Australian Government
Department of Industry, Innovation and Science
National Measurement Institute

Proficiency Testing in Australia and the NMI PT Program

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Australian PT Providers

- Accreditation to ISO17043
  - offered by National Association of Testing Authorities NATA
  - 11 accredited providers
- Medical
- Mining
- Food
  - chemical testing
  - microbiology
- Australian laboratories also participate in international PT
  - import restrictions can make this difficult

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Inorganic Analytes

Hydrocarbons and PAHs

Forensic Drugs

Allergens

Vitamins

Pesticide Residues

Poly and per-fluorinated compounds

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The Role of NMI PT

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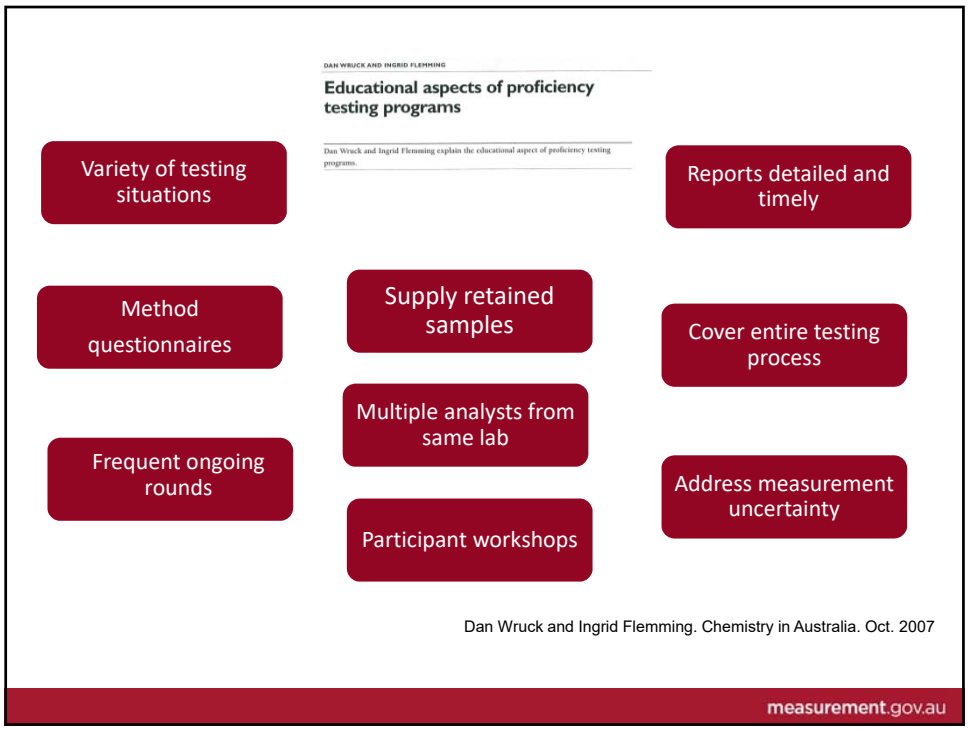

NMI PT and Laboratory Performance

- Not blind
  - laboratories know it is a PT sample
- Limited range of target analytes
  - list provided to participants
- Blank sample provided
- Long turn around time
  - four weeks
- So what we see is the laboratory's best attempt
- But:
  - PT is just a snapshot
  - anyone can make a mistake
- The purpose is quality improvement

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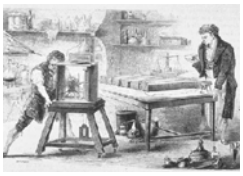
Types of errors

- Two-thirds of errors are technical
  - extraction method
  - instrumental technique
  - dilution factors
  - interference correction
  - calibration
  - etc
- One-third are blunders
  - wrong units
  - transcription error
  - calculation error
  - sample mix-up
- NMI will not accept changes to results after the issue of the interim report.



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24 Years of Pesticide in Fruit and Vegetable PT

1994

- 11 labs sent results – 10 Australian
- Most used Luke method
  - liquid/liquid acetone, dichloromethane, hexane
- GC with ECD, FPD and NPD

2018

- 22 labs, 10 Australian
- 1 survivor from 1994
- QuEChERS
- LC/MS/MS, GC/MS GC/ECD and FPD

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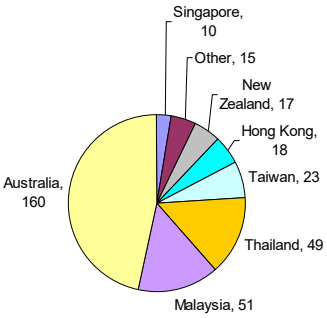
Participant Labs by Country

Most participants are Australian

Significant number from SE Asia in the Fruit and Vegetable Program.

Others include Brazil, Vietnam, Kenya, India, Mexico



Fruit and Vegetable

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Possible analytes 2019

2,4-D	Diazinon	Methidathion
Abamectin	Dicofol	Methomyl
alpha-Endosulfan	Dieldrin	Methomyl oxime
Azinphos-methyl	Dimethoate	Mevinphos
Azoxystrobin	Dithiocarbamates	Monocrotophos
beta-Endosulfan	Endosulfan Sulfate	Omethoate
Bifenazate	Fenamiphos	Parathion
Bifenthrin	Fenitrothion	Parathion Methyl
Buprofezin	Fenthion	Penconazole
Captan	Fenthion sulfone	Permethrin
Carbaryl	Fenthion sulfoxide	Pirimicarb
Carbendazim	Fenvalerate	pp-DDT
Chlorfenvinphos	Imazalil	Procymidone
Chlorothalonil	Imidacloprid	Profenofos
Chlorpyrifos	Indoxacarb	Propargite
Clothianidin	Iprodione	Pyraclostrobin
Cyfluthrin	Linuron	Spinosad
Cyhalothrin	Maldison	Thiabendazole
Cypermethrin	Metalaxyl	Triadimefon
Deltamethrin	Methamidophos	

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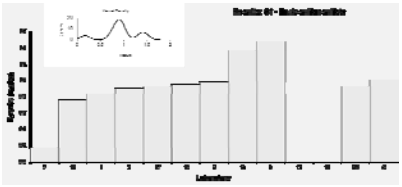
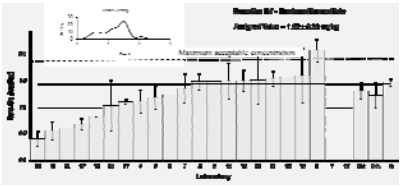
Endosulfan sulfate in tomato

1994
- agreement with spike
- uncertainties?



2018
- similar lab performance
- uncertainties reported



Md = Median
S = Spike
RA = Robust average

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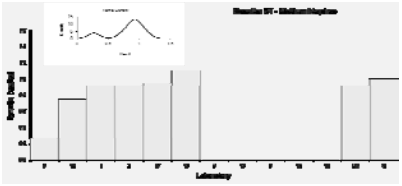
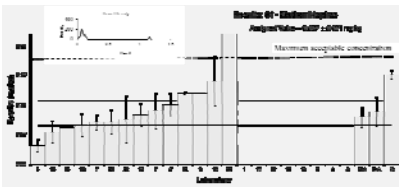
Methamidophos in tomato

1994
- agreement with spike
- 5 of 11 labs did not report



2018
- similar lab performance
- 8 of 22 labs did not report



Md = Median
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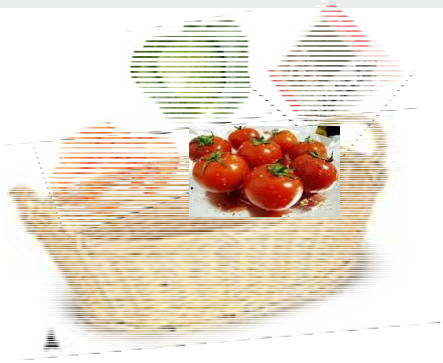
PT Studies of Metals in Food

- Matrix:
  - prawn
  - prawn fortified with shark tissue
  - wine
  - cabbage
  - cabbage digest
  - tomato paste
  - seaweed
  - wheat flour
  - bovine liver
  - oyster tissue
  - wheat



- Analytes

Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Se, Sb, Sn, Sr, Th, U, V and Zn

Iodine and Inorganic As.

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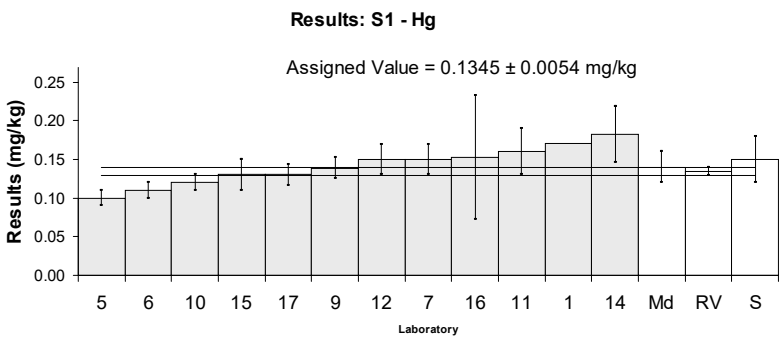
Assigned Value Hg in Prawn

- Double Isotope Dilution Mass Spectrometry



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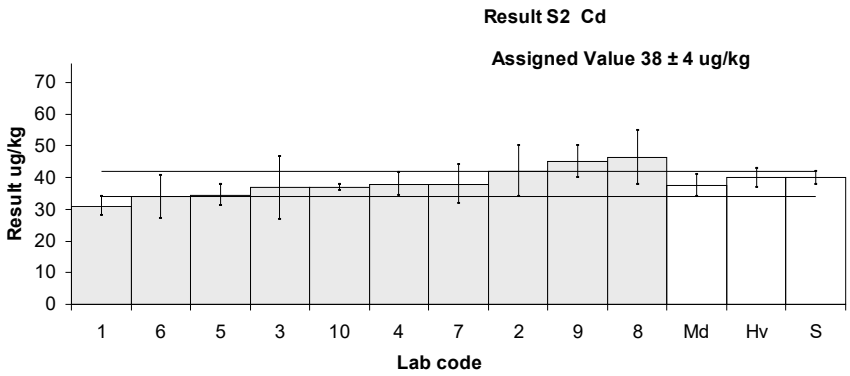
Assigned Value Cd in Wine

- Robust average (ISO 13528)



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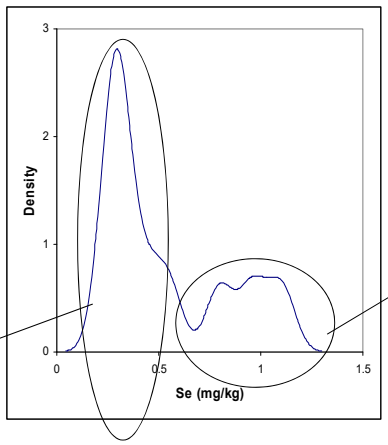
Se in Food

Results mg/kg	Instrument
0.29	ICP-MS-ORS
0.29	ICP-MS-ORS
0.3	ICP-MS-DRC
0.33	ICP-MS
0.44	ICP-MS-ORS



Results mg/kg	Instrument
0.55	ICP-MS
0.8	ICP-MS
0.96	ICP-MS
1.1	ICP-OES

Homogeneity value: by ICP-MS-DRC =0.28 mg/kg and by HR-ICP-MS = 0.25 mg/kg

ICP-MS without reaction/collision cell may not be a good choice for Se measurements in food.

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Using PT data to Estimate MU

- A single round of PT is a snapshot of a laboratory's performance
- Ongoing participation build a record of performance
  - including the MU estimates
- Data from PT can be used for MU estimation

Interlaboratory Studies

- Validation trial
  - all laboratories use the same method
  - the method is being evaluated
  - reproducibility standard deviation is an estimate of standard uncertainty
  - Eurachem has an example of fibre in feed
- Proficiency test
  - laboratories use their own methods
  - the laboratories are being evaluated
  - between-laboratory standard deviation is an estimate of standard uncertainty
  - Nordtest Guide has an example of MU estimation

PT History of Laboratory X Ni in water

PT Study No.	Sample	Laboratory X result µg/L	PT Assigned value µg/L	Robust CV of all results (%)	Number of Results
AQA 08-02	Fresh	53 ± 8	52.0 ± 3.1	9.9	18
AQA 08-10	Fresh	19.5 ± 2.5	18.9 ± 0.6	7.8	26
	Fresh	200 ± 30	191 ± 5	5.5	26
AQA 09-05	Saline	49	44.7 ± 3.3	10.8	18
AQA 09-18	Fresh	5.4 ± 1.5	5.04 ± 0.27	7.4	14
	Fresh	49 ± 7	48.9 ± 1.2	3.3	16
AQA 10-06	Potable	50 ± 7	50 ± 1	5.9	20
	Potable	50 ± 7	50 ± 1	3	20
AQA 10-17	Saline	5.2 ± 1.6	4.93 ± 0.25	12	14
	Saline	5.3 ± 1.6	4.93 ± 0.25	8.9	13
			Average	**7.5**	

MU from Lab. X's PT Data

- The average robust between laboratory CV was 7.5 %
  - this is an estimate of the relative standard uncertainty
    - could also use a pooled relative standard deviation (7.7% in this case)
- A coverage factor of 2 give an estimated relative expanded uncertainty of 15%
  - at a confidence level of approximately 95%

MU in the Unit of Measurement (µg/L)

Result µg/L	Uncertainty µg/L
5.0	0.8
20	3
50	8
200	30

The estimate of MU from the PT data is quite similar to the estimates reported by Lab. X in the PT.
E.g. Lab. X reported: 200 ± 30, 53 ± 8, 5.2 ± 1.6

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MU from PT: Limitations

- Aggregated data
  - different method, different laboratories
- Applied to a particular measurement in a single laboratory
  - All measurements get the same estimate of MU
    - the estimate that would apply to a hypothetical 'typical' sample
    - measured in a hypothetical 'typical' laboratory
- PT sample may not cover all aspects of the measurement process
  - e.g. extraction, sub-sampling
- Consensus assigned value may be biased
- Three years of PT participation is a long time to wait before making an MU estimate.

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