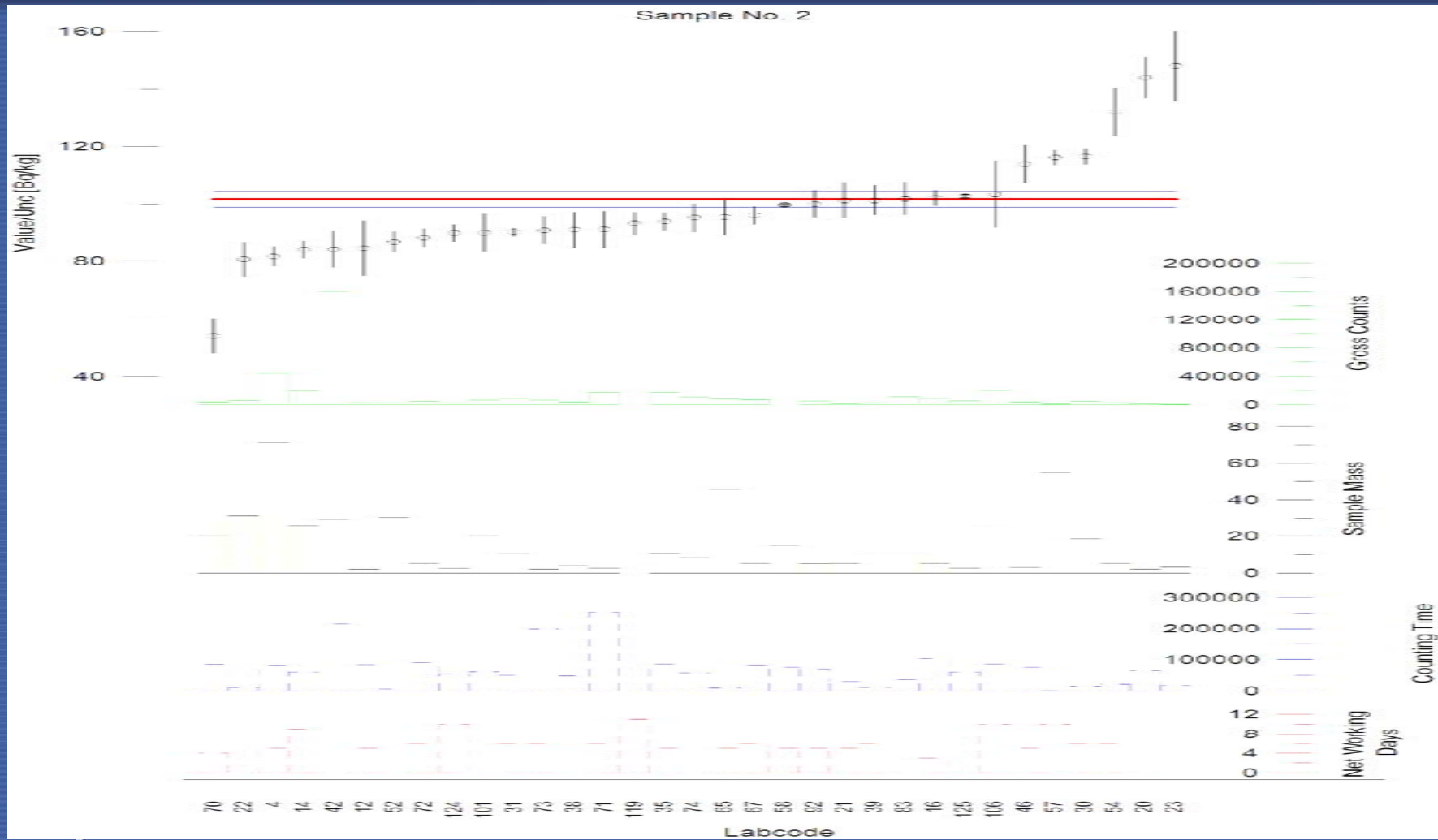
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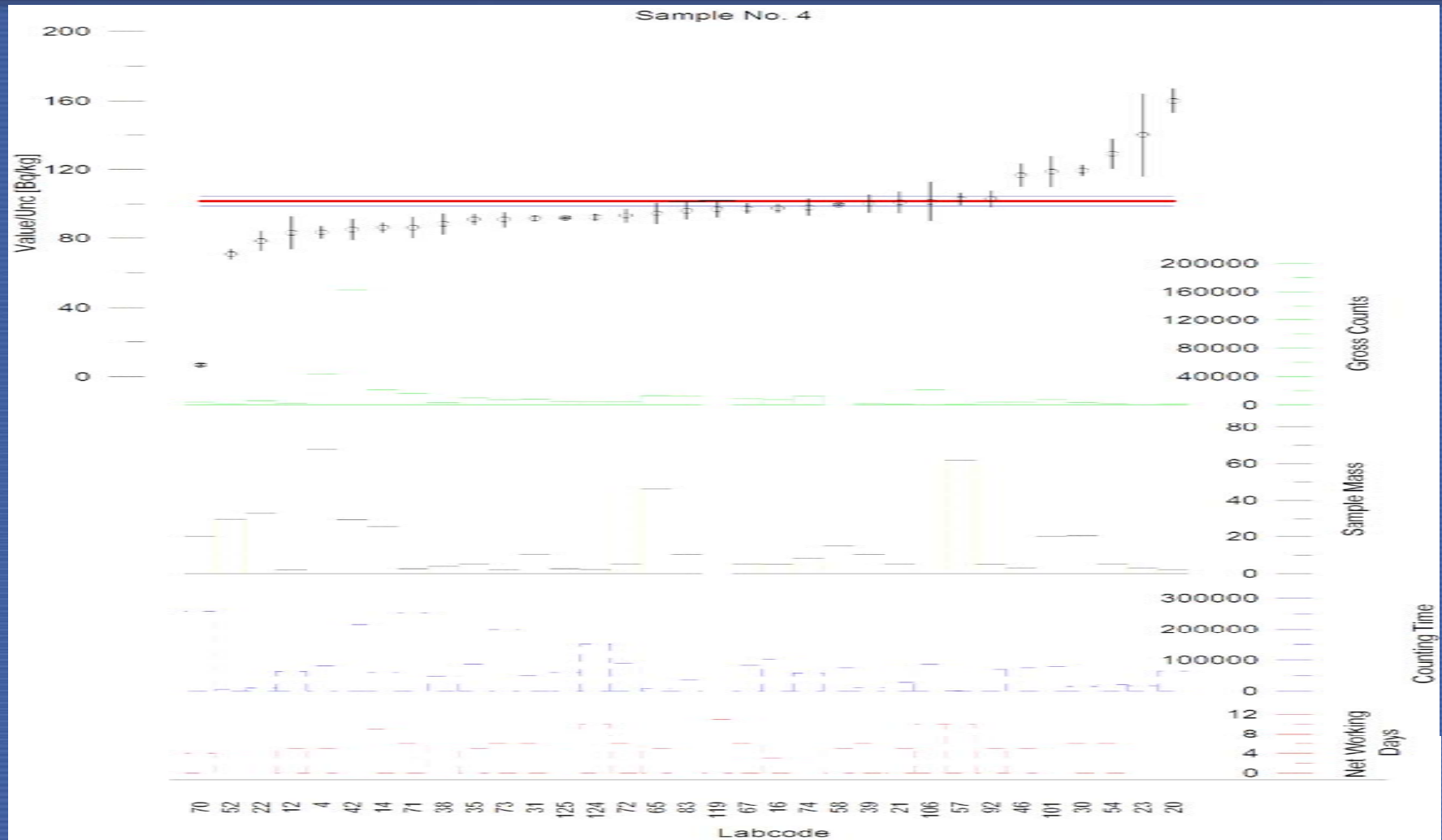
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FEED BACK from LABORATORIES

- Just Po-210 addition to a demineralised water sample is NOT even difficult enough.
- Asking relative (%) errors for background is not relevant.
- Typing mistakes in the electronic forms

IAEA-CU-2007-09 ALMERA PT: Conclusions

- The PT was successfully conducted,
- Most of the participants were able to report the results within the deadline,
- Although the matrix was not difficult and the activity concentration was high, 18 % of the reported results did not fulfil the PT criteria,
- False positive were reported might be mainly from cross contamination or unstable analytical procedure.
- Some of the laboratories should verify the performance characteristics in their laboratory conditions (method validation-verification).
- Proposal to establish an ALMERA harmonised-standard analytical procedure for the determination of Po-210 in water in emergency

IAEA-CU-2006-04 ALMERA PT: Acknowledgment

- Contributions of all laboratories are highly appreciated,
- Support of all colleagues at the Chemistry Unit is appreciated and acknowledged,



Thank you for your attention