

# Use of assigned reference values: Revisiting a small scale inter- laboratory comparison for residual pesticides in tea

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# Content

- A proficiency testing programme (HKGL0903) [residues of organochlorine pesticides (a-endosulfan, b-endosulfan and endosulfan sulfate) in tea ] organised in 2009
- Performance evaluation -
  - z-scores, using consensus values and standard deviation that was estimated from the Horwitz equation
  - assigned reference values derived from gas spectrometry-isotope dilution mass spectrometry with higher metrological traceability
- Observable differences
- Recommendations



# Test material

- About 7 kg of dried green tea samples (pre-screened to contain trace level of target pesticides) were ground to powder and filtered through 200  $\mu\text{m}$  sieves. Fine tea powder was thoroughly mixed and about 20 g each was packed into a cleaned and nitrogen-flush amber glass bottle.
- All bottles were capped, disinfected by  $\gamma$ -irradiation at a dose of about 1 kGy and stored at about 25 °C before dispatch to participants. Homogeneity and stability studies of the test materials were performed using an in-house validated GC- $\mu$ ECD method and treatment of the respective analytical data was in accordance with ISO 13528:2005
- Stability and homogeneity tests passed





# Performance Evaluation

- two bottles of test material provided
- requested to determine the mass fraction ( $mg/kg$ ) of the three pesticides in the sample as received Participants' z-scores were determined as:

$$z = (x_i - x) / \sigma_R$$

where

$x_i$  is participant's reported analytical data and  $x$  is consensus value

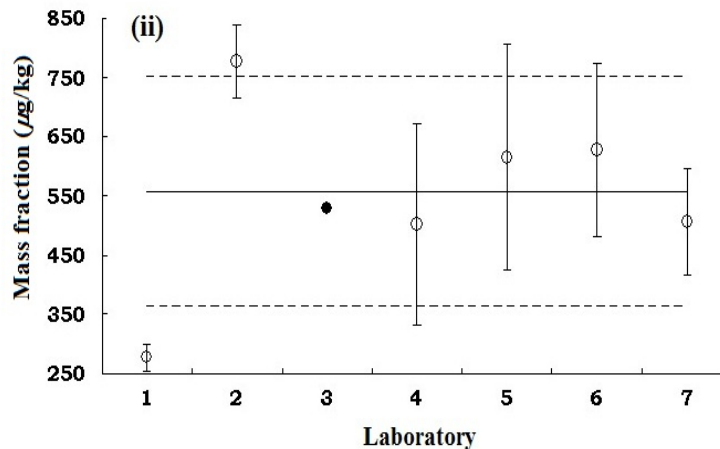
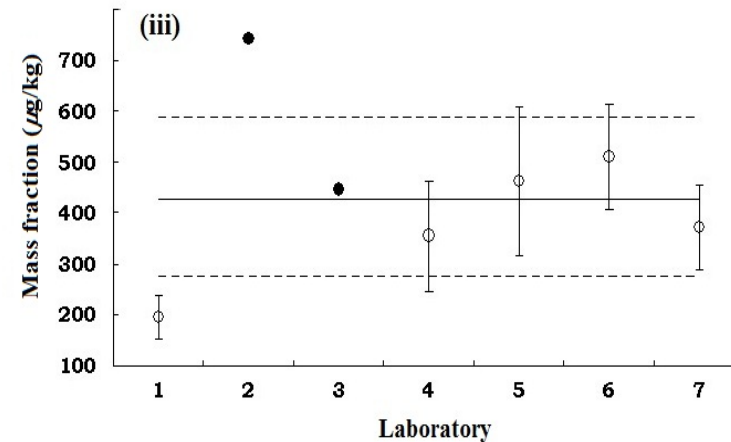
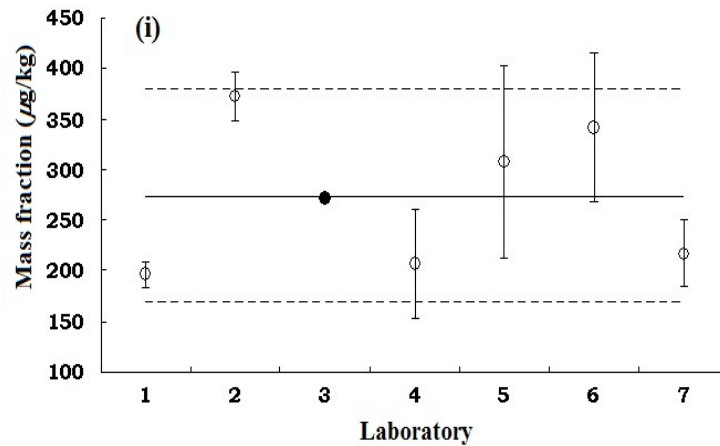
$\sigma_R$  was derived using the Horwitz function of  $2 c^{0.85}$ , where  $c$  is the mean concentration of analytes expressed as mass fraction in percent from the homogeneity study



## Participant's methods

- Sample preparation: Extraction by mechanical shaking or ultrasonication with ethyl acetate and other commonly used solvents for OC pesticides (acetonitrile and dichloromethane) for the duration from 5 to 45 min
- Sample cleanup: none (1), GPC, SPE or both (6)
- Method used: GC-ECD (3), GC-MS (3) and both techniques (1)
- Majority of them used internal standards
- Extraction efficiencies with respect to the spike standards were reported ranging from 79 to 120 %

# Performance of participants



i)  $\alpha$ -endosulfan ii)  $\beta$ -endosulfan and iii) endosulfan sulfate  
Solid lines represent the consensus values, dotted lines embrace the conc. ranges within  $|z| = 2$ , error bars represent U at 95 % confidence level ( $k = 2$ )

## Summary of participants results in HKGL0903

Parameter	a-Endosulfan	b-Endosulfan	Endosulfan SO <sub>4</sub>
Data submitted (n)	7	7	7
Consensus value, $\bar{x} \pm u(x)$ (mg/kg)	273 $\pm$ 75	556 $\pm$ 127	429 $\pm$ 127
Median (mg/kg)	272	530	445
Range (mg/kg)	196 – 372	278 – 777	196 – 741
Between-laboratory standard deviation (%)	28.9	23.9	31.0

$u(x)$ : Standard uncertainty of the consensus value estimated using the equation of  $1.25 \cdot \sigma / \sqrt{x}$  in accordance with ISO13528







## Revisiting

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- Duplicate analysis using GC-IDMS at 4 different days
- The mean assigned reference values were:
  - 346 ± 18 µg/kg for α-endosulfan
  - 708 ± 25 µg/kg for β-endosulfan
  - 464 ± 17 µg/kg for endosulfan sulfate
- U was contributed by weighing of sample, standard solutions of the natural and labeled isotopes high purity (<sup>13</sup>C<sub>9</sub>-α-endosulfan, <sup>13</sup>C<sub>9</sub>-β-endosulfan and <sup>13</sup>C<sub>9</sub>-endosulfan sulfate), purity of standards, and the bias of the peak area ratio of the natural and labeled isotopes respectively in the samples and calibrants



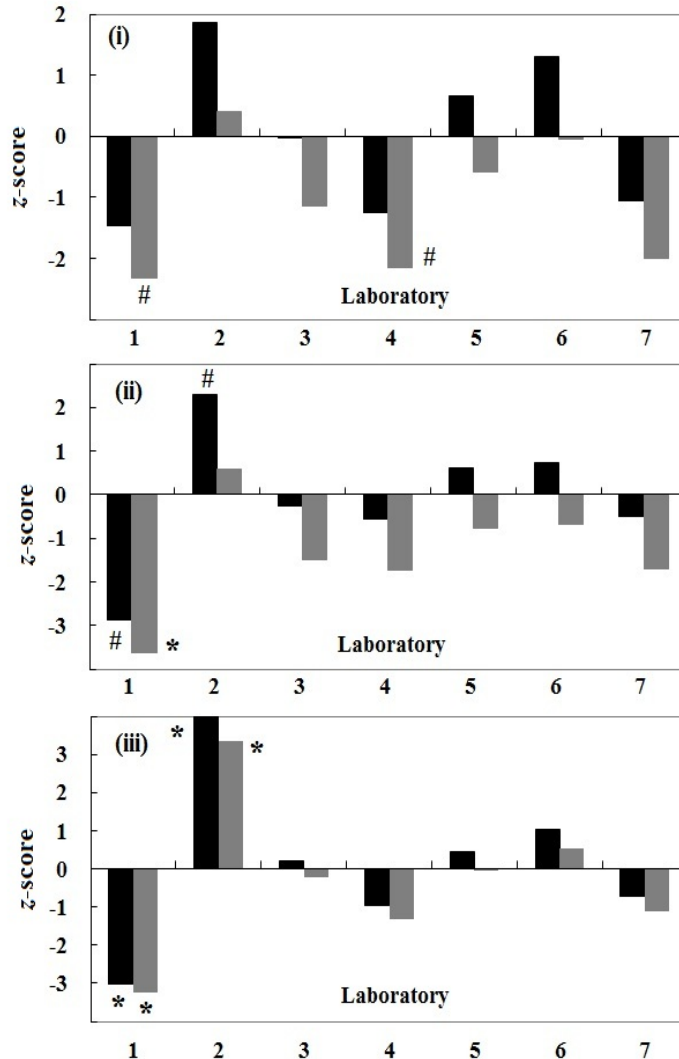


## Percentage deviation of participants' results from the assigned reference values

the consensus values from participants: +27 % for both  $\alpha$ - and  $\beta$ -endosulfan, and +8 % for endosulfan sulfate respectively when comparing with the GC-IDMS values

Lab	Deviation (%)		
	$\alpha$ -Endosulfan	$\beta$ -Endosulfan	Endosulfan SO <sub>4</sub>
1	-43.3	-60.7	-57.8
2	7.6	9.7	59.7
3	-21.3	-25.1	-4.1
4	-40.1	-29.1	-23.5
5	-10.9	-13.1	-0.4
6	-1.0	-11.3	9.7
7	-37.2	-28.4	-19.8

# Assigned values vs Consensus values



Histograms of z-scores assessed by consensus (black columns) and assigned reference values (gray columns) for i)  $\alpha$ -endosulfan, ii)  $\beta$ -endosulfan and iii) endosulfan sulfate. # denotes a questionable z-score and \* an unsatisfactory z-score

# Findings

- Observable differences - 2 satisfactory z-scores became questionable and 2 questionable ones become 1 unsatisfactory and 1 satisfactory respectively. Overall, the laboratories that having either questionable or unsatisfactory changed from 2 to 3
- The majority were lower than the reference values, - probably due to overestimated recoveries or incomplete extraction of residual pesticides.
- Unlike **spike** samples, a certain portion of incurred pesticide residues were absorbed and embedded within the plant matrices which could not be easily extracted by organic solvents alone.
- The underestimation of a wide variety of **incurred** pesticides in samples without hydration was found to be from 25 to 74 %.



# Conclusions & Recommendations

- The present study is an illustrative example to show that although the operation of test materials and statistical analysis of the PT program met the stipulated international requirements; the outcome of participant's performance will be much influenced by the choice of assigned values.
- The 2010 official IUPAC/CITAC Guide - **consensus values are not suitable to evaluate participants' performance in terms of z-score with participation number fewer than thirty ( $n < 30$ ).**

# Acknowledgements

- Thanks to Ms. Pat Chu and Ms. Janet Yeung of the Government Laboratory, and participants of HKGL0903



National Health Commission