Proficiency Testing for the Determination of Pesticides in Mango Pulp: A View of the Employed Chromatographic Techniques and the Evaluation of Laboratories' Performance

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Abstract

The proficiency testing for determination of pesticides residues in mango pulp was the third work of the partnership established by INMETRO and INCQS/Fiocruz. Three mango pulp samples were sent to each participant laboratory, two being spiked with the pesticides and one exempt of pesticides. The added pesticides were: deltamethrin, ethion, fenitrothion, malathion, and permethrin. The evaluation of the results of the homogeneity and the stability tests, as well as the determination of the assigned value was made in agreement with ISO GUIDE 35 and ISO 13528, assuming the samples were considered homogeneous and stable for the studied period. The assigned values and the standard deviation for proficiency evaluation was calculated using the robust algorithm, according to ISO 13528, and the evaluation of the results was carried through in accordance with ABNT ISO/IEC Guide 43-1. The z-score graphs and confidence ellipse was also used in the evaluation of the results. In the evaluation carried through from the values of the z-scores, 71% of the reported results were considered satisfactory based on the results found for this index. The evaluation of the analytical viability for the determination of each pesticide and of the analytical capacity of the participant laboratories was carried through. A summarized view of the chromatographic techniques and of preparation of sample used by the participant laboratories was also carried through in this work.

Introduction

Several proficiency testings propitiate the participant laboratories: evaluation of the performance and continuous monitoring; evidence of reliable results; identification of problems related to the systematic nature of assays; possibility of taking corrective and/or preventive actions; evaluation of the efficiency of internal controls; determination of the performance characteristics and validation of methods and technologies; standardization of the activities in the market and national and international recognition of assays results. Although the number of proficiency testing providers in the food industry is great, the costs charged for the participation in the schemes are abnormally high, which makes it impractical for laboratories to participate in many rounds (1).

An evaluation of pesticides residues in food is extremely important to indicate to producers how good agriculture practice is and for studying prevention and control actions before these chemical contaminants affect the environment and the health of the population or cause serious economic losses. The international market demands reduced levels of residues in these contaminants in foods (1).

Due to its potential harm to people's health, the environment, and the consequent necessity of preventative actions, the standards of these residues in foods or other matrices are very low (sub-mg/kg, mg/kg) (2). The data on residues are used in the evaluation of exposition by authorities from the health and security area where accurate measurements are required in any level of residue including values below limit of detection (LOD) (3–5). The main challenge for the laboratories is to be able to analyze a great number of different pesticides (about 400 active ingredients) having validated methodologies for a great number of foods, and demonstrate the ability to trustfully detect occurrences with values below the LOD, which is frequently low (6).

Multi-residues methods are normally used for the determination of hundreds of pesticides in one single analysis. These methods cannot be used for substances that do not share physical chemical properties with a great number of pesticides, for which specific methods are used. Different techniques of extraction have been used for the preparation of samples in multi-residues analyses. The technique of extraction with solvent

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followed by liquid–liquid partition and clean-up is still used frequently due to its simplicity. However, in aiming for optimization, toxics, and inflammable cost reduction, other techniques were developed, such as: pressurized liquid extraction (PLE), micron-assisted extraction (MAE), and solid-phase extraction (SPE). Beyond the miniaturized techniques, there is also: solid-phase micron-extraction (SPME), matrix solid-phase dispersion (MSPD), stir-bar sorptive extraction (SBSE), and supercritical fluid extraction (SFE) (2). All these techniques lead to a solvent-use reduction, but some are extremely complex, slow and need specialized personnel for its development. The extraction technique called QuEChERS (quick, easy, cheap, effective, and disembarrasses - fast, easy, cheap, efficient, and safe) was recently developed in aiming for high quality in extractions and minimizing the practical difficulties of the cited methods since it uses a lesser number of steps and simpler materials and glasses (7).

The chromatographic techniques coupled to selective detectors [electron capture detector (ECD), flame photometry detector (FPD), nitrogen phosphorous detector (NPD), fluorescence detector (FD), diodes arrangement detector (DAD), and UV detector, and to mass spectrometers (MS)] have been used and have been considered appropriate for multi-residues analyses (2).

Independent of the method, the laboratories must permanently evaluate their efficiency, comparing findings to previously defined criteria of acceptance. A widely used criteria, for instance, is that the method must be able to furnish a mean recovery tax between 70–120% (8). The results obtained in proficiency testing are also tools for the identification of the possible critical points in all the steps of the methodology analysis and for the set up of corrective actions and the improvement of measurements.

This work presents the methodologies used and the performance obtained by the participants of the third round of the proficiency testing for the determination of pesticides in foods organized by INMETRO and INCQS/FIOCRUZ. This round focuses on the determination of pesticides in mango pulp.

Organization of the Proficiency Testing

Preparation and sending of the test item

The mango pulp samples were acquired in a city market in Rio de Janeiro, and the absence of pesticide residues was confirmed through analytical determination. So, this pulp was considered adequate for being spiked with pesticides. The mango pulp was peeled, cut in cubes, and triturated using a blender. Part of the exempt pulp was separated and frozen to be used as a blank matrix. The remaining pulp was spiked with deltamethrin, ethion, fenitrothion, malathion, and permethrin pesticide solutions, then homogenized and divided in aliquots of approximately 50 g, which were then transferred to glass bottles and stored in a freezer (–15ºC) before being sent to the participant laboratories. A list of possible 49 pesticides present in the mango pulp sample was informed to the participants as well as that only one to six of these would be indeed spiked.

The solutions of pesticides were prepared from their reference materials following the Good Laboratory Practice standards. The final theoretical mass fractions of the pesticides added to the mango pulp were: 0.249 mg/kg (deltamethrin); 0.128 mg/kg (ethion); 0.126 mg/kg (fenitrothion); 0.074 mg/kg (malathion); 0.281 mg/kg (permethrin).

Ten spiked samples representative of the lot were separated for the homogeneity test. Each test item was divided in two parts, and each part was analyzed in an independent way. For the stability test, the mango pulp samples were evaluated in three different periods of time, comprehended between the moment the laboratories received the test item and the deadline for the sending of results. In this period, the samples were all stored at –15ºC. The one-way analysis of variance (ANOVA) was used for the evaluation of the homogeneity of mango pulps regarding the concentration of the spiked pesticides, as recommended in the ISO Guide 35 (9). The analysis of residues was also used to evaluate the stability of the mango pulp samples compared with the theoretical spiked value of each pesticide. The variance of the values used in the linear regression was also estimated through ANOVA as recommended in the ISO Guide 35 (9).

Each participant laboratory received three test items containing approximately 50 g of the frozen sample: two of them containing the spiked pulp and one sample pulp exempt of pesticides (blank matrix).

Orientation to the participant laboratories

Twenty-four laboratories were subscribed in the third round of the INMETRO-INCQS Scheme for the Determination of Pesticides in Foods, and twenty laboratories (83.3%) sent the results. The laboratories were instructed to analyze each of the received samples in duplicate. Being so, each of them informed at most for each pesticide twelve analytical results (four per sample). The analytical results were reported in mg/kg. The laboratories also recorded the techniques and equipments used in the assays and some parameters of the methodology, such as the recovery (%), LOD, and the limit of quantification (LOQ).

Establishment of the assigned values

To minimize the influence of the extreme results, the assigned values for each pesticide were calculated using the robust statistics presented in Item 5.6 of the lSO 13528:2005 (10). The results obtained by INCQS in the homogeneity test were also included in this statistical analysis.

Evaluation of the laboratories performance

Coefficient of variation

The coefficient of variation (CV) was used to evaluate the reproducibility of the data sent by the participant laboratories. According to Codex Alimentarius (Alinorm 03/24A) (11), the CV must be ≤ 15% for pesticides analyses in spiked foods before the extraction, and in mass fraction levels > 0.1 mg/kg and ≤ 1 mg/kg.

Z-score

For the qualification of the results of the laboratories, the Z-score was calculated, which represents a measure of the relative distance of the result of the laboratory in relation to the assigned

value established for the pesticide. The values of Z-score were interpreted as shown below:

$|z| \leq 2$: Satisfactory result
$2 < |z| < 3$: Questionable result
$|z| \geq 3$: Unsatisfactory result

Confidence ellipse

Since a pair of the spiked sample was sent to each laboratory, confidence ellipse graphs, or the Youden plot (12), was constructed, which aimed to verify compatibility among laboratories. The experimental planning for the construction of the Youden plot foresees the distribution of a pair of similar samples, not necessarily of equal concentrations but similar ones. In the plot, each laboratory was represented by a point. The straight lines that pass in the laboratories averages in *x* (relative result of one of the analyzed sample) and in *y* (relative result of the other analyzed sample) divide the diagram in quadrants. When only random errors are present, the points must be distributed in a uniform way in all the quadrants. If the points are more concentrated in the superior right and inferior left one, that is interpreted as evidence of occurrence of bias, which means that the laboratories tend to get high or low values in both the samples of the pair (13).

Analytical viability and analytical capacity

The analytical viability (AV) of the participant laboratories for the determination of the spiked pesticides was calculated for this proficiency testing. The AV was determined using the Equation 1:

$$AV = 10^{-4} \times (a \times b) \quad \text{Eq. 1}$$

where a = percentage of laboratories that analyzed the pesticide, and b = percentage of satisfactory results for that pesticide.

The result represents the viability of determination of one pesticide for the set of laboratories that participated in the round.

The Analytical capacity (AC) of each participant laboratory was also determined, using the Equation 2:

$$AC = 10^{-4} \times (a \times b) \quad \text{Eq. 2}$$

where a = percentage of pesticides analyzed for each laboratory, and b = percentage of satisfactory results for the analyzed pesticides.

In this analysis, the results reported as "not detected" were not considered unsatisfactory.

Results and Discussion

Homogeneity study

Despite efforts to ensure homogeneity of the test item prepared for a proficiency test and other inter-laboratorial studies, these materials as a rule have a certain degree of heterogeneity. When this material is divided in portions (test items) and distributed to the laboratories, it presents a small variation in the composition among them. In this study it was determined through the ANOVA if the variation in the composition among the distributed samples is sufficiently small enough for the purpose of proficiency testing.

The values of *F* calculated through ANOVA were compared with the value of tabled *F* with a 95% confidence level. As shown in Table I, the samples were considered homogeneous regarding the concentration of the pesticides deltamethrin, ethion, fenitrothion, and malathion. The obtained values had not show significant variation within samples (lines) in comparison with the variations between samples once the values of calculated *F* are less than the critical *F* for a confidence level of 95% for these pesticides. However, for the permethrin pesticide, it obtained a degree of heterogeneity in the test items. The dispersion of the relative values obtained for permethrin in each of the 10 analyzed samples in the homogeneity test is shown in Figure 1.

Through a visual analysis of this graph, it can be assumed that the cause of the inhomogeneity in permethrin is the values obtained for the concentration of permethrin in sample 10, which are not compatible with the values of the other samples.

To evaluate if the heterogeneity of permethrin pesticide significantly influences the result of the participant laboratories, the homogeneity test was done again, this time using the approach presented in ISO 13528: 2005 (10). The standard deviation (SD) between samples (s_s) is calculated and compared with the SD of the proficiency test, which is represented by the SD calculated through the robust algorithm, also presented in ISO 13528: 2005

Table I. ANOVA Results for the Homogeneity Test

Pesticide	F	P-value	Critical F
Deltamethrin	2.880	5.739×10^{-2}	3.020
Ethion	1.355	3.200×10^{-1}	3.020
Fenitrothion	1.235	3.712×10^{-1}	3.020
Malathion	2.863	5.837×10^{-2}	3.020
Permethrin	3.234	4.077×10^{-2}	3.020

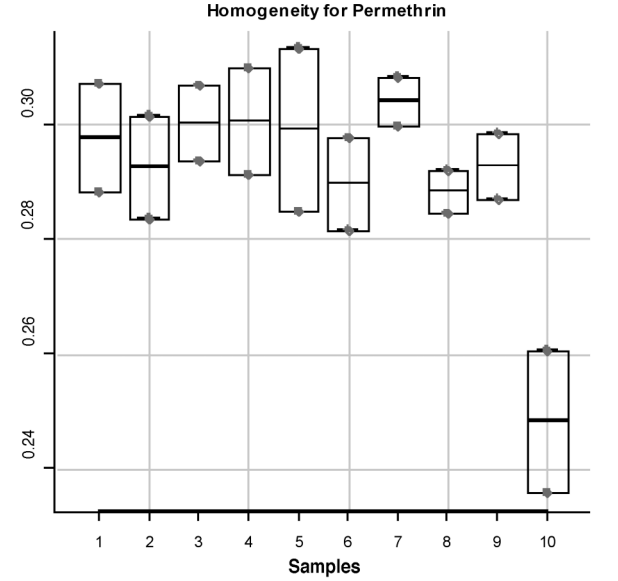

Figure 1. Graph of dispersion in the study of homogeneity of permethrin.

(10). The samples were considered sufficiently homogeneous since they comply with the condition established in this norm ($s_s \leq 0.3 \times SD$). The value of s_s was calculated, and the condition above has been answered. It shows that the item of test had been properly homogeneous for this proficiency testing with respect to the pesticide permethrin.

Stability study

To ensure that the samples used in the proficiency test were stable in this third round, a stability study was done to identify if there is a reproducibility of the results along time. The evaluation was done using the analysis of residues of the linear regression. Table II represents the results obtained in the estimate of the variance of the values used in the linear regression according to ISO Guide 35 (9).

Considering that the angular coefficient of the straight line obtained in the regression analysis was ~0 for all the studied pesticides, the samples were considered stable. The results had also shown that the calculated values of P was higher than 0.05 (95% confidence), which means there was no significant difference between the values, so the test items were considered stable in the study conditions.

Table II. Angular Coefficient and P-Value Obtained in the Regression Analysis

Pesticide	Angular coefficient	P-value
Deltamethrin	–0.0008624	5.29×10^{-1}
Ethion	0.0002370	5.18×10^{-1}
Fenitrothion	–0.0003599	1.82×10^{-1}
Malathion	–0.0001464	2.67×10^{-1}
Permethrin	–0.0007196	5.82×10^{-1}

Table III. Assigned Values Obtained Through the Robust Average

Pesticide	Assigned value (mg/kg)	SD (mg/kg)
Deltamethrin	0.219	0.073
Ethion	0.106	0.023
Fenitrothion	0.100	0.026
Malathion	0.045	0.019
Permethrin	0.239	0.047

Determination of the assigned values

The assigned values of the pesticides used in this proficiency testing, as well as their respective SD, were calculated according to statistical procedure described in Item 5.6 of the Norm lSO 13528: 2005 (10) and are presented in Table III.

Lab 16 detected the pesticide fenitrothion; however, its results were below the LOQ reported for the proper laboratory, so it was not considered in the calculation of the assigned value.

Evaluation of the performance of the participant laboratories

The data reported for the proficiency test participant laboratories was treated according to the procedures of ABNT ISO/IEC Guide 43-1 (14). Table IV presents the mean mass fraction values among the samples obtained by the laboratories as well as the CV and the Z-score values.

Reproducibility of the laboratories results

For the calculation of the CV, it was considered the average of the results obtained for one pesticide concentration for the two spiked samples reported by a laboratory. Lab 18 detected the

Table IV. Average Values Obrained by the Laboratories (mg/kg), Coefficients of Variation (CV), and Z-Score

	Deltamethrin			Ethion			Fenitrothion			Malathion			Permethrin		
Lab	Mean	CV	Z	Mean	CV	Z	Mean	CV	Z	Mean	CV	Z	Mean	CV	Z
Lab 1	0.354	5.6	1.8	0.139	1.3	1.4	0.130	2.7	1.2	0.101	1.7	2.9	0.223	4.8	–0.3
Lab 2	0.418	2.5	2.7	0.450	9.4	15.3	0.218	8.1	4.5	ND*	–	–	0.453	19.5	4.5
Lab 3	0.162	7.4	–0.8	0.085	11.2	–0.9	0.074	4.3	–1.0	0.051	7.0	0.3	0.210	7.7	–0.6
Lab 4	0.162	7.4	–0.8	0.085	11.2	–0.9	0.074	4.3	–1.0	0.049	20.8	0.2	0.234	3.8	–0.1
Lab 5	0.189	6.0	–0.4	0.119	7.1	0.6	0.123	7.7	0.9	NT†	–	–	0.213	2.5	–0.5
Lab 6	0.275	5.1	0.8	0.113	3.1	0.3	0.123	2.9	0.9	0.050	0.0	0.3	ND	–	–
Lab 7	0.223	13.0	0.0	0.110	2.9	0.1	NT	–	–	ND	–	–	0.174	7.3	–1.4
Lab 8	NT	–	–	NT	–	–	NT	–	–	NT	–	–	NT	–	–
Lab 9	0.209	10.1	–0.1	0.100	1.4	–0.3	0.088	2.6	–0.5	0.030	3.0	–0.8	0.271	6.2	0.7
Lab 10	0.150	9.4	–1.0	0.092	13.1	–0.7	0.102	11.8	0.1	0.035	10.2	–0.5	0.205	10.3	–0.7
Lab 11	0.295	2.4	1.0	ND	–	–	ND	–	–	ND	–	–	ND	–	–
Lab 12	0.213	8.3	–0.1	0.123	2.9	0.7	0.103	1	0.1	0.030	1.2	–0.8	0.335	4.2	2.0
Lab 13	0.159	3.6	–0.8	0.106	5.0	0.0	NT	–	–	ND	–	–	0.250	1.4	0.2
Lab 14	NT	–	–	NT	–	–	NT	–	–	NT	–	–	NT	–	–
Lab 15	0.168	2.1	–0.7	0.121	1.5	0.7	0.090	0.0	–0.4	0.050	0.0	0.3	0.199	4.4	–0.9
Lab 16	NT	–	–	ND	–	–	0.023	–	–3.0	ND	–	–	ND	–	–
Lab 17	0.223	1.6	0.0	0.087	1.8	–0.9	0.090	0.2	–0.4	0.054	1.0	0.5	0.489	1.1	5.3
Lab 18	0.140	–	–1.1	0.090	–	–0.7	0.092	–	–0.5	0.031	–	–0.7	0.200	–	–0.8
Lab 19	NT	–	–	ND	–	–	NT	–	–	ND	–	–	NT	–	–
Lab 20	NT	–	–	0.006	6.0	–4.4	0.009	18	–3.5	0.008	5.7	–1.9	NT	–	–
Lab 21	0.300	3.0	1.1	0.118	1.0	0.5	0.111	4.2	0.4	0.069	1.0	1.2	0.291	0.8	1.1

*ND= Not detected; †NT= Not tested

pesticides in only one of the samples; therefore, it did not have its CV calculated. In accordance with the obtained results presented in Table IV, only Lab 2, Lab 4, and Lab 20 presented CV > 15% for the pesticides permethrin, malathion, and fenitrothion, respectively. However, only the result of Lab 2 for permethrin can be considered unsatisfactory because the other laboratories presented results in a mass fraction inferior to the one stipulated in Codex Alimentarius (> 0.1 mg/kg and ≤ 1 mg/kg), so that the limit (CV > 15 %) can be considered (11). According to Figure 2, permethrin displayed a big dispersion of the values gotten for this laboratory beyond its incompatibility with the other laboratories and with values distant from the average.

Many participant laboratories reported results for only one sample, so it was not possible to calculate their CV. All the other laboratories obtained acceptable CV according to the Codex Alimentarius (Alinorm 03/24A) (11). It is important to point out that the analysis of the laboratories' results reproducibility presented in Table IV considers the average results obtained in the sample analysis. This does not evaluate repeatability of the laboratory (analysis of each replicate, of each portion, of each sample), as well as the reproducibility of the analysis of one single sample. It is important to note again that it was requested of each laboratory to analyze two portions of each sample. It was observed that some laboratories presented high dispersion in its measurements. This indicates a deficiency in their repeatability and/or reproducibility.

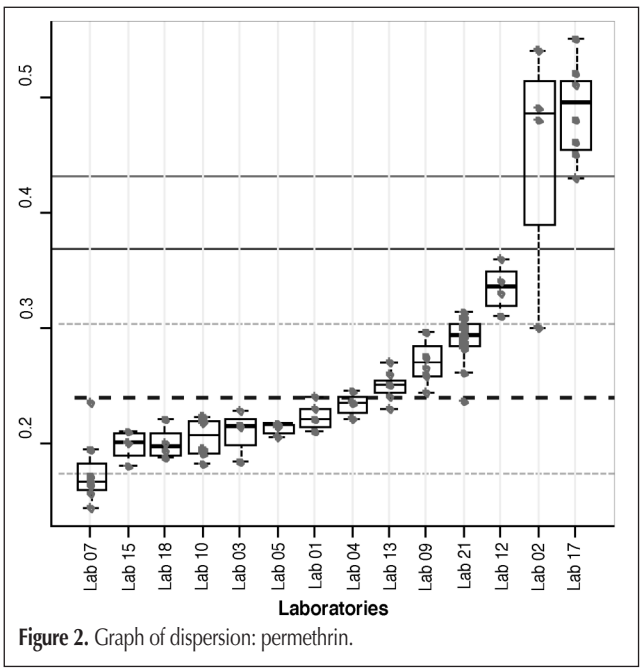

Figure 2. Graph of dispersion: permethrin.

Calculation of Z-score

The evaluation of performance of the participant laboratories and the INCQS, expressed through Z-score, is presented in Table IV.

"Not detected" (ND) results were considered unsatisfactory results. According to the obtained results, ten of the twenty participant laboratories obtained questionable or unsatisfactory results for at least one of the analyzed pesticides. From a total of eighty-three reported results (average values), approximately 71% was considered satisfactory (59 results), 2.4% was considered questionable (two results), and 26% unsatisfactory (22 results, considering ND). Seven laboratories did not detect at least one of the pesticides present in the samples.

Confidence ellipse

Figures 3–5 present the graphs of the confidence ellipse (Younden plot) for the pesticides ethion, fenitrothion, and permethrin. It can be observed that the results of Lab 2 are out of the plot because its results are not compatible with the results of the other participants. This laboratory also presented unsatisfactory results for these pesticides in the performance evaluation through Z-score. Some laboratories also in prominence, although their results inside of the plot are far away from others throughout the biggest axle of the ellipse, which indicates that

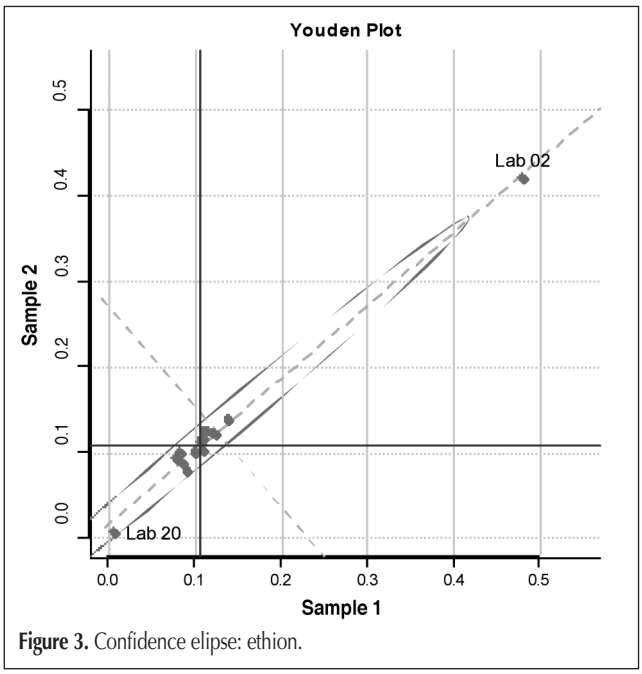

Figure 3. Confidence elipse: ethion.

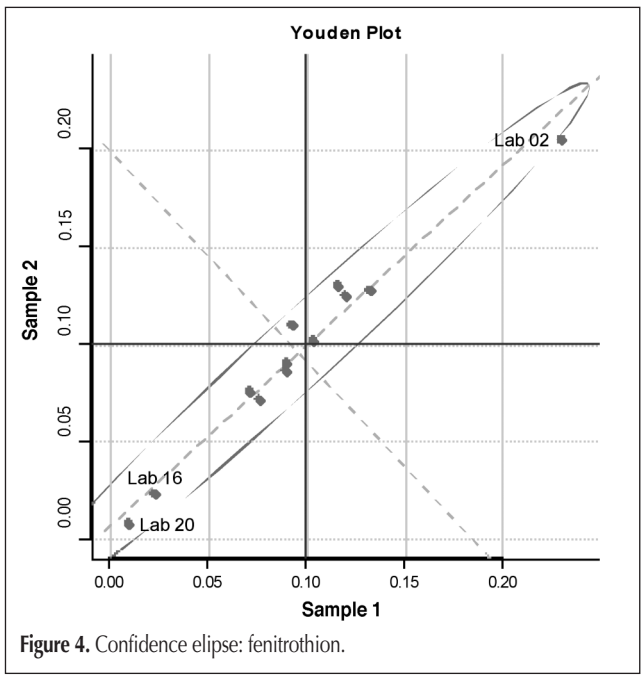

Figure 4. Confidence elipse: fenitrothion.

their results are subjected to systematic errors. All the graphs display a format extended in the direction of the biggest axle of the ellipse with an inclination that is ~45°. This indicates an occurrence of systematic errors bigger than random errors. Such trends can be related to the methodology used by the laboratories.

Analytical viability and analytical capacity

If the AV for a pesticide is equal to 1, all the participant laboratories are analyzing it and are doing so in a satisfactory way. If the AV for a pesticide is equal to 0, no laboratories were able to analyze it in a satisfactory way.

According to Table V regarding the AV, the following shows the order of difficulty in the determination of the pesticides by the laboratories of this proficiency testing: deltamethrin < ethion < fenitrothion = permethrin <malathion.

If the CA for a laboratory equals 1, it analyzed all the pesticides present in the test item and did it in a satisfactory way. If the CA equals 0, the laboratory did not analyze any of the pesticides present in a satisfactory way, meaning it did not detect the pesticide or got a unsatisfactory Z-score. It was observed that of the twenty participant laboratories, eleven (55%) had reached CA indices between 0.80–1.0; two laboratories (10%) reached CA indices between 0.60–0.80, and five laboratories (25%) reached CA indices less than 0.60. Lab 8 and Lab 14 analyzed none of the pesticides present in the sample, so the CA for these laboratories was not determined.

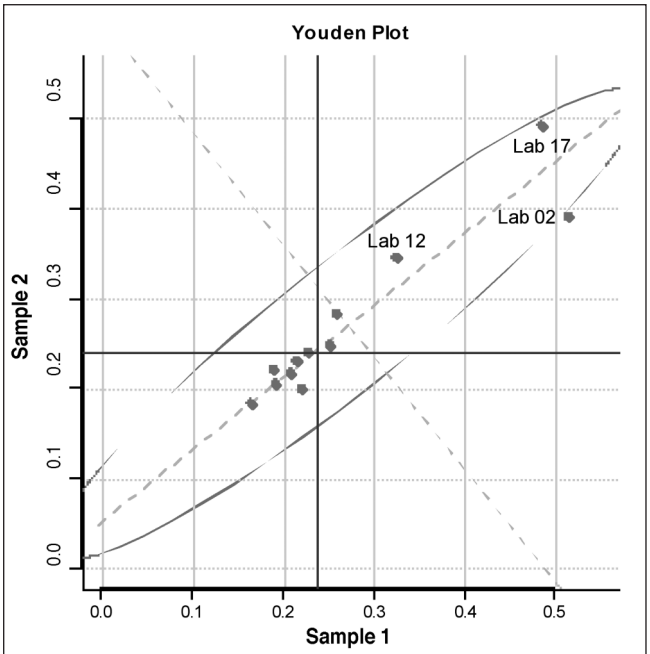

Figure 5. Confidence elipse: permethrin.

Table V. Viability of Determination of the Pesticides Spiked in the Sample

Pesticide	% of Labs analyzing the pesticide (*a*)	% of satisfactory results for pesticide (*b*)	VA* = 10^{-4} a × *b*
Deltamethrin	75	93	0.70
Ethion	90	72	0.65
Fenitrothion	75	73	0.55
Malathion	85	59	0.50
Permethrin	80	69	0.55

Pesticides found by the laboratories

Table VI shows which laboratories that detected pesticides different from the ones spiked in the sample. For example, Lab 18 found in sample 3 the same pesticides spiked in samples 1 and 2.

Methodologies used by participant laboratories

A summary of the methods used by the laboratories in each analytical step can be observed in Table VII. In this round, the participant laboratories were asked to supply some information about the techniques and equipment used in the assays and on the inherent parameters of the methodology. From the information presented in Table VII, it can be observed that among the

Table VI. Pesticides Found by the Laboratories

Laboratory	Detected pesticides
Lab 8	Diazinon, Gamma-HCH
Lab 10	Total DDT
Lab 11	Endrin, Pirimiphos-methyl
Lab 16	Aldicarb, Total DDT, Dichlorvos, Dicofol, Fenarimol
Lab 18	Total DDT, (Deltamethrin, Ethion, Fenitrothion, Malathion, Permethrin)*
Lab 19	Total DDT

* Pesticides found in sample 3.

Table VII. Methodology Used by the Participant Labs

Analytical step	Method	Number of times reported
Extraction	LLE	5
	QuEChERS	1
	Modified Luke	7
Solvent	Acetone	2
	Acetonitrile	1
	Dichloromethane	1
	Ethyl Acetate	2
	Hexane	1
Clean-up	MSPD	1
	GPC	1
	C18	1
	Centrifuge	1
Chromatography	GC–ECD	9
	GC–FPD	3
	GC–MS or MS–MS	5
	GC–NPD	3
	HPLC–MS or MS–MS HPLC–UV	2
Injection mode (GC)	Splitless	15
	On column	1
Calibration curve	Matrix matched	7
	Solvent	10

laboratories that reported these information only five used the technique of high-performance liquid chromatography (HPLC). The other laboratories used the technique of gas chromatography (CGAR) and the splitless sample injection method. In this round, a great number of the participant laboratories used the mass spectrometry detection, which demonstrates an evolution in infrastructure of the laboratories. One of the laboratories found incompatible results compared to the other ones for three of the analyzed pesticides. The analytical methodology used by this laboratory was MSPD and acetonitrile as the solvent of extraction. The application of MSPD is based on the simplification of the stage of preparation of sample for matrices with high fat content. However, as for any other technique, some of its procedures must be analyzed with caution. In the case of the MSPD, it is recommend to wash and pre-condition the dispersant material for the elimination of interferents and exercise caution to prevent the degradation of the analyte while waiting the analysis (15). Moreover, the small amount of sample used in this method (0.1–2 g) can lead to an unrepresentative sampling of all. As a solvent of extraction, for instance, acetonitrile was used by some participant laboratories. Despite its higher toxicity and cost, acetonitrile has an advantage because of its high polarity, allowing a lesser amount of fats to be extracted together with pesticides. It can also be verified that extraction with the QuEChERS method is not yet a widely used method by the pesticide analyses laboratories.

Due to the great number of variables, no concrete correlation can be defined between the employed techniques and the result of the laboratory. But the proper laboratory can evaluate step-by-step its procedures and come to the conclusion about the improvements that could be adopted.

The laboratories also were questioned about the accreditation of testing they conducted. Among the 18 laboratories that reported this information, nine have accreditation for at least one of the tests issued.

Conclusions

The establishment of corrective actions and the continuous participation in similar proficiency testing are great tools for measuring the improvement of laboratories.

Regarding the performance of the laboratories as a role, it can be considered satisfactory for those that reported results, once most of them (71%) got a satisfactory Z-score. However, it fits to note that 50% of the laboratories that reported results for at least one of the pesticides present in the samples got at least one unsatisfactory or questionable result. This performance is reflected in the CA index: only 35% of the participant laboratories got CA = 100%; the other 15% of the laboratories got CA = 0.

For the laboratories that found results incompatible with others (unsatisfactory or questionable, false-positives results, or did not detect any of the pesticides present in the sample), corrective actions should be adopted for the improvement of its measurements. A detailed evaluation, including the receiving of materials and its storage, the fulfilling of the Form for Results Register, and the evaluation of all the steps of the analysis methodology, is important for the identification of critical points.

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