



1



## CONTROL CHARTS TO EVALUATE LONG-TERM PERFORMANCE IN PROFICIENCY TESTS

*Angela Sorbo*

*European Union Reference Laboratory for Chemical  
Elements in Food of Animal Origin (EU-RL CEFAO)*

EURACHEM Workshop October 10-11, 2012



2

## CONTENTS

- ✓ **ROLE OF THE EUROPEAN UNION REFERENCE LABORATORIES**
- ✓ **EURL CEFAO AS PT PROVIDER AND RATIONALE FOR ITS SCHEME**
- ✓ **PERFORMANCE EVALUATION: Z-SCORES USING "FITNESS FOR PURPOSE APPROACH"**
- ✓ **CONTROL CHARTS OF Z-SCORES**
- ✓ **CONCLUSIONS**

*This work has been produced with the financial support of the SANCO 2005/Food SAFETY/003-Residues Program of the European Commission. The contents of this presentation are the sole responsibility of the author and can in no way be taken to reflect the views of the European Commission*

EURACHEM Workshop October 10-11, 2012

3



## ROLE OF THE EUROPEAN REFERENCE LABORATORIES

COMMUNITY REFERENCE LABORATORIES FOR RESIDUES OF VETERINARY MEDICINES AND CONTAMINANTS IN FOOD OF ANIMAL ORIGIN WAS DESIGNATED IN COUNCIL DIRECTIVE 96/23/EC AND REFIXED IN COMMISSION REGULATION (EC) No 776/2006 of 23 May 2006 AMENDING ANNEX VII TO REGULATION (EC) No 882/2004

**Art. 12 CR (EC) 776/2006** ASSIGNED TO THE ISTITUTO SUPERIORE DI SANITÀ (ROME) THE COMMUNITY REFERENCE LABORATORY FOR THE RESIDUES LISTED IN ANNEX I, GROUP B 3(C) TO DIR. 96/23/EC



**EURL (FORMER CRL) IS RESPONSIBLE FOR CHEMICAL ELEMENTS IN FOOD OF ANIMAL ORIGIN (EU-RL CEFAO)**

*EURACHEM Workshop October 10-11, 2012*

4



## ROLE OF THE EUROPEAN REFERENCE LABORATORIES

### Tasks of the CRLs (Art. 32-Reg. 882/2004)

- a) providing national reference laboratories with details of analytical methods, including reference methods
- b) coordinating the national reference laboratories in the application of the methods referred to in (a), **in particular by organising comparative testing and by ensuring an appropriate follow-up of such comparative testing in accordance with internationally accepted protocols, when available**
- c) coordinating, within their area of competence, practical arrangements needed to apply new analytical methods and informing national reference laboratories of advances in this field
- d) conducting initial and further training courses for the benefit of staff from national reference laboratories and of experts from developing countries

*EURACHEM Workshop October 10-11, 2012*

5



## EURL CEFAO AS PT PROVIDER AND RATIONALE FOR ITS SCHEME

**EU-RL CEFAO IS ACCREDITED AS PT PROVIDER ACCORDING TO ISO/IEC 17043:2010 (BEFORE 2010: ISO GUIDE 43-1)**

**THE LABORATORY IS ALSO ACCREDITED IN CONFORMITY WITH ISO/IEC 17025:2005, ENLARGED WITH FLEXIBLE SCOPE**

**MATRICES, ANALYTES AND LEVEL OF CONCENTRATION FOR PTs ARE SELECTED TAKING INTO ACCOUNT BOTH THE RELEVANT EUROPEAN REGULATION (EXISTING MAXIMUM LEVELS) AND NATIONAL RESIDUES CONTROL PLANS**



**THE CONCENTRATION OF THE SAMPLES IS OFTEN ADJUSTED TO THIS AIM**

*EURACHEM Workshop October 10-11, 2012*

6



## EURL CEFAO AS PT PROVIDER AND RATIONALE FOR ITS SCHEME

### PROFICIENCY TESTS ORGANIZED IN THE FIVE-YEAR PERIOD 2006-2011

2006	2007	2008	2009	2010	2011
Meat freeze-dried 2 samples	Meat freeze-dried 1 sample	Liver freeze-dried 1 sample	Fish freeze-dried 1 sample	Meat Frozen 1 sample	Liver Frozen 1 sample
Milk freeze-dried 2 samples	Milk Liquid 2 samples	Milk Liquid 2 samples	Milk Liquid 2 samples	Milk Liquid 1 sample	Meat freeze-dried 1 sample
	Fish freeze-dried 1 sample	Meat freeze-dried 1 sample		Fish Frozen 1 sample	

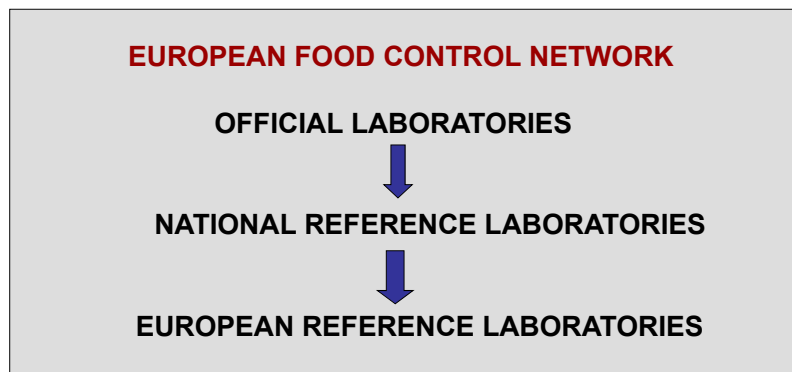
**Analytes: Cadmium (Cd), Lead (Pb), total Arsenic (As) and Mercury (Hg)**

*EURACHEM Workshop October 10-11, 2012*



7

PROFICIENCY TESTS ORGANIZED BY EU-RL CEFAO ARE ADDRESSED TO THE NATIONAL REFERENCE LABORATORIES (NRLs) OF THE EU MEMBER STATES NETWORK IS NOW CONSTITUTED BY 27 PARTICIPANTS



EURACHEM Workshop October 10-11, 2012



8

### GENERAL OBJECTIVES OF PTs according to EU-RL TASKS

*TO IMPROVE THE PERFORMANCE OF THE NRLs ANALYTICAL METHODS AROUND THE MLs*

*TO HARMONIZE THE INTERPRETATION OF RESULTS IN TERMS OF THE SAMPLE ACCEPTANCE (CR (EC) 333/2007)*

*TO ASSIST NRLs IN FINDING THE CAUSE OF ANALYTICAL PROBLEMS LEADING TO AN UNSATISFACTORY PERFORMANCE*

EURACHEM Workshop October 10-11, 2012



PERFORMANCE EVALUATION

“FITNESS FOR PURPOSE” APPROACH PROPER FOR THE ROLE OF NRLs

PERFORMANCE REQUIRED FROM NRLs SHOULD BE BETTER THAN THAT OF ROUTINE CONTROL LABORATORIES

STANDARD DEVIATION FOR PROFICIENCY ASSESSMENT ( $\sigma_{pEU-RL\ CEFAO}$ ) LOWER THAN THE ONE DERIVED FROM HORWITZ EQUATION

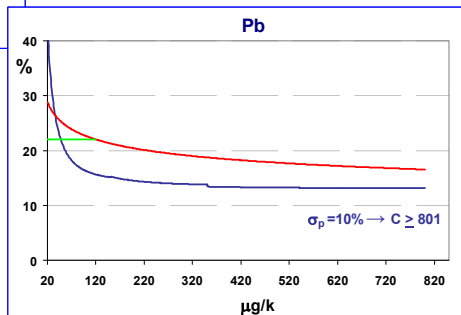
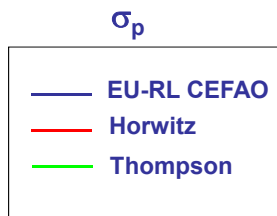
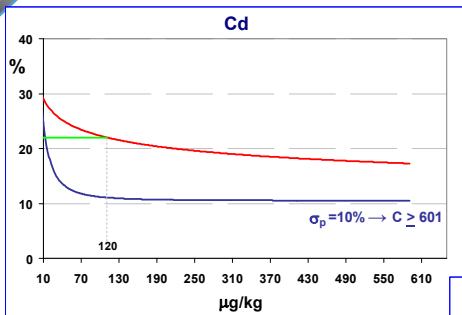
EU-RL CEFAO HAS DEVELOPED PROPER EQUATIONS GIVING A  $\sigma_p$  CORRESPONDING TO THE PERFORMANCE LEVEL THAT NRLs ARE EXPECTED TO ACHIEVE FOR THE DIFFERENT COMBINATION MATRIX/ANALYTE/CONCENTRATION LEVEL

EURACHEM Workshop October 10-11, 2012



PERFORMANCE EVALUATION

MEAT AND FISH



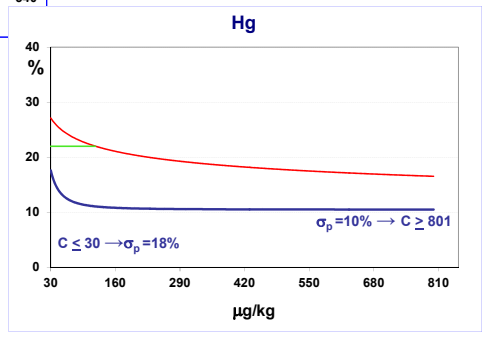
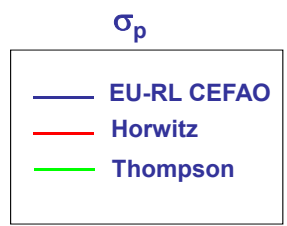
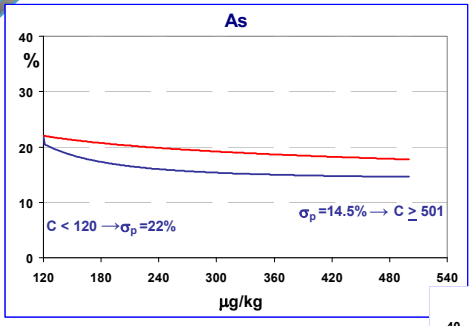
EURACHEM Workshop October 10-11, 2012

11



### PERFORMANCE EVALUATION

## MEAT AND FISH



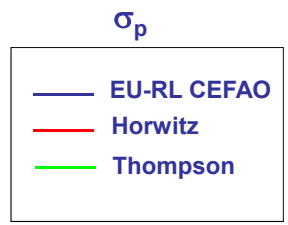
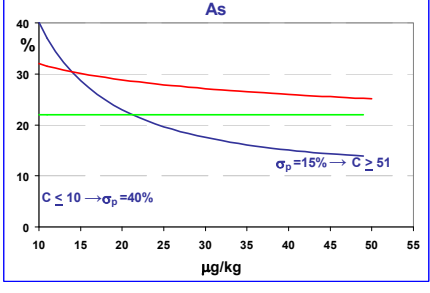
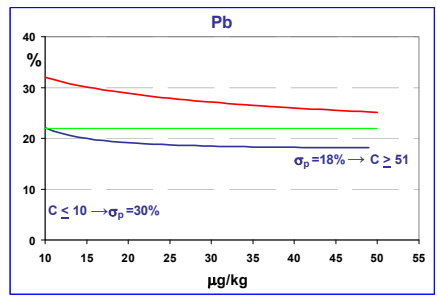
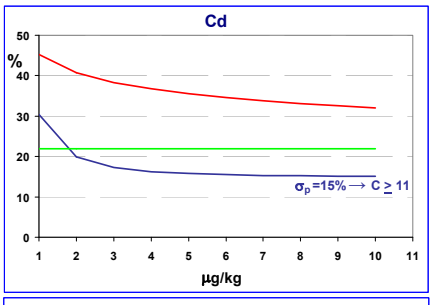
EURACHEM Workshop October 10-11, 2012

12



### PERFORMANCE EVALUATION

## MILK



EURACHEM Workshop October 10-11, 2012



### Shewhart Control Chart for z-scores (ISO 13528:2005\*, Par. 9.2.1)

To prepare this charts the z-scores for a laboratory are plotted as individual points, with action and warning limit set at  $\pm 2.0$  and  $\pm 3.0$  (...). When several characteristics are measured in each round, the z-scores for different characteristics may be plotted on the same graph (...)

The Shewart control chart is an effective method of identifying problems that cause large erratic values of z-scores

\* ISO 13528:2005: Statistical methods for use in proficiency testing by interlaboratory comparisons

*EURACHEM Workshop October 10-11, 2012*



### Rules (ISO 13528:2005\*, Par. 9.2.1)

**An out of control signal is given when:**

- a) a single point falls outside the action limits ( $\pm 3,0$ )**
- b) two out of three successive points fall outside the same warning limit ( $\pm 2,0$ )**

\* ISO 13528:2005: Statistical methods for use in proficiency testing by interlaboratory comparisons

*EURACHEM Workshop October 10-11, 2012*



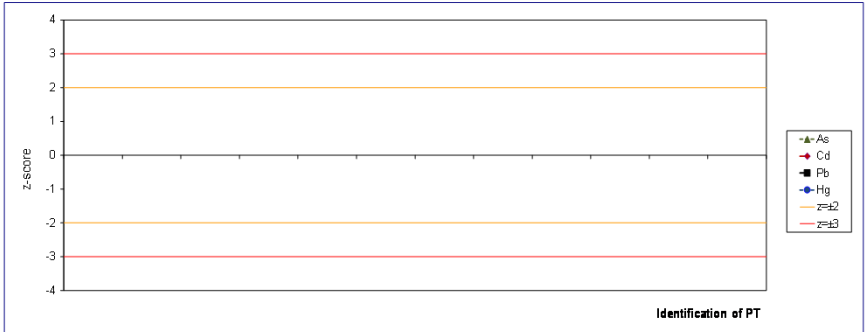
### CONTROL CHARTS OF Z-SCORES

Shewart Control Chart of z-scores: EU-RL CEFAO PTs - EU-RL z-scores  
 NRL Code: code assigned to the last PT



Updated ~~data~~ ~~yyyy~~

PT	Year	Matrix																
As	$\bar{X}$	$\sigma_s$																
mean	$\bar{X}$	$\sigma_s$																
Cd	$\bar{X}$	$\sigma_s$																
mean	$\bar{X}$	$\sigma_s$																
Pb	$\bar{X}$	$\sigma_s$																
mean	$\bar{X}$	$\sigma_s$																
Hg	$\bar{X}$	$\sigma_s$																
mean	$\bar{X}$	$\sigma_s$																



EURACHEM Workshop October 10-11, 2012



### CONTROL CHARTS OF Z-SCORES



## EU - NATIONAL REFERENCE LABORATORIES CONTROL CHARTS OF THE z-scores (2005-2011) Meat, Fish and Offal

Edited by: A. Colabucci  
 Verified by: L. Ciaralli (QM)  
 Issued: 29.12.2011

EURACHEM Workshop October 10-11, 2012



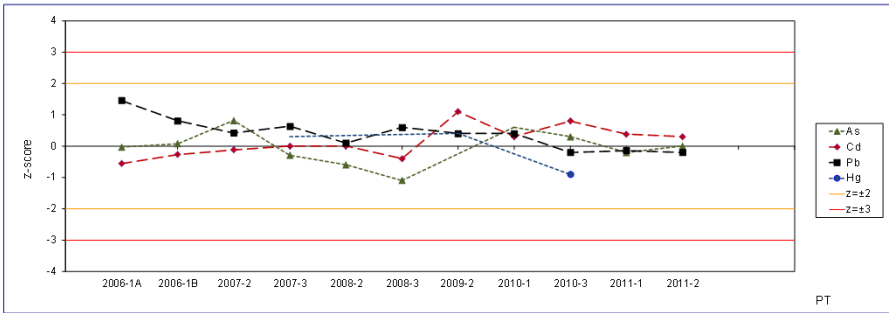
### CONTROL CHARTS OF Z-SCORES

Shewart Control Chart of z-scores: EU-RL CEFAO PTs - EU-RL z-scores  
 NPL Code (19<sup>th</sup> PT 2<sup>nd</sup> Round on Freeze-Dried Meat): 18



Updated 29/12/2011

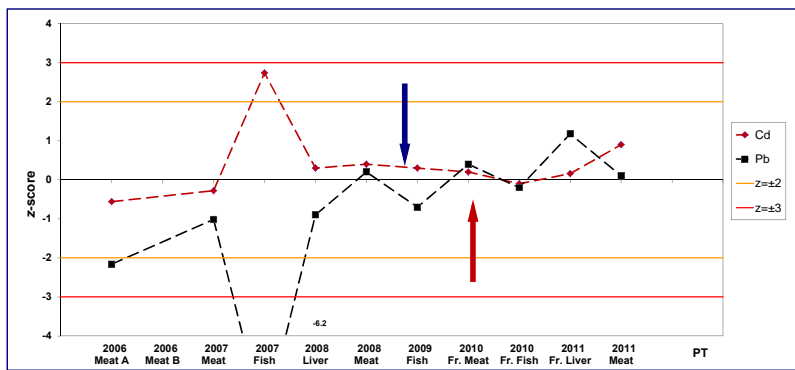
PT	10 <sup>th</sup> -1A	10 <sup>th</sup> -1B	11 <sup>th</sup> -2	11 <sup>th</sup> -3	12 <sup>th</sup> -2	12 <sup>th</sup> -3	13 <sup>th</sup> -2	14 <sup>th</sup> -1	14 <sup>th</sup> -3	15 <sup>th</sup> -1	15 <sup>th</sup> -2
Year	2006	2006	2007	2007	2008	2008	2009	2010	2010	2011	2011
Matrix	Meat	Meat	Meat	Fish	Liver	Meat	Fish	Fr. Meat	Fr. Fish	Fr. Liver	Meat
As mg/kg	$\bar{x}$ 0.231	0.547	0.770	9.11	7.63	0.214		0.402	0.926	0.159	0.225
	$\sigma$ 0.0372	0.0793	0.112	1.32	1.15	0.032		0.0596	0.134	0.0298	0.0365
Cd mg/kg	$\bar{x}$ 0.0636	0.0047	0.042	0.025	0.513	0.064	0.281	0.043	0.075	0.600	0.060
	$\sigma$ 0.0068	0.0108	0.0061	0.0050	0.054	0.008	0.031	0.0062	0.0089	0.0631	0.0084
Pb mg/kg	$\bar{x}$ 0.0825	0.138	0.114	0.224	0.532	0.171	0.276	0.141	0.370	0.415	0.142
	$\sigma$ 0.0141	0.0210	0.0179	0.0321	0.069	0.026	0.039	0.0214	0.0496	0.0553	0.0216
Hg mg/kg	$\bar{x}$			0.711			1.25		0.222		
	$\sigma$			0.0747			0.125		0.0237		



EURACHEM Workshop October 10-11, 2012

### CONTROL CHARTS OF Z-SCORES

#### CC Meat, Fish and Offal



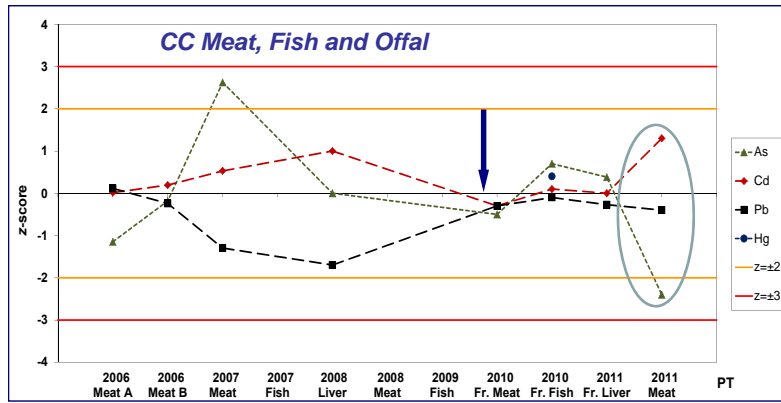
2009: Visit of the EU-RL CEFAO representatives

2010: Change of analytical technique

EURACHEM Workshop October 10-11, 2012



### CONTROL CHARTS OF Z-SCORES



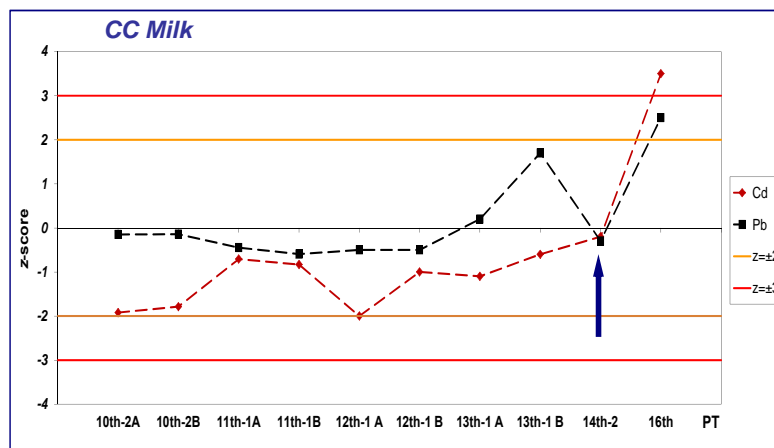
2010: Change of staff and technique (from more to less sensitive!)

EURACHEM Workshop October 10-11, 2012



### CONTROL CHARTS OF Z-SCORES

2010: Change of technique (from less to more sensitive!)



EURACHEM Workshop October 10-11, 2012



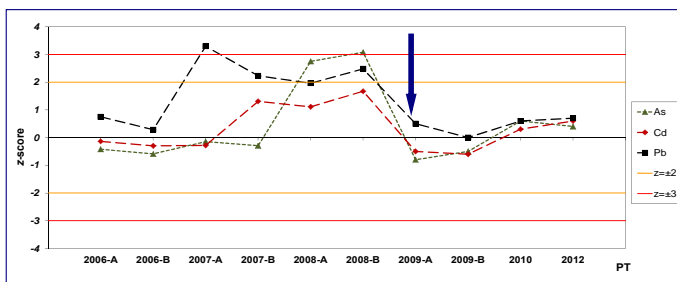
**EU-NATIONAL REFERENCE LABORATORIES  
CONTROL CHART OF THE z-scores  
(2006-2012)  
MILK**

Edited by: A. Colabucci  
Verified by: L. Ciaralli  
Issued: 19.07.2012

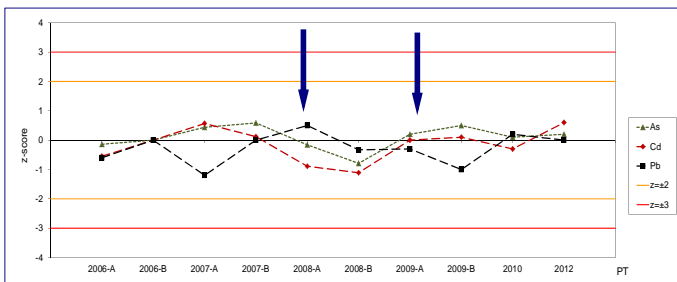
EURACHEM Workshop October 10-11, 2012

**CC Milk**

**Change of staff:  
improved performance**



**Change of the staff in a laboratory with high standard of QS:  
excellent and steady performance**

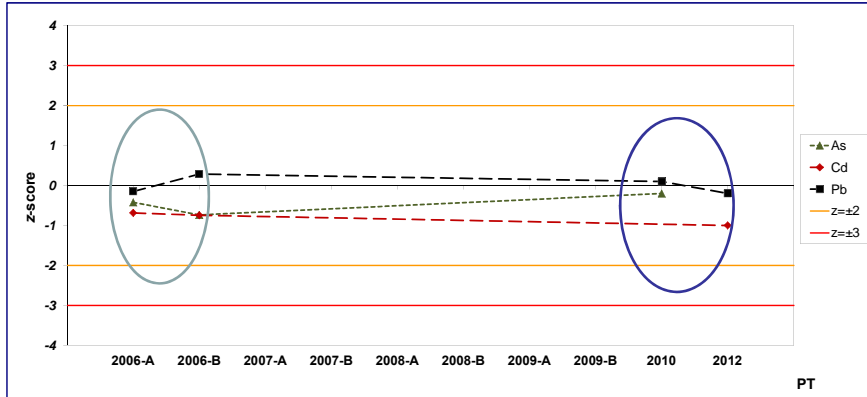


EURACHEM Workshop October 10-11, 2012



CONTROL CHARTS OF Z-SCORES

CC Milk

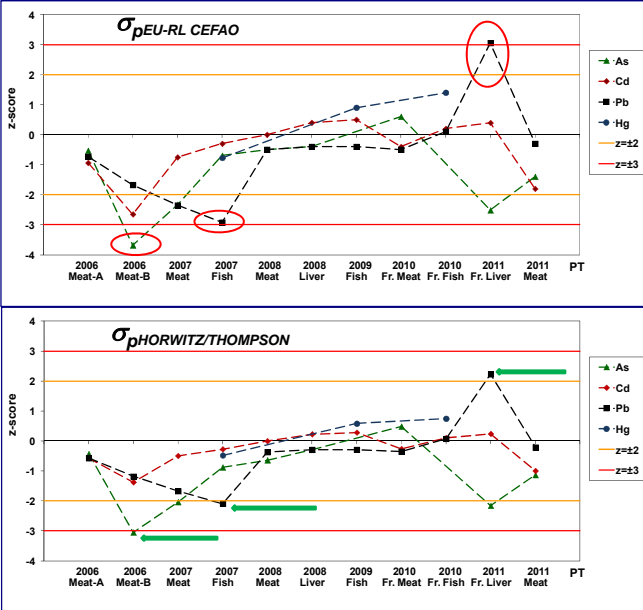


Steady performance in spite of no participation in PTs for 3 years and the change of the sample physical state

Analytical method under control



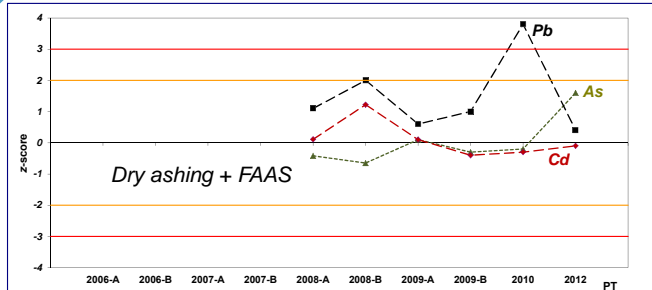
CONTROL CHARTS OF Z-SCORES



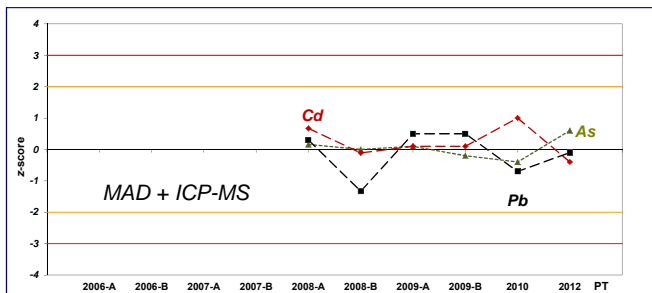
CC Meat, Fish and Offal



## CONTROL CHARTS OF Z-SCORES



**The NRL was advised to accredit the method based on the most sensitive technique**



EURACHEM Workshop October 10-11, 2012



## CONTROL CHARTS OF Z-SCORES

### CUSUM Control Chart for z-scores (ISO 13528:2005\*, Par. 9.3.1)

To prepare this chart, the cumulative sum (cusum) of the z-scores achieved by a laboratory over several rounds of a PT is calculated and plotted.

The CUSUM control chart is an effective method of identifying problems that cause a bias in the determination of a characteristic that persists over several rounds.

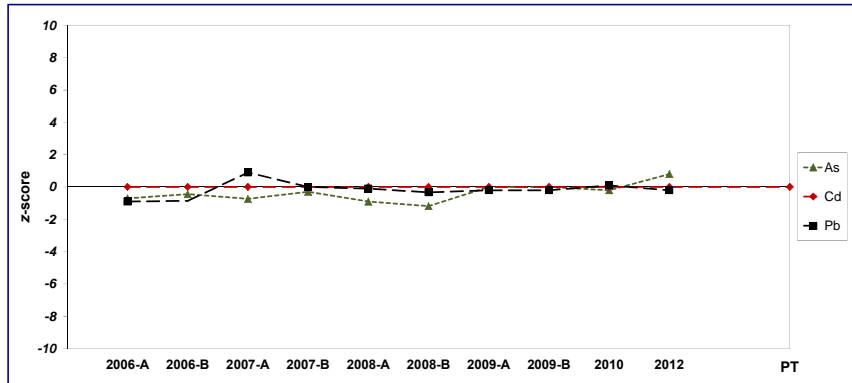
\* ISO 13528:2005: Statistical methods for use in proficiency testing by interlaboratory comparisons

EURACHEM Workshop October 10-11, 2012



### CONTROL CHARTS OF Z-SCORES

#### THE 'PERFECT' CUSUM CHART



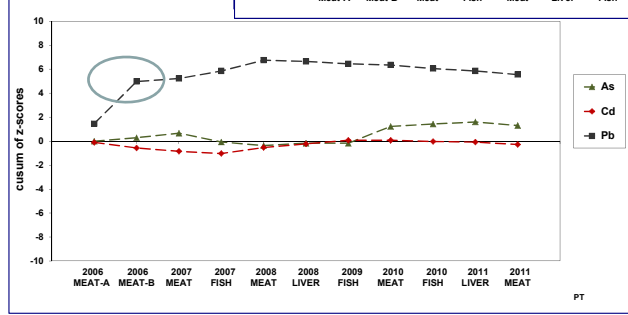
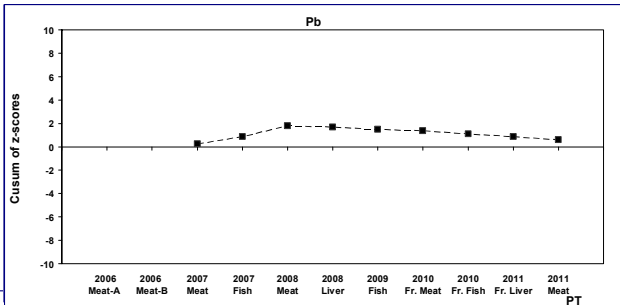
EURACHEM Workshop October 10-11, 2012



### CONTROL CHARTS OF Z-SCORES

#### Meat, Fish and Offal

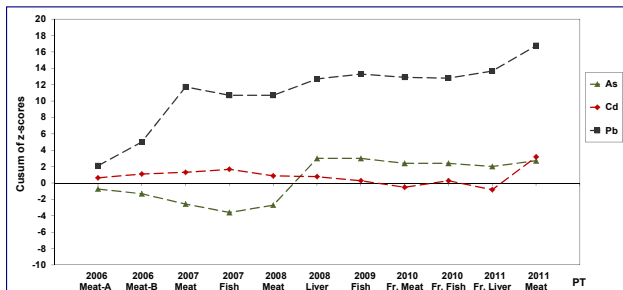
Shewart CC →



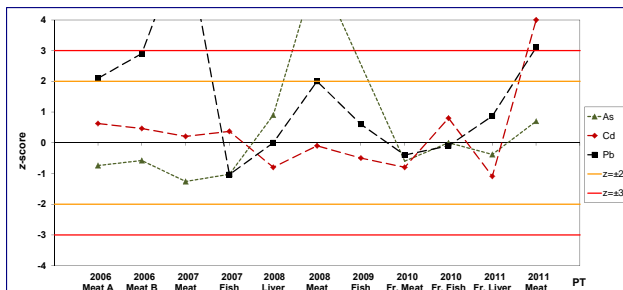
← Cusum CC

EURACHEM Workshop October 10-11, 2012

## CONTROL CHARTS OF Z-SCORES



← Cusum CC



← Shewart CC

EURACHEM Workshop October 10-11, 2012

## CONCLUSIONS

- *The organization of recurrent PTs on the same matrix/analyte combination and at a similar level of concentration allows participants to monitor the performance of their analytical methods and the PT provider to constantly check the quality level of the network*
- *The use of proper Control Charts is an effective means of monitoring the trends in the results produced by the laboratory*
- *The evaluation of CUSUM Charts together with Shewart Control Charts can be a useful way of highlighting bias in the analytical methods*
- *The analytical background of the Provider is an important basis to join all the information from the PT to assist participants in understanding their performance*

EURACHEM Workshop October 10-11, 2012

Many thanks to dr. Rosa Giordano  
for the invaluable support  
Attention!  
Thank you for your



EURACHEM Workshop October 10-11, 2012