



Outcome from your “Results Form”

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Community Reference laboratory for Chemical Elements in Food of Animal Origin

- Uncertainty and Interpretation of Results
- LoD and LoQ
- Use of CRM
- Other considerations

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Lab Code

10

13th PT 1st Round Milk

<i>Interpretation of results</i>			
	Acceptance	Expanded Uncertainty (mg/kg)	Coverage Factor K
Pb Sample A	No	0,034 +/- 0,03	2
Pb Sample B	Yes	0,022 +/- 0,02	2

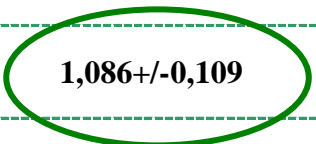
Uncertainty of ~ 100%

Lab Code

18

13th PT 2nd Round Fish

Cd	Swordfish	Yes	0,268+/-0,27	2
Pb	Swordfish	Yes	0,253+/-0,25	2
Hg	Swordfish	Yes	1,086+/-0,109	2



LoD and LoQ

COMMISSION REGULATION (EC) No 333/2007
of 28 March 2007

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LOD	For inorganic tin less than 5 mg/kg. For other elements less than one tenth of the maximum level in Regulation (EC) No 1881/2006, except if the maximum level for lead is less than 100 µg/kg. For the latter, less than one fifth of the maximum level
LOQ	For inorganic tin less than 10 mg/kg. For other elements less than one fifth of the maximum level in Regulation (EC) No 1881/2006, except if the maximum level for lead is less than 100 µg/kg. For the latter, less than two fifth of the maximum level

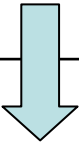
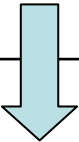
13th PT 1st Round Milk

Lab Code: 16	As	Cd	Pb
LoD of the Method	40 µg/kg	5 µg/kg	10 µg/kg
LoQ of the Method	50 µg/kg	5 µg/kg	12 µg/kg

Three light blue arrows point downwards from the LoD values to the LoQ values for As, Cd, and Pb.

13th PT 2nd Round: Fish

Same Laboratory

Lab Code 4	As	Cd	Hg	Pb
LoD of the Method	40 µg/kg	5 µg/kg	0.4 µg/kg	20 µg/kg
LoQ of the Method	 50 µg/kg	 5 µg/kg	0.7 µg/kg	40 µg/kg

13th PT 1st Round Milk


Lab Code 20	As	Cd	Pb
LoD of the Method	--	0.005 mg/kg	0.02 mg/kg
LoQ of the Method	--	0.02 mg/kg	0.06 mg/kg

Lab Code

20

Cd		Pb	
<i>Concentration (mg/kg)</i>	<i>SD</i>	<i>Concentration (mg/kg)</i>	<i>SD</i>
0,0056	0,00098	0,0265	0,0029

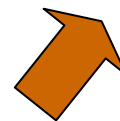
Cd		Pb	
<i>Concentration (mg/kg)</i>	<i>SD</i>	<i>Concentration (mg/kg)</i>	<i>SD</i>
0,0081	0,0013	0,0215	0,0022



13th PT 1st Round Milk: Results

Lab Code: 4	Cd	Pb
Sample A (mg/kg)	0.0049	0.013
Sample A (mg/kg)	0.0066	0.0088

$2.1 \leq z\text{-scores} \leq 3.5$
(σ_p CRL)



Comments	Results were low and outside our normal work range (.....)
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Lab Code: 4	Cd	Pb
LoD of the method (mg/Kg)	0.002	0.001
LoQ of the method (mg/Kg)	<i>0.004</i>	<i>0.002</i>

Method LoD and LoQ

Perform n determinations of a blank matrix and n determinations of a blank matrix (n>20) fortified with a small amount of the analyte of interest

LoD is numerically equal to 3 times the standard deviation of the mean of the determinations.

LoQ is numerically equal to 6 or 10 times the standard deviation of the mean of the determinations.

Example:

$$\text{LoD} = 3 * \text{Dil} * (\text{V/w}) * \sigma_B * \text{C}_{\text{spiked}} / (\text{I}_{\text{spiked}} - \text{I}_{\text{Blk}})$$
$$\text{LoQ} = (6 \text{ or } 10) * \text{Dil} * (\text{V/w}) * \sigma_B * \text{C}_{\text{spiked}} / (\text{I}_{\text{spiked}} - \text{I}_{\text{Blk}})$$

where:

Dil is the final dilution of the sample (after preparation, before introducing in the instrument)

V/w is the typical ratio (Final Volume/Sample Weight)

σ_B is the standard deviation of the signal considering n determinations of a blank (n>20)

C_{spiked} is the conc, of the spike on the blank

I_{spiked} is the mean of the intensity of the signal for the spiked blank

I_{Blk} is the intensity of the mean of the blank

LoD and LoQ

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LoD and LoQ for Lead in Milk

Maximum level Regulation EC 0.020 mg/kg (fresh material)

- max LoD: $(1/5) \times 0.020 = 0.004 \text{ mg/kg}$
- max LoQ $(2/5) \times 0.020 = 0.008 \text{ mg/kg}$

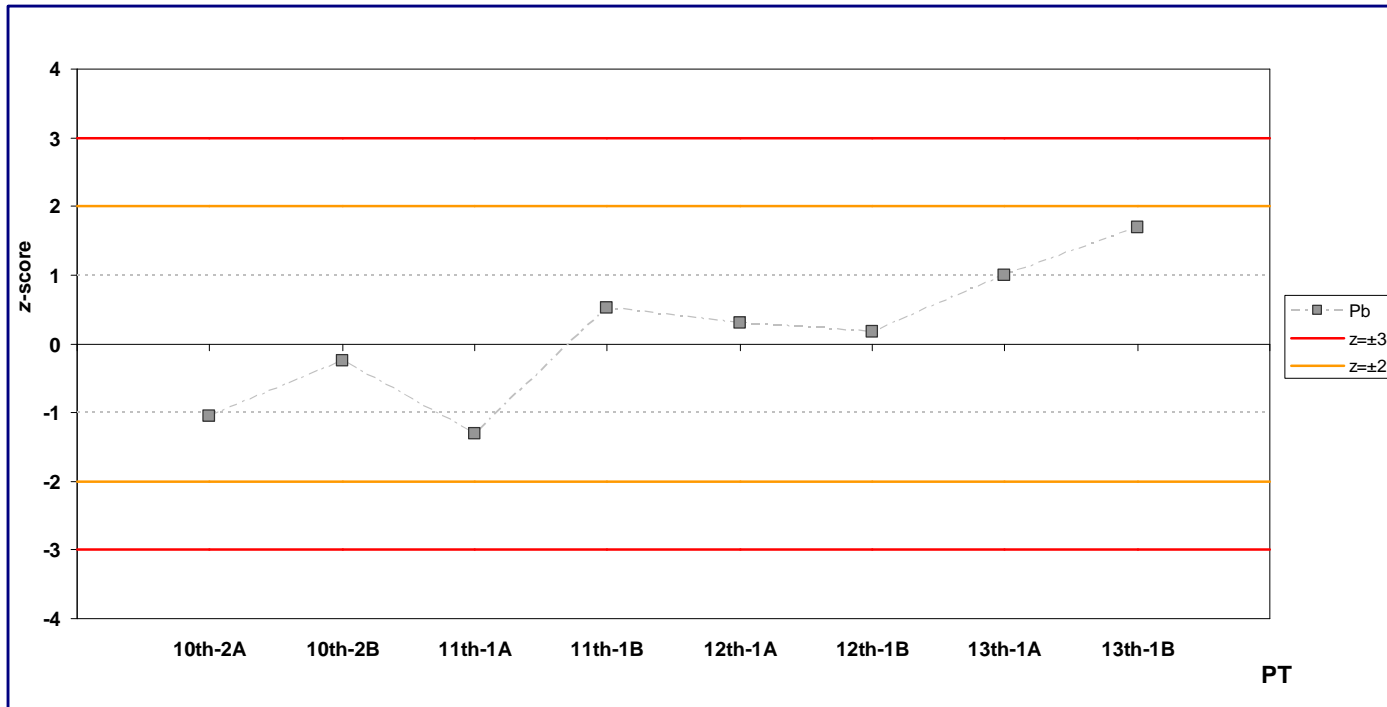
Lab Nr.	LoD (mg/kg)	LoQ (mg/kg)	Technique	Accreditation
2	0.005	0.01	AAS	Yes
9	0.006	0.012	FAAS	Yes
12	0.009	0.018	ICP-MS	Yes
16	0.010	0.012	AAS	Yes
21	0.007	0.015	FAAS	Yes
23	0.009	0.015	AAS	No

Lab Code 12 (13th PT Milk)

12th proficiency test on milk:

LoQ for Pb = 0.025 mg/kg

Control Chart for Pb in Milk



LoD and LoQ

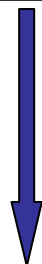
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LoD and LoQ for Lead in Milk

Lab Nr.	LoD (mg/kg)	LoQ (mg/kg)	Technique	Accreditation
6	0.0003	0.0008	AAS	Yes



Instrument: **Perkin Elmer SIMAA 6000**

weight 5g; final volume 20ml → 0.2ppb* (instrumental output)

This means that, with a signal of about 0.4 mabs, the analyte can be measured with reasonable statistical certainty.

* considering a single sample injection of 20 μ l

LoD and LoQ for Lead in Milk

Lab Nr.	LoD (mg/kg)	LoQ (mg/kg)	Technique	Accreditation
9	0.00022	0.00044	AAS	Yes



Instrument **Perkin Elmer AAnalyst 600**

weight 2g; final volume 25ml → 0.0352ppb

This means that, with a signal of about 0.1 mabs, the analyte can be measured with reasonable statistical certainty.

* considering a single sample injection of 20 μ l

CRMs Milk

	BCR 150	BCR 151	NIST 1549	NIST 1568a	NIST 8414	IAEA 155 (RM)	BCR 185r
	Skim milk	Skim milk	Non-fat milk	Rice flour	Bovine muscle	Milk whey	Bovine liver
As*		0.101	0.0019	0.29	0.009	0.049	0.009
Cd*	0.0218		0.0005	0.022	0.013	0.016	0.013
Pb*	1.00	2.002	0.019	<0.010	0.38	0.104	0.38

* values expressed as mg/kg

Milk: some considerations.....

the most widely used CRMs are BCR 150 and 151

BCR 150 is not certified for As; Cd 0.0218 mg/kg

BCR 151 is not certified for Cd; As 0.101 mg/kg

Values for Pb 1.00 mg/kg (BCR 150) and 2.002 mg/kg (BCR 151)

are very far from the maximum levels stated in CR 1881/2006

13th PT 1st Round Milk

It's not easy to find a suitable reference material.....

Lab Code: 30

Use of three different RMs

BCR 150, IAEA 155*, NIST 1549

BCR 150 Cd: 0.0218 mg/kg

IAEA 155 As: 0.049 mg/kg

NIST 1549 Pb: 0.019 mg/kg

*not certified

z-scores (σ_p CRL)			
	As	Cd	Pb
A	-0.8	-0.5	0.5
B	-0.5	-0.6	0.0

13th PT 1st Round Milk

It's not easy to find a suitable reference material.....

Lab Code: 27 (same technique as lab 30)

Use of 12th PT Sample A and B

Consensus Values 12 th PT			
	As	Cd	Pb
A	0.125	0.0058	0.0265
B	0.179	0.0059	0.0330

z-scores (σ_p CRL)			
	As	Cd	Pb
A	0.1	0.1	0.5
B	-0.2	0.1	0.5

CRMs Fish

	Dorm-3	IAEA 407 (RM)	NIST 8414	BCR 185r	Dorm-2	BCR 278r	Tort-2	Dolt-2
	Fish protein	Fish muscle	Bovine muscle	Bovine liver	Fish muscle	Muscle tissue	Lobster epatop.	Fish liver
As*	6.88	12.6	0.009	0.033	18	6.07	21.6	16.6
Cd*	0.290	0.189	0.013	0.544	0.043	0.348	26.7	20.8
Pb*	0.395	0.12	0.38	0.172	0.065	2.00	0.35	0.22
Hg*	0.382	0.222			4.64	0.196	0.27	2.14

* values expressed as mg/kg

13th PT 2nd Round Fish

It's not easy to find a suitable reference material.....

Lab Code 1: BCR 185R – NIST 8414 – IAEA 407

Lab Code 22 : DOLT 2 – Dorm 3 – TORT 2

Consensus Values 11 th PT Fish				
	As	Cd	Hg	Pb
A	9.11	0.0025	0.711	0.224

Consensus Values 13 th PT Fish			
	Cd	Hg	Pb
A	0.281	1.252	0.276

Calibration ranges

Lab Code

13

Technique AAS

Calibration: external linear

Calibration Range

0.01-0.05 mg/kg Lead

Sample Amount 4g

Ratio V/w = 3.75

Final Volume 15ml

Maximum level 0.020 mg/kg

µg/kg

Instrumental Output for Lead (ML) = $20 / 3.75 = 5.3$

For PT Sample A (value from NRL 13) = $28 / 3.75 = 7.5$

For PT Sample B (value from NRL 13) = $18 / 3.75 = 4.8$

Calibration ranges

Lab Code

30

Technique ICP-MS

Calibration: external linear

Calibration Range

1-10 $\mu\text{g}/\text{kg}$ for Cd and Pb

Final Dilution 1:100

Instrumental Output for Lead (ML) = $20 / 100 = 0.2$

For PT Sample A (value from NRL 13) = $38 / 100 = 0.38$

For PT Sample B (value from NRL 13) = $23 / 100 = 0.23$

$\mu\text{g}/\text{kg}$



Results

Lab Code

7

13th PT 2nd Round Fish

Replicates			
As	1.083	1.039	1.012
Hg	1.144	1.154	1.163

	Mean Reported	Mean
As	1.074	1.045
Hg	1.186	1.154

Results

Lab Code

2

13th PT 2nd Round Fish

As	1.450	1.501	1.586	1.592	1.594	1.658	1.641
Cd	0.240	0.266	0.270	0.272	0.272	0.281	0.276
Pb	0.286	0.279	0.284	0.274	0.279	0.283	0.300

	Mean Reported	Mean
As	1.628	1.575
Cd	0.276	0.268
Pb	0.292	0.284

Use of PTs schemes results

Biases from interlaboratory comparisons (Nordtest Report TR 537)

- interlaboratory comparisons may be used in the same way as a reference material
- a laboratory should participate at least 6 times
- the way forward is very similar to that for reference materials

CRL-ISS PTs on Milk: Lead

- find the between laboratory standard deviations, s_R , for the exercises

	X PT		XI PT		XII PT		XIII PT	
	1	2	1	2	A	B	A	B
Cons value	17.3	39.7	0.0144	0.0247	0.0265	0.033	0.035	0.023
SDrob	4.22	4.51	0.0047	0.0037	0.0041	0.006	0.005	0.003
$s_R\%$	24.4%	11.4%	32.6%	15.0%	15.5%	18.2%	14.3%	13.0%

the s_R has been on average of 18.0%

mean number of participants (n) = 23

$$u(\text{Cref}) = s_R / \sqrt{n} = 18 / \sqrt{23} = 3.8\%$$

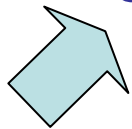
Laboratory X

	X PT		XI PT		XII PT		XIII PT	
	1	2	1	2	A	B	A	B
Found	17.3	44	0.0139	0.0267	0.028	0.035	0.036	0.026
Cons Value	17.3	39.7	0.0144	0.0247	0.0265	0.033	0.035	0.023
s _R %	0.0%	10.8%	3.5%	8.1%	5.7%	6.1%	2.9%	13.0%

$$\text{RMS}_{\text{bias}} = \sqrt{(\sum (\text{bias}_i)^2 / n)} = 7.4 \%$$

$$u = \sqrt{(\text{RMS}_{\text{bias}})^2 + u(\text{Cref})^2} = \sqrt{(7.4)^2 + (3.8)^2} = 8.31\%$$

$$\mathbf{U = k * u = 16.62 \%}$$



no other contributions to uncertainty were considered

U_{dich}
U_{dich}

Found	Uncertainty	Ratio
0.036	0.005	14%
0.026	0.004	15%

Some advices:

- check your results before sending them
- check the consistency of your figures of merit
- for any question contact us at crl@iss.it

Thank you for your attention