



Federal Office of
Consumer Protection
and Food Safety

Coming up to standards: Usefulness of standard solutions as test items

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Proficiency tests (PTs) conducted by the EURL Berlin (residues of veterinary medicinal products)

PTs: Mandatory task of European Reference Laboratories (EURLs)

- National Reference Laboratories (NRLs) are **required to participate**
- Objective: **harmonisation** of lab performance, identification of areas of **improvement**
- EURL Berlin has long-standing experience in PT organisation (since 1996), has held **ISO 17043 accreditation** since 2016
- Focus on PTs using **incurred samples**

substance group /matrix	anthelmintics	β -agonists	coccidiostats	nitroimidazoles	NSAIDs	multi
egg			X	X		
milk	X			X	X	X
liver		X	X			
muscle	X		X	X	X	
plasma				X	X	
urine		X				
hair		X				
retina		X				

Substance group-matrix combinations previously investigated in EURL PTs

Why conduct a PT on standard solutions?

Picture this:

You are an **analytical chemist** participating in a **proficiency test (PT)**. You just received **your results**.



100 % accurate depiction!





FAIL

How do you proceed?

Why conduct a PT on standard solutions?

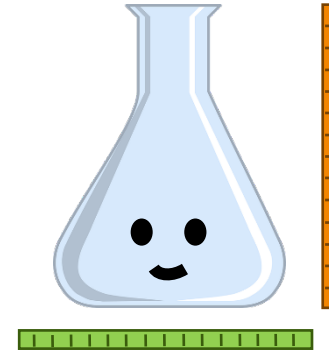
PT Follow-up

Was it really a bad result?

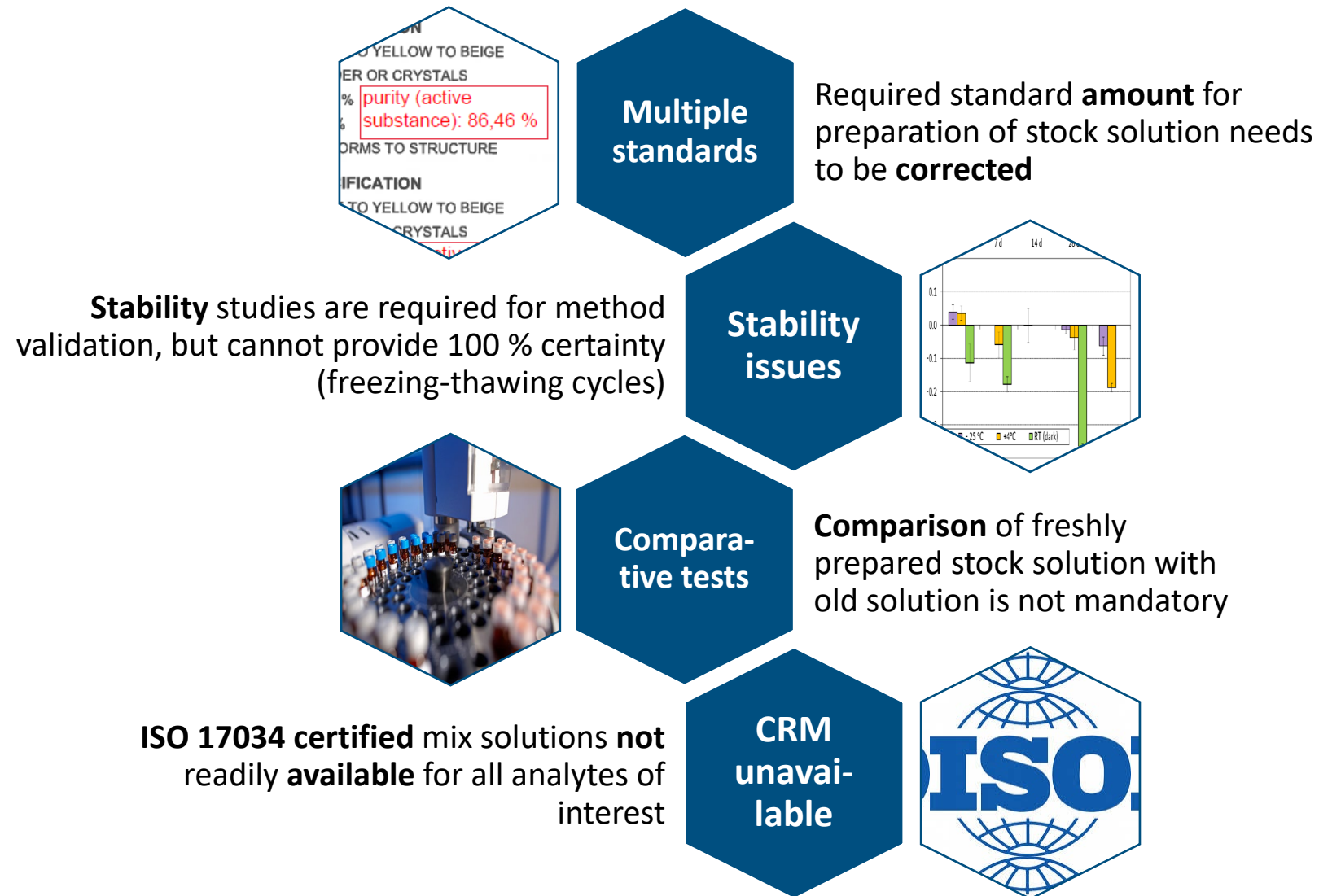
- Critically evaluate the PT design
- Results reported correctly?

A bad result indeed:

- Check **QC** samples
- Check for **anomalies** in analytical series
- Check **appropriateness** of analytical **method** (with CRM)
- Inexperienced **operator**?
- **Check the employed standard solutions!**



Standard solutions – a common cause of errors

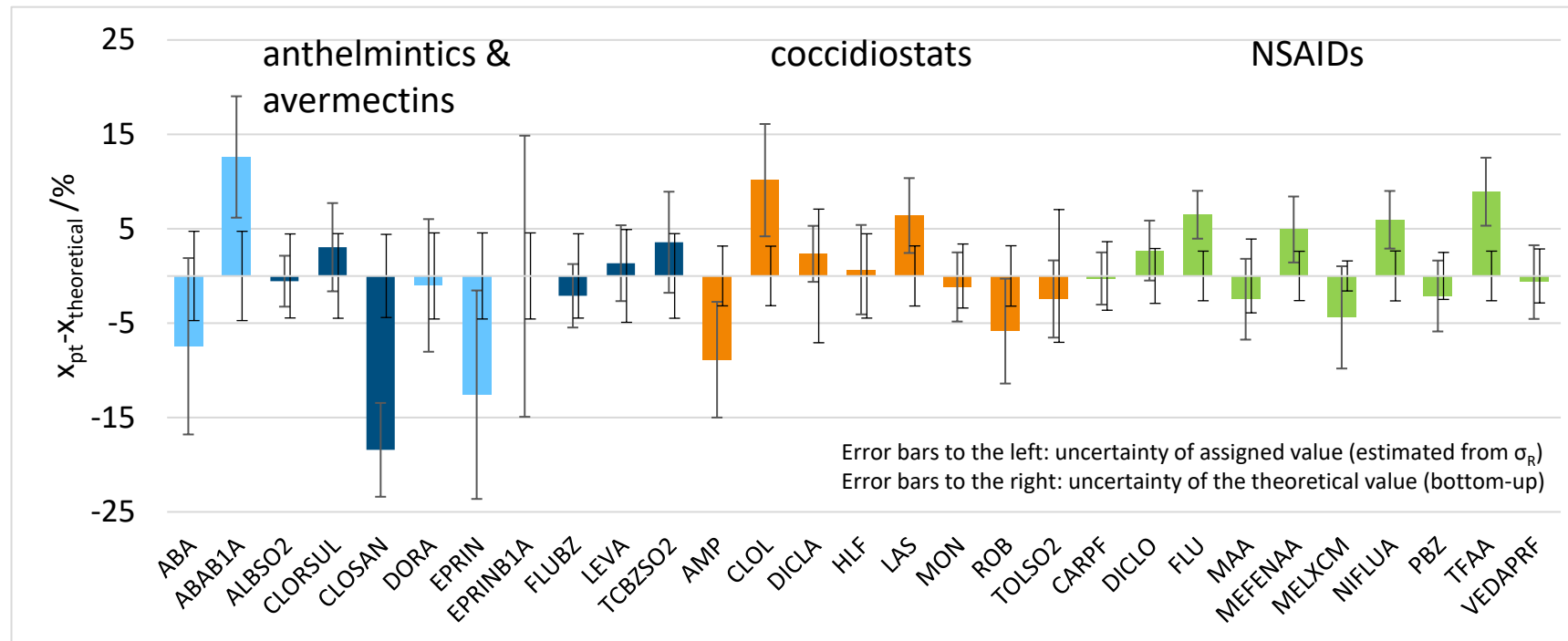


- Participants: EU **NRLs**, NRLs from **Third Countries**, **German official labs**
 - 50 participants in total, 34-39 per substance group
- **3 samples** of standard mixes containing anthelmintics, coccidiostats and NSAIDs
- Participants were asked to dilute samples as they wished (recommended 1/9), report **results for undiluted sample**
- All samples **homogeneous** and sufficiently **stable**
- **Free choice** of method
- Assigned value: **consensus mean**; target std. dev.: **HORWITZ, reproducibility**

Sample	Solvent	Analytes	Σ	Concentration /(ng/mL)
ANTH_B	EtOH	ABA, ALBSO2, CLOSAN, CLORSUL, DORA, EPRIN, FLUBZ, LEVA, TCBZSO2	9	100-2000
COCC_B	EtOH	AMP, CLOL, DICLA, HLF, LAS, MON, ROB, TOLSO2	8	100-1000
NSAI_B	ACN/MeOH 9/1 v/v	MAA, CARPF, DICLO, FLU, MEFENA, MELXCM, NIFLUA, PBZ, TFAA, VEDAPRF	10	50-1500

Results: Consensus values vs. reference values

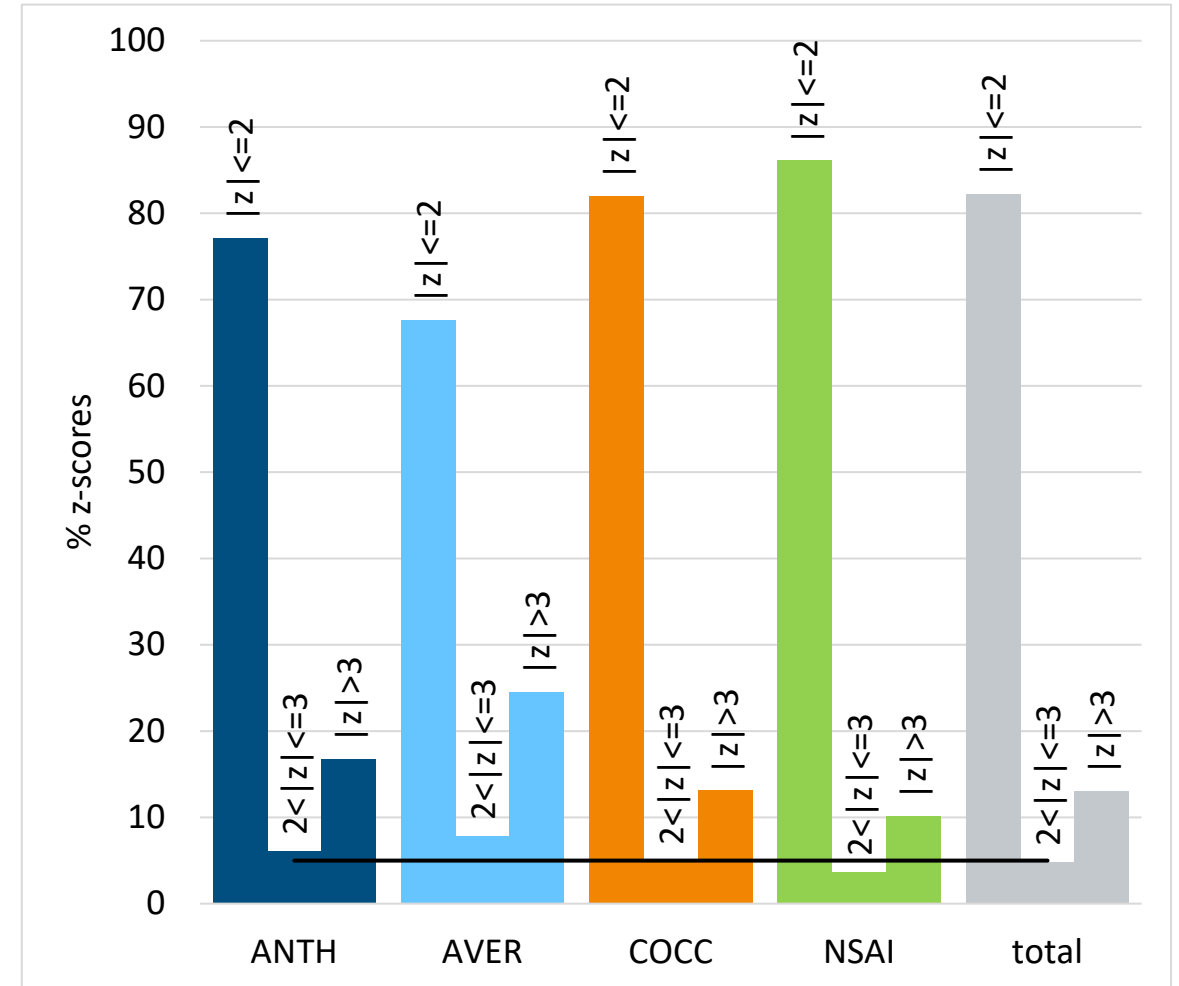
- **Good correlation** between consensus value and reference value under consideration of the respective uncertainties
- Indicates that all **relevant uncertainty** contributions were **considered**



>5 % of results with $|z'| > 2$

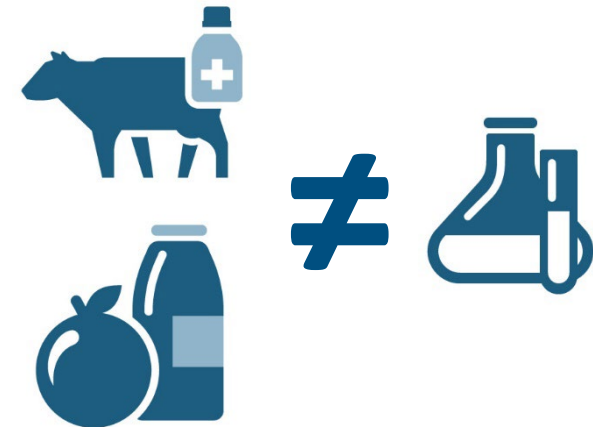
Possible reasons:

- In some cases use of **HORWITZ** instead of σ_R
- **Lack of experience** with quantification of standard solutions
- Gross **errors** (incorrect units, incorrect dilution factors)



Comparison with matrix PTs – same same but different

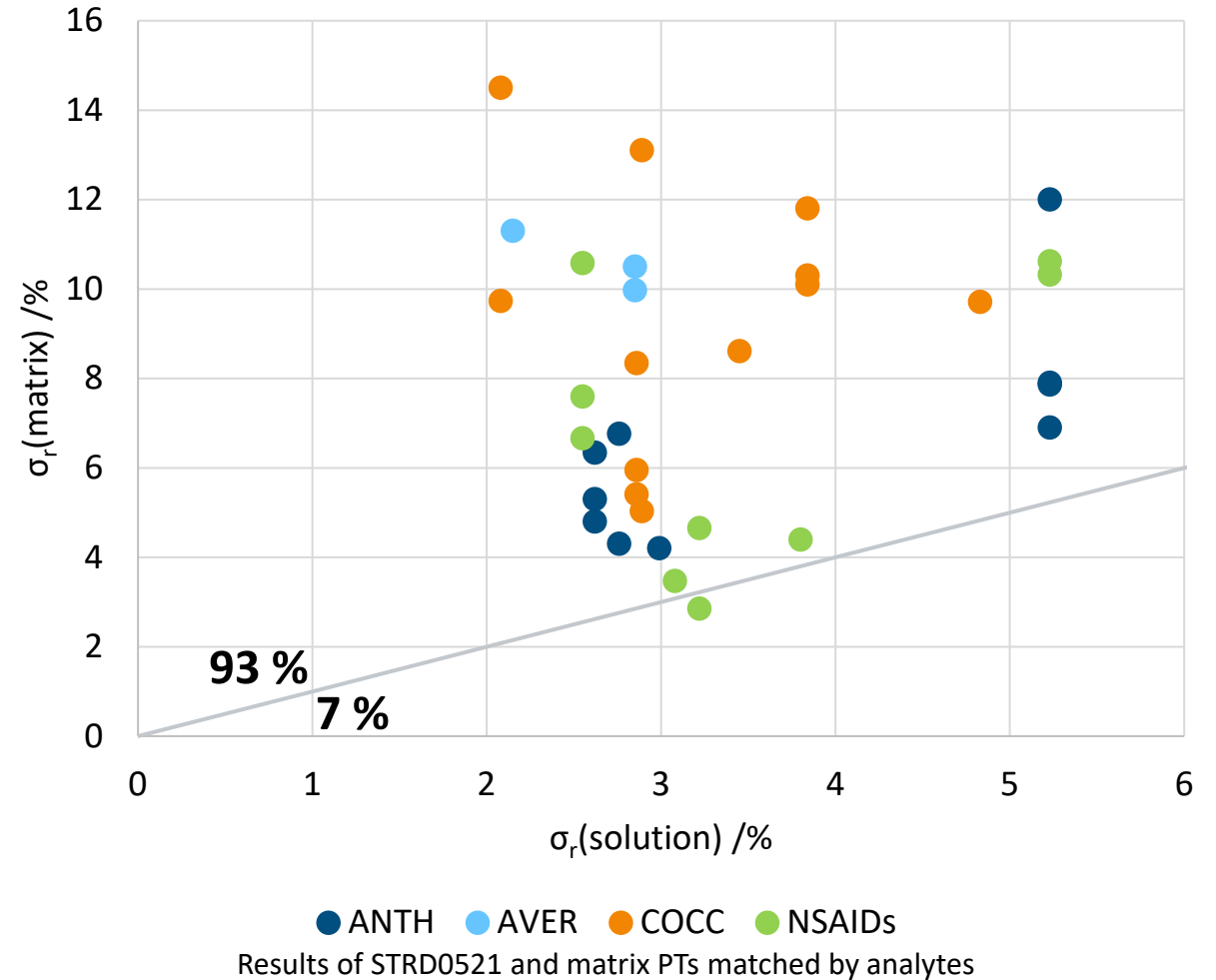
- **Comparison** of results from **standard solution** PT STRD0521 with results from **matrix** PTs
 - Matrices include milk, egg, liver, muscle
 - Several results from matrix PTs per analyte
- Concentrations in the range 0.175-369 ppb
- **Robust statistics**
 - consensus mean: HAMPEL
 - repeatability, reproducibility: Q-method



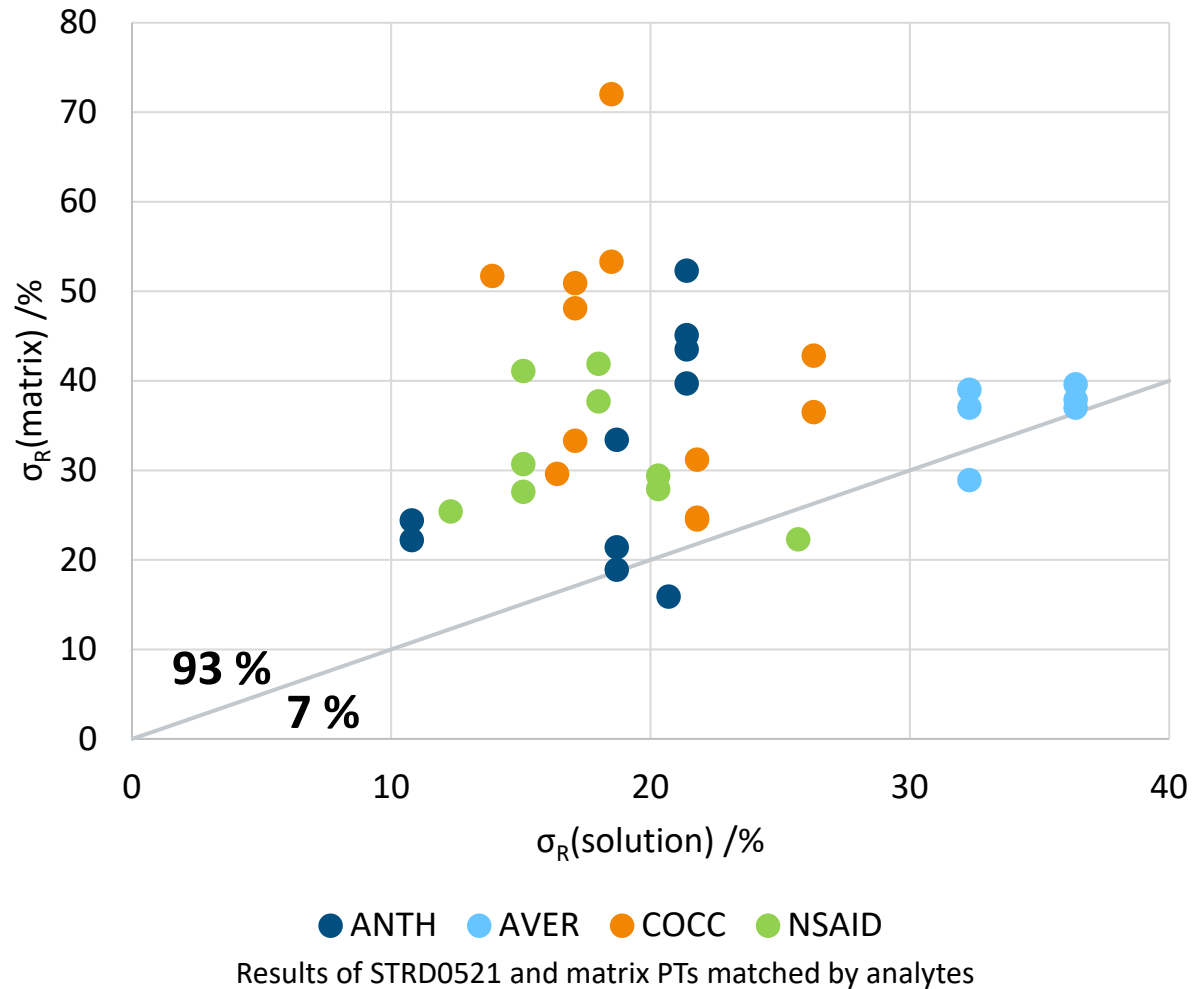
Comparison with matrix PTs – repeatability σ_r

Observations:

- σ_r differs between analytes
- σ_r often similar for same analyte in different matrices
- **Repeatability is higher in matrix samples**
 - Up to 7x higher in matrix samples,
 - **Median ratio: 2**
 - More factors influence analysis of matrix samples



Comparison with matrix PTs – reproducibility σ_R



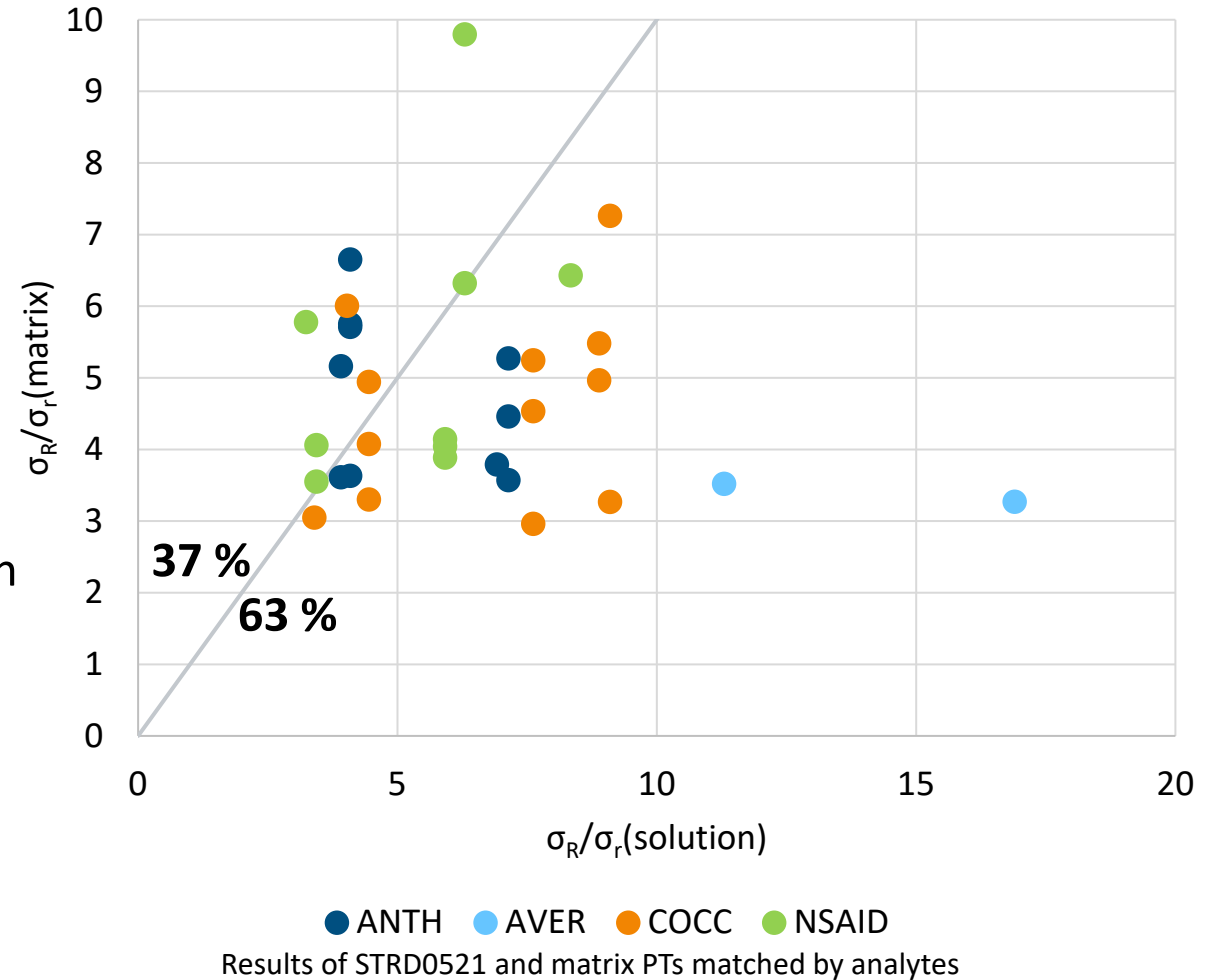
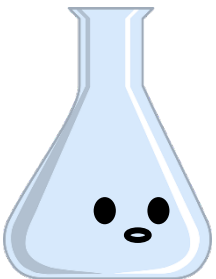
Observations:

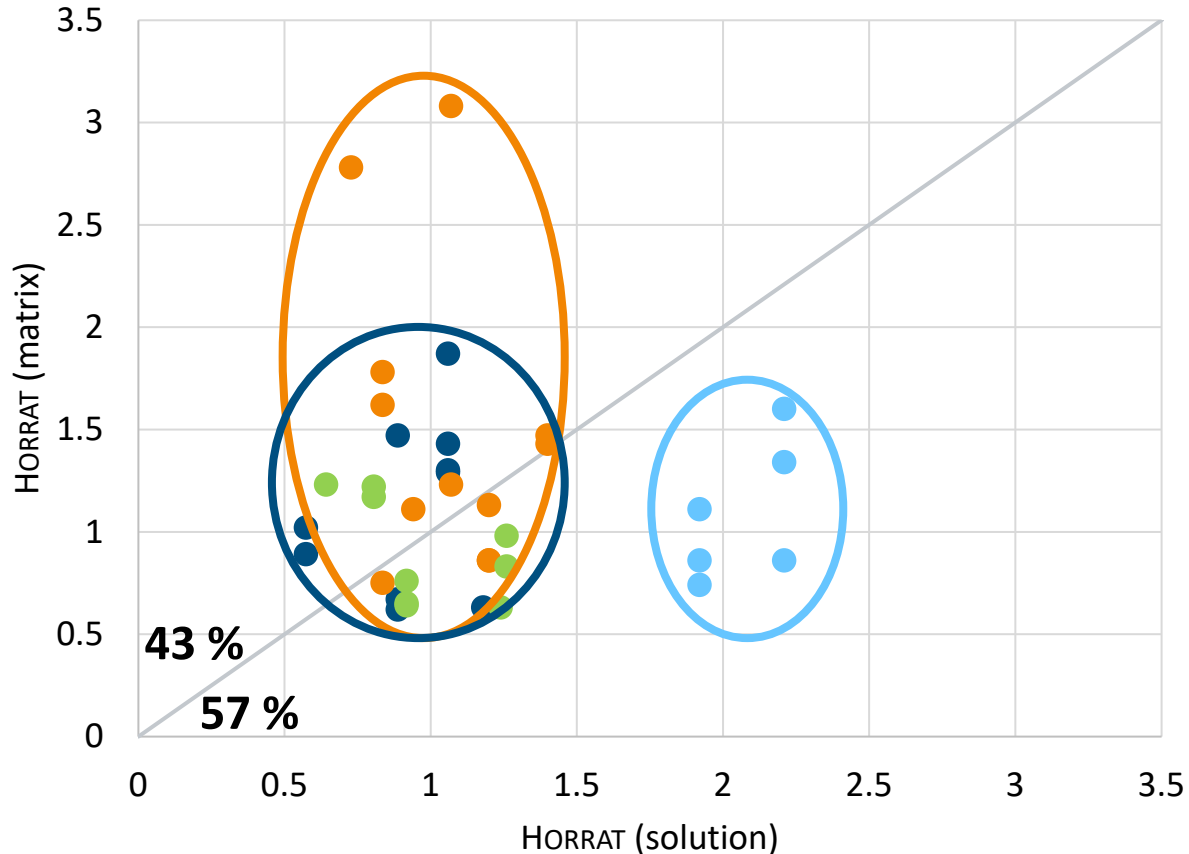
- σ_R differs between analytes
- Larger concentration for same analyte often comes with larger σ_R
- **Reproducibility is higher in matrix samples**
 - Up to 4x higher in matrix samples,
 - **Median ratio: 1.5**
 - More factors influence analysis of matrix samples

Comparison with matrix PTs – ratio σ_R/σ_r

Observations:

- Ratio for solutions often higher
 - Up to 5x higher in solutions
 - **Median ratio: 0.84**
 - Ratio for solutions about 20 % higher
- **Lower σ_r and same or higher σ_R in solution**
 - Labs are very good at analysis of their own solutions, but solutions might differ significantly between labs





● ANTH ● AVER ● COCC ● NSAIDs

Results of STRD0521 and matrix PTs matched by analytes

Observations:

- HORRAT dependant on analyte
 - HORRAT for AVER higher in solution
 - HORRAT for ANTH, COCC mostly higher in matrix
- Overall **good correlation** between HORRAT in solution and HORRAT in matrix
 - **Median ratio: 0.9**
 - If corrected for concentration, laboratory performance for matrix samples is comparable to performance for standard solutions

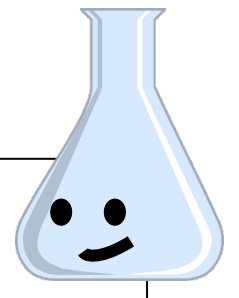
Taking stock



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- **PTs on matrix samples and standard solutions differed**
 - σ_r and σ_R for standard solutions often **lower**
 - **Ratio σ_R/σ_r for standard solutions often higher**
- **External control of standard solutions is a valuable tool**
 - **Pitfalls** of matrix sample analysis are **eliminated**
 - **Immediate feedback** on a common source for errors
- **PTs with standard solutions come with their own set of challenges**
 - Participants' **methods** are optimised for **matrix**
 - Participants are **unfamiliar** with analysis of standard solutions

An improvement of the quality of the employed standard solution leads to an overall improvement in performance of the laboratory network.



Acknowledgement

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Thank you for your attention and good luck with your upcoming proficiency tests!

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