

Proficiency Testing (PT) for the Determination of Dithiocarbamate Pesticides in Mango Matrix.

Armi W. Nóbrega¹, Damares S. Santos², Heloísa C. A. Gôes¹, Paulo R. F. Santos², Vanderléa Souza², Adherlene V. Gouvêa¹, Adriana S. de São José¹, Denise de P. Dias¹, Fernando G. M. Violante², Janaína M. R. Caixeiro², Lucia Helena P. Bastos¹, Maria Helena W. M. Cardoso¹, Raquel D. C. C. Bandeira², Renato R. R. de Almeida¹, Tânia M. Monteiro²

¹ Fundação Oswaldo Cruz- FIOCRUZ/INCQS, Rio de Janeiro-RJ-Brazil, E-mail: armi@incqs.fiocruz.br
² Instituto Nacional de Metrologia, Normalização e Qualidade Industrial-INMETRO, Rio de Janeiro-RJ-Brazil
 E-mail: prsantos@inmetro.gov.br



1 – Introduction

In order to enhance the reliability of results of complex pesticide determinations, participation in Proficiency Tests is a fundamental tool in any laboratory as prerequisite of the Quality System Program based on the ISO/IEC 17025. Although there is a large offer of assays by international PT providers, many factors limit the participation of Brazilian laboratories: difficulties on importing, which frequently result in receiving samples in inadequate integrity or temperature conditions, and the high cost of the participation. INCQS is the only Brazilian PT provider of samples for the determination of pesticide residue in foods. This work presents the results of twelve Brazilian and one Dutch (VWA/KWV) Laboratories in a PT organized by INCQS and INMETRO, with samples of dithiocarbamate thiram in mango pulp.

2 – Objectives

The objective of this PT was to provide information to the participating laboratories to help them to identify problems in the analytical procedures being used or/and to increase the confidence in the analytical results produced.

3 – Methodology

Sample preparation

The mangoes were bought in a market of Rio de Janeiro, tested to be dithiocarbamate-free, blended and the resulting pulp transferred to plastic recipients. 100mL of a 13.15 mg/mL solution of thiram (Thiram®, Dr. Ehrenstorfer, Germany) in ethylic alcohol was prepared and distributed in 5mL ampoules. The reference material used had a declared purity of 97.5%.

The samples consisted of two sets of 1 ampoule of thiram and one recipient of mango pulp. Each set was to be mixed right before the performing of the assay, according to the instructions.

Homogeneity and stability tests

The homogeneity of the samples was tested in 20 ampoules and 20 mango pulp recipients and the stability in 10 ampoules and 10 mango pulp recipients. These analyses were performed in INCQS, using Keppel methodology. Variance analysis (ANOVA) was used for homogeneity statistical evaluation and confirmed the homogeneity of the samples provided. The stability study lasted 5 weeks, the result was evaluated through residue analysis and the results demonstrated the stability of the samples.

4 - Laboratory performance criteria

The laboratory performance criteria was evaluated according to the ABNT ISO/IEC Guia 43-1. The parameter for evaluation of the performance of an individual laboratory was the z-score.

Equation 1:

$$Z_i = \frac{Y_i - Y_{ref}}{S} \quad (1)$$

Z_i : z-score
 Y_i : result of the laboratory i
 Y_{ref} : designated value
 S : new standard deviation

Criterion for acceptability of performance:

$$\begin{array}{l}
 |Z| \leq 2 \rightarrow \text{acceptable} \\
 2 < |Z| < 3 \rightarrow \text{questionable} \\
 |Z| \geq 3 \rightarrow \text{unacceptable}
 \end{array}$$

The repeatability of the results given for each laboratory was evaluated. According to the CODEX it was considered to have an acceptable repeatability those laboratories that presented a relative standard deviation minor to 15%.

5 – Results:

5.1 Homogeneity

Table 1: Analysis of variance of the samples used in PT.

Variation Source	SS	df	MS	F	P-value	F _{critic}
Different days	0,001208	9	0,000134	1,20	0,386783	3,02
Same day	0,001116	10	0,000112			
TOTAL	0,002324	19				

SS = sum of squares; df= degrees of freedom; MS = mean square

5.2 Stability

Table 2: Represents the results of stability thiram in mangoes.

	df	SS	MS		
Regression	1	0,000129	0,000129		
Residue	8	0,000416	5,1993E-05		
Total	9	0,000545			
	Coefficients	Standard error	t Stat	P-value	
Intercept	0,453644	0,003803	119,300132	2,72403E-14	
Variable X1	-0,000307	0,000195	-1,575381	0,15	

df= degrees of freedom; SS = sum of squares; MS = mean square

5.3 Designated value

The designated value calculated by using the robust statistic presented at ISO 13528 was **0.377 mg/kg of CS₂**, with a standard deviation of 0.0931.

6 - Results

Of the twelve participating laboratories, two ones presented an unsatisfactory-score and a RSD greater than 15%. Two laboratories presented questionable-scores, despite the fact that they have presented acceptable RSD.

Table 3: Results of laboratories.

Laboratories	Z-score	CV (%)	Laboratories	Z-score	CV (%)
PEP4.2/01	0.38	11.79	PEP4.2/11	-2.26	
PEP4.2/01	1.19		PEP4.2/11	-2.42	
PEP4.2/02	-0.32	5.55	PEP4.2/12	0.30	
PEP4.2/02	-0.61		PEP4.2/13	0.08	
PEP4.2/04	342.84	120.51	PEP4.2/13	0.17	
PEP4.2/04	23.65		PEP4.2/14	0.07	
PEP4.2/05	-2.26	10.58	PEP4.2/14	0.02	
PEP4.2/05	-1.97		PEP4.2/16	0.17	
PEP4.2/06	-3.89	10.88	PEP4.2/16	-0.16	
PEP4.2/06	-3.86		PEP4.2/17	-0.44	3.22
PEP4.2/08	1.10	8.18	PEP4.2/18	0.84	2.43
PEP4.2/08	0.54				
PEP4.2/09	0.61	1.05			
PEP4.2/09	0.68				

CV = coefficient of variation of the results from the laboratories; Laboratory PEP-4.2/12 had one measurement value.

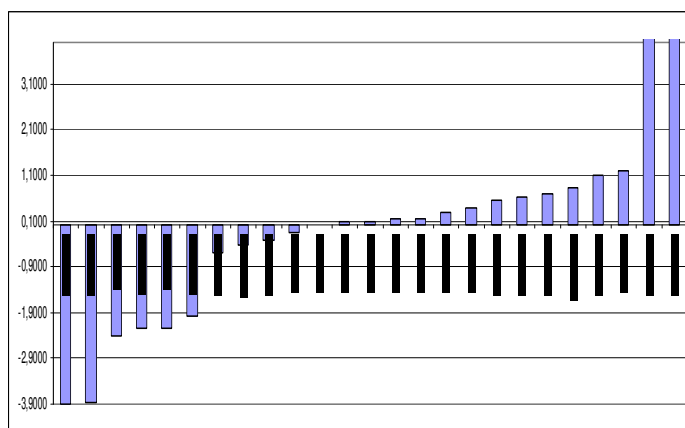


Figure 1: Proficiency Testing (PT) for the Determination of Dithiocarbamate Pesticides in Mango Matrix: z-scores for the participating laboratories.

7– Conclusion

The results of this proficiency testing indicated that efforts are needed to increase the quality of the measurements of pesticide residues, in mangos, performed by some of the participating laboratories. The results now presented could suggest that a better recovery was obtained by using the photometric method. However, it has been demonstrated previously that the photometric and the chromatographic methods are equivalent even though the chromatographic method seems to be more sensitive.

8 – Acknowledgments

