

# Materials for Proficiency Tests and Results of 9<sup>th</sup> PT in Fish

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# What is a (laboratory) Proficiency Testing (PT)?

- ✓ determination of laboratory testing performance by means of interlaboratory comparisons;
- ✓ interlaboratory comparisons are organisation, performance and evaluation of tests on the same or similar items by two or more laboratories in accordance with predetermined conditions;

## Types of Proficiency Testing?



### Interlaboratory Testing Schemes

- ✓ randomly selected sub-samples from a source of material are distributed simultaneously to participant testing laboratories;

*ISO/IEC Guide 43 part 1:1997*

## What kind of materials are distributed?

- ✓ test materials should be as close as possible to the materials generally analysed, so that the laboratory can work under routine conditions;
- ✓ sufficiently homogeneous so that the results later identified as extreme are not attributed to any significant test item variability;

## What is the main purpose of a PT?

- ✓ to help laboratories to identify problems and initiate remedial actions which may be related to, for example, individual staff performance or calibration of instrumentation;

*ISO/IEC Guide 43 part 1:1997*

## What are the limits of the PT?

- ✓ provides the participant laboratories only with the indication that there is a problem, but it does not solve it;
- ✓ the success obtained for an element does not indicate that the laboratory is equally competent for the other elements;

# PROFICIENCY TEST

ORGANISATION and DESIGN



PRODUCTION of MATERIAL

TESTS on MATERIAL

FITNESS of the MATERIAL

DISPATCHING of MATERIAL

SCHEME REPORT

EVALUATION of  
PERFORMANCE



PARTICIPANTS



# CRL-ISS

9<sup>th</sup> and 10<sup>th</sup> PT (1<sup>th</sup> and 2<sup>nd</sup> round)

## Fish

As, Cd, Cr, Cu, Fe, Hg, Pb, Zn



## Milk

As, Cd, Pb

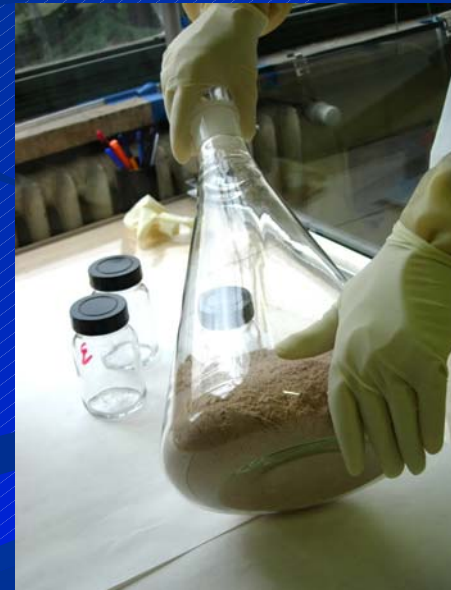


## Meat

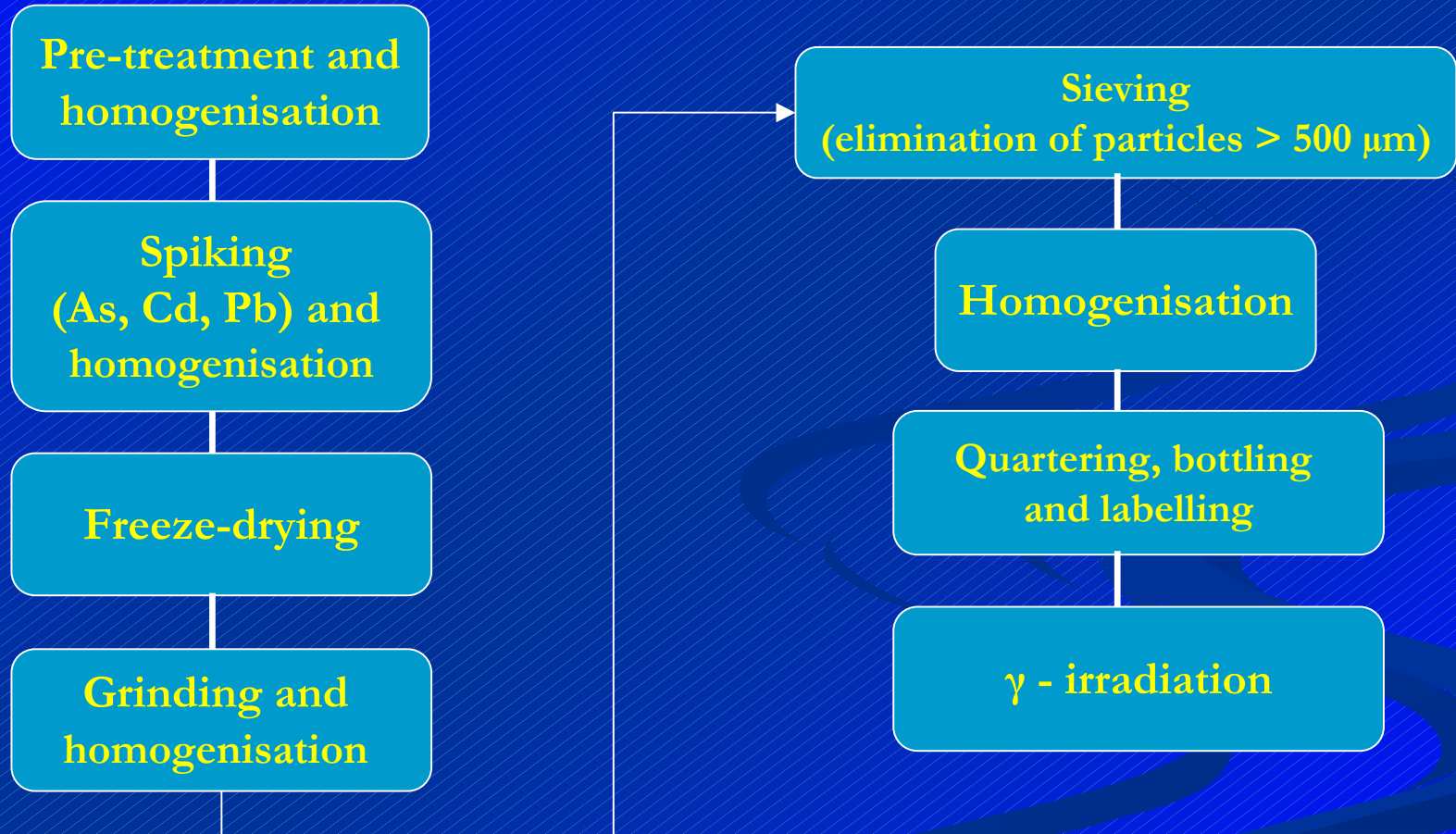
As, Cd, Pb



# PRODUCTION of MATERIAL: BOVINE MUSCLE



## PRODUCTION of MATERIAL: BOVINE MUSCLE



## PRODUCTION of MATERIAL: MILK

**Sampling  
(partially skimmed milk)**

**Homogenisation  
and spiking (As, Cd, Pb)**

**Stirring  
and homogenisation**

**Sub-sampling  
and bottling**

**Freeze-drying  
and labelling**

The freeze-drying process on bovine muscle and milk was performed at the Centre of the Italian National Agency for New Technologies, Energy and the Environment (ENEA) of Trisaia, Matera



The bottles of bovine muscle were  $\gamma$ - irradiated ( $^{60}\text{Co}$ , 25 KGray) by Johnson & Johnson Medical Holding of Pomezia, Rome

# TESTS on MATERIAL: Fish and bovine muscle MOISTURE CONTENT

## FISH

CRL-ISS mean value: 7.0 %

sd 0.9 – CV 13.4 %

PT mean value : 6.2 %

sd 2.2 – CV 35.4 %

Bottle	H <sub>2</sub> O %
1	6.4
2	6.4
3	6.5
4	6.9
5	8.0
6	8.6
7	6.7
8	6.4
9	8.1
10	5.7

## MEAT

	<b>LEVEL A</b>	<b>LEVEL B</b>
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CRL-ISS mean value:	4.2 %	4.3%
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sd/CV%	0.3/6.2 %	0.1/3.5%
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PT mean value :	4.4 %	4.2 %
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sd/CV %	0.7/16.4 %	0.8/19.0%
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Bottle	H <sub>2</sub> O %	
	Level A	Level B
1	3.8	4.5
2	4.3	4.1
3	4.4	4.4
4	4.8	4.1
5	4.1	4.2
6	4.1	4.4
7	4.1	4.4
8	4.4	4.5
9	4.3	4.4
10	4.2	4.3

## TESTS on MATERIALS

### Homogeneity, Test for acceptable between-sample variance

The homogeneity of the test material was assessed by the use of the statistical test “sufficient homogeneity”.

The adopted procedure was that of Thompson and Fearn, which is an improvement of the process described in the International Harmonised Protocol.

The number of the bottles to be tested for the homogeneity was obtained according to this formula  $(n - 1)^{1/2}$ ; while, the selection of the bottles to be analysed was performed by a table of records generated by a computer package.

Two portions of the materials were taken from the same bottle, digested by microwave oven and analysed by means of ICP-AES and ICP-MS.

Fearn, T. and Thompson, M, A new test for ‘sufficient homogeneity’, *Analyst*, 2001, 126, 1414-1417.  
M. Thompson and R. Wood, The International Harmonised Protocol for the Proficiency Testing of (Chemical) Analytical Laboratories, *Pure & Applied Chemistry*, 1993, 65 (9), 2123-2144.

# TESTS on MATERIALS

Identification of outliers, Cochran's test

Homogeneity, Test for acceptable between-sample variance

The outliers were identified by the Cochran's test; when found they have been eliminated.

The homogeneity was estimated by calculating the between-sample variance  $S^2_{sam}$  and comparing it with the critical value  $C$ . The critical value  $C$  depends on the analytical variance  $S^2_{an}$ , and the target standard deviation  $\sigma_p$  (according to Horwitz) is connected with the concentration of the analyte:

$$\begin{aligned}\sigma_p &= 0.22 \cdot c / mr && (c < 120 \text{ ppb}) \\ \sigma_p &= 0.02 \cdot c^{0.8495} / mr && (120 \text{ ppb} \leq c \leq 13.8\%) \\ \sigma_p &= 0.01 \cdot c^{0.5} / mr && (c > 13.8\%) \end{aligned}$$

where  $c$  is the assigned concentration and  $mr$  is the dimensionless mass ratio (1 ppm= $10^{-6}$ , %= $10^{-2}$ ).

When  $S^2_{sam}$  is lower than the critical value  $C$ , it means the test passed and the material is sufficiently homogeneous.

**TESTS on MATERIAL: Fish**  
**Identification of outliers, Cochran's test**

<b>Element</b>	<b>Test value C</b>	<b>Critical value CV (5 %)</b>	<b>C-CV</b>	<b>Results</b>
As	0.2699	0.50595	<0	Passed/No evidence of analytical outliers
Cd	0.2891	0.50595	<0	Passed/No evidence of analytical outliers
Hg	0.2556	0.50595	<0	Passed/No evidence of analytical outliers
Pb	0.3298	0.50595	<0	Passed/No evidence of analytical outliers

**TESTS on MATERIAL: Meat and Milk**  
**Identification of outliers, Cochran's test**

<b>Meat</b>	<b>Test value</b>	<b>Critical value</b>	<b>C-CV</b>	<b>Results</b>
<b>Element</b>	<b>C</b>	<b>CV (5 %)</b>		
	Level A/Level B	Level A/Level B		
Cd	0.283/0.625	0.801	<0	Passed/No evidence of analytical outliers
Pb	0.384/0.608	0.801	<0	Passed/No evidence of analytical outliers

<b>Milk</b>	<b>Test value</b>	<b>Critical value</b>	<b>C-CV</b>	<b>Results</b>
<b>Element</b>	<b>C</b>	<b>CV (5 %)</b>		
	Level A/Level B	Level A/Level B		
Cd	0.411/0.798	0.877	<0	Passed/No evidence of analytical outliers
Pb	0.756/0.602	0.877	<0	Passed/No evidence of analytical outliers

**TESTS on MATERIAL: Fish**  
**Homogeneity, Test for acceptable between-sample variance**

<b>Element</b>	<b>Between-sample variance, <math>S^2_{sam}</math></b>	<b>Critical value <math>C</math></b>	<b><math>S^2_{sam} - C</math></b>	<b>Results</b>
As	0.0301	0.3636	<0	Passed, the material is sufficiently homogenous
Cd	0.000130	0.000207	<0	Passed, the material is sufficiently homogenous
Hg	0.0004	0.0013	<0	Passed, the material is sufficiently homogenous
Pb	0.00006	0.0018	<0	Passed, the material is sufficiently homogenous

**TESTS on MATERIAL: Meat and Milk**  
**Homogeneity, Test for acceptable between-sample variance**

<b>Meat</b>	<b>Between-sample variance, <math>S^2_{sam}</math></b>	<b>Critical value C</b>	<b><math>S^2_{sam} - C</math></b>	<b>Results</b>
<b>Element</b>	Level A/Level B	Level A/Level B		
Cd	0.525098/0.748418	20/82	<0	Passed, the material is sufficiently homogenous
Pb	3.42156/7.177457	63/45	<0	Passed, the material is sufficiently homogenous

<b>Milk</b>	<b>Between-sample variance, <math>S^2_{sam}</math></b>	<b>Critical value C</b>	<b><math>S^2_{sam} - C</math></b>	<b>Results</b>
<b>Element</b>	Level A/Level B	Level A/Level B		
Cd	0.001/0.019	0.302/0.995	<0	Passed, the material is sufficiently homogenous
Pb	0.400/0.687	10.869/13.284	<0	Passed, the material is sufficiently homogenous

## EVALUATION of PERFORMANCE STATISTICAL TREATMENT of DATA

The robust mean by Huber's H15 method, using the AMC algorithm, allowed to obtain the consensus value.

The appropriate formula of the Horwitz/Thompson equation was used to obtain the target standard deviation ( $\sigma_p$ ).

Analytical Methods Committee, Robust Statistics – How not to reject outliers Part 1. Basic Concepts. *Analyst*, 1989, 114, 1693-1697.

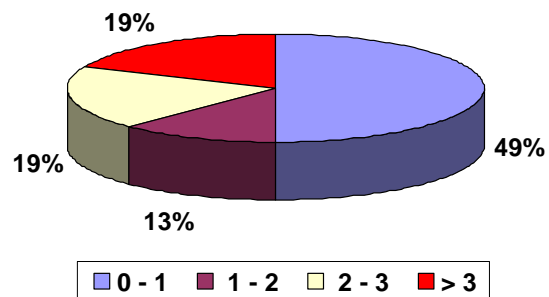
Analytical Methods Committee, Robust statistics: a method of coping with outliers.

Technical Brief No 6, Apr 2001, <http://www.rsc.org/pdf/amc/brief6.pdf>

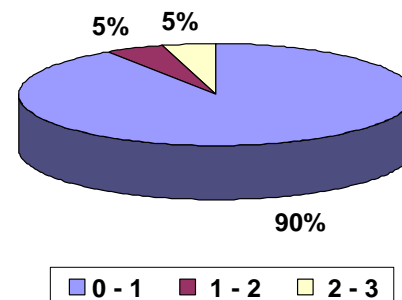
# The Results on fish

# Percentage distribution of z-scores for fish

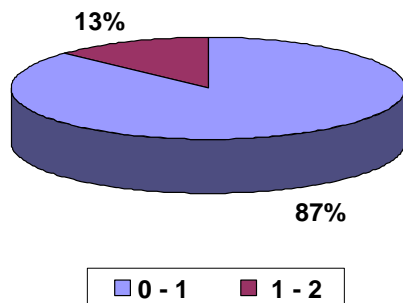
As



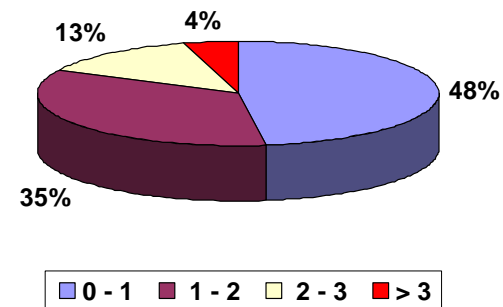
Hg



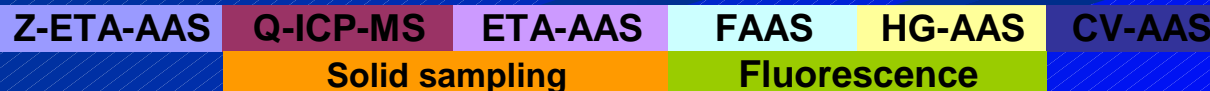
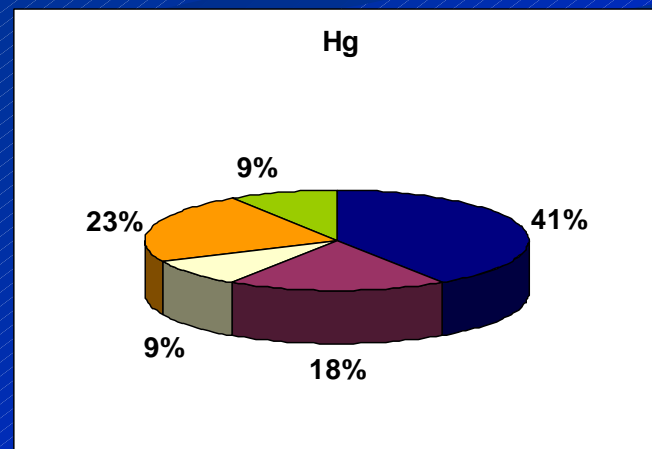
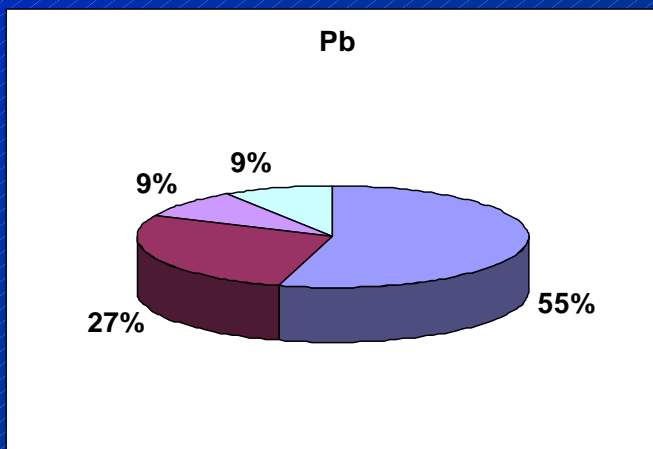
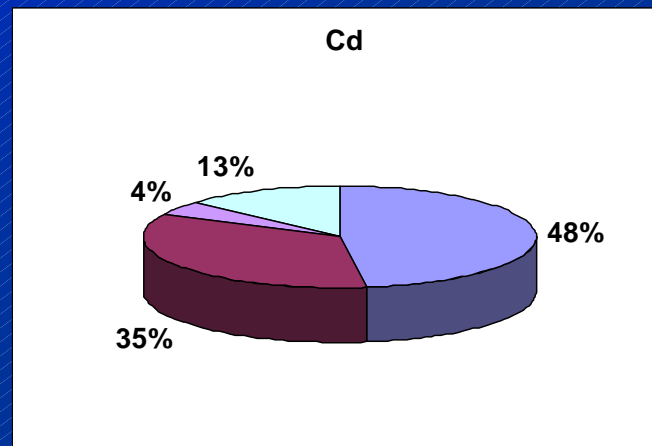
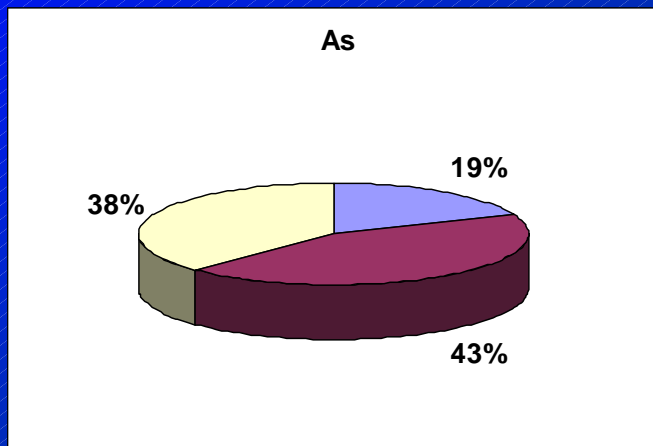
Cd



Pb



# Percentage distribution of analytical techniques for fish



## Summary and conclusion: fish

Concentration in  $\mu\text{g g}^{-1}$

	Cd	Hg	Pb
<i>No. of Results</i>	24	22	23
<i>min</i>	0.197	0.322	0.178
<i>max</i>	0.376	0.621	0.632
<i>Mean</i>	0.310	0.429	0.415
<i>SD</i>	0.041	0.057	0.115
<i>Median</i>	0.321	0.431	0.421
<i>Robust mean</i>	0.314	0.426	0.416
<i>Robust SD</i>	0.035	0.042	0.124
<i><math>\sigma</math> target (<math>\sigma_p</math>)</i>	0.060	0.077	0.076
<i>Standard error of the Robust Mean (Robust SD/<math>n^{1/2}</math>)</i>	0.01	0.01	0.03



**Thank you for your attention**