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IMEP-37: Determination of pesticides in grapes

Interlaboratory Comparison Report

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IMEP®

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Executive Summary

The institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate-General of the European Commission, operates the International Measurement Evaluation Programme (IMEP). It organises interlaboratory comparisons (ILC's) in support to EU policies. This report presents the results of a proficiency test exercise (PT) which focussed on the determination of pesticides in grapes in support to Regulation 396/2005/EC of the European Parliament and of the Council on maximum residue levels of pesticides in or on food and feed of plant and animal origin. This PT was run in collaboration with the European Union Reference Laboratory for Pesticide Residues in Fruit and Vegetables (EURL-FV) in Almeria, Spain.

Eighty-seven participants from thirty-three different countries registered to the exercise, of which eighty-one reported results. From these eighty-one participants, forty were from EU countries while forty-one were from outside the EU.

The test item was a grape sample spiked with 20 selected pesticides (azoxystrobin, carbendazim, chlorpyrifos, cyprodinil, difenoconazole, fenhexamid, fludioxonil, imidacloprid, indoxacarb, iprodione, kresoxim methyl, lambda-cyhalothrin, methoxyfenozide, myclobutanil, penconazole, pyraclostrobin, pyrimethanil, quinoxyfen, tebuconazole and triadimenol). The assigned values used to benchmark the participants were obtained as the average of results reported by five expert laboratories having demonstrated experience in the analysis of pesticides in vegetable and fruit matrices. The standard uncertainties related to the assigned values (u_{ref}) were calculated combining the uncertainty of the characterisation (u_{char}) with a contribution for homogeneity (u_{bb}) and for stability (u_{st}). u_{char} was calculated following the ISO Guide 35.

Participants were invited to report their measurement uncertainties. This was done by the majority of laboratories having submitted results in this exercise.

Laboratory results were rated with z- and zeta (ζ-) scores in accordance with ISO 13528 and ISO 17043. The z-score compares the participant's deviation from the reference value with the standard deviation for proficiency assessment $\hat{\sigma}$ used as common quality criterion. The ζ-score states if the laboratory result agrees with the assigned value within the respective uncertainties. The standard deviation for the proficiency assessment, $\hat{\sigma}$, was set by the advisory board of this PT at 25% for the 20 measured pesticides based on previous experience with similar measurands. Participants were not scored for triadimenol due to the large u_{ref} associated to the assigned value.

The percentage of satisfactory z-scores for the 19 scored pesticides ranged from 81 % (carbendazim) to 97 % (azoxystrobin, penconazole, pyrimethanil). When analysing the results of the group of non-EU countries separately, similar results were obtained. It can be concluded that the performance in this PT is satisfactory for the laboratories world-wide.

1 Introduction

The IMEP-37 exercise was organized to assess the world-wide performance of control laboratories on the determination of pesticides in vegetable food.

The PT supports the implementation of Regulation 396/2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin [1]. According to this regulation official controls of maximum residue levels of pesticides have to be carried out. Indeed, one of the most important drivers behind pesticide residue analysis remains regulatory compliance. Local requirements for maximum residue levels for a variety of pesticides must be met before food products can enter a particular market [2]. Pesticide residue analysis is a challenging area in food analysis because of the large number of target analytes and the wide variety of complex food matrices [3]. Therefore reliable and sensitive analytical methods that are able to quantify the low limits set by legislation are needed [4]. Regarding the pesticides investigated in this study, legal limits are set by legislation for pesticides in table grapes ranging from 0.2 mg kg^{-1} (for lambda-cyhalothrin and penconazole) to 10 mg kg^{-1} (for iprodione) [5].

The PT was run in 2013 in collaboration with the European Union Reference Laboratory for Pesticide Residues in Fruit and Vegetables (EURL-FV) in Almeria (Spain) making use of a grape homogenate. Grapes were grown in Almeria in the southeast of Spain. The grapes were treated post-harvest using commercial formulations and analytical standards which were applied using a microspray technique. In total 20 pesticides were spiked (azoxystrobin, carbendazim, chlorpyrifos, cyprodinil, difenoconazole, fenhexamid, fludioxonil, imidacloprid, indoxacarb, iprodione, kresoxim methyl, lambda-cyhalothrin, methoxyfenozide, myclobutanil, penconazole, pyraclostrobin, pyrimethanil, quinoxyfen, tebuconazole and triadimenol) in concentrations ranging from 0.031 mg kg^{-1} (lambda-cyhalothrin) to 0.332 mg kg^{-1} (difenoconazole).

This report summarises and evaluates the outcome of IMEP-37.

2 IMEP support to EU policy

IMEP is owned by the JRC – IRMM and provides support to the European measurement infrastructure in the following ways:

IMEP disseminates metrology from the highest level down to routine laboratories. These laboratories can benchmark their measurement result against the IMEP certified reference value which is established according to the metrological best practice.

IMEP helps laboratories to assess their estimate of measurement uncertainty. The participants are invited to report the uncertainty on their measurement results. IMEP integrates the estimate into the scoring, and provides assistance for the interpretation.

IMEP supports EU policies by organising interlaboratory comparisons in the frame of specific EU legislation, or on request of a specific EC Directorate-General. IMEP-37 provided specific support to the following stakeholders:

- The European Cooperation for Accreditation (EA) in the frame of a Memorandum of Understanding on a number of metrological issues, including the organisation of interlaboratory comparisons. National accreditation bodies were invited to nominate a limited number of laboratories for participation in IMEP-37. Mrs Hanna Tugi from the Polish Centre for Accreditation (PCA) liaised between EA and IMEP for this ILC.
- The Asia Pacific Laboratory Accreditation Cooperation (APLAC) in the frame of collaboration with APLAC. Mrs Cynthia Chen (APLAC PT committee) liaised between APLAC and IMEP, announcing the exercise to the accreditation bodies in the APLAC network.
- The InterAmerican Accreditation Cooperation (IAAC). Mrs Barbara Belzer liaised between IAAC and IMEP. She announced the exercise to the accreditation bodies in the IAAC network.

3 Scope and aim

The scope of this PT was to monitor the performance of control laboratories world-wide in the determination and quantification of pesticide residues in vegetable food.

The assessment of the measurement results followed the administrative and logistic procedures of IMEP, which is accredited according to ISO 17043:2010 [6]. This PT is identified as IMEP-37.

4 Set-up of the exercise

4.1 Time frame

The exercise was announced on the IMEP webpage in May 2013 (Annex 1). Additionally, the exercise was announced to EA, to APLAC and to IAAC. These announcements were made on 6 May 2013 (Annexes 2-4).

Registration was opened till 30 August 2013. The sample dispatch was done during the second half of October 2013. The deadline for reporting results was 20 December 2013.

Expert laboratories received the samples during the second half of October 2013 and they were asked to report within two months after sample reception.

4.2 Confidentiality

The following confidentiality statement was made to EA, IAAC and APLAC: "Confidentiality of the participants and their results towards third parties is guaranteed." In the case of EA the following was added: "However, IMEP will disclose details of the participants that have been nominated by EA to the EA working group for ILCs in Testing coordinator for this exercise. The EA accreditation bodies may wish to inform the nominees of this disclosure."

4.3 Distribution

Test items were dispatched to the participants in the period 7 to 16 October 2013. Each participant received a package containing:

- one bottle containing approximately 220 g of the test item;
- one bottle containing approximately 220 g of blank material;
- a "Confirmation of Receipt" form to be sent back to IRMM after receipt of the test material (Annex 5);
- an accompanying letter (Annex 6).

4.4 Instructions to participants

Participants were asked to perform two or three independent measurements and report on the reporting website their calculated mean (mg kg^{-1}), the associated expanded uncertainty (mg kg^{-1}), together with the coverage factor and the technique used.

Participants received an individual code to access the online reporting interface, to report their measurement results and to complete the related questionnaire. The questionnaire was used to extract all relevant information related to measurements and laboratories (Annex 7).

Participants were asked to follow their procedure as used in routine analyses as closely as possible.

5 Test material

5.1 Preparation

The organic grapes were grown in Almeria (southeast of Spain). The test items (1 treated and 1 blank) were prepared by the European Union Reference Laboratory for Pesticide Residues in Fruit and Vegetables (EURL-FV) in Almeria, Spain. Eighty kilograms of grapes were treated using a microspray. Some of the pesticides were applied as commercial pesticide formulations dissolved in water (azoxystrobin, carbendazim, cyprodinil, difenoconazole, fenhexamid, fludioxonil, imidacloprid, indoxacarb, iprodione, kresoxim methyl, methoxyfenozide, myclobutanil, penconazole, pyrimethanil, tebuconazole, lambda-cyhalothrin and triadimenol). Others were applied in the form of analytical standards dissolved in organic solvent (chlorpyrifos, pyraclostrobin and quinoxyfen). After all the pesticides had been spiked, a portion of the treated grapes was taken and analysed to check if the residue levels present were close to the target levels or whether any additional spraying was necessary. When the residue levels in the grapes were close to the target ones, the entire sample was frozen and processed using liquid nitrogen and a mincer. The frozen minced grapes were mixed in a constantly-spinning container until a homogeneous material was obtained. 210-250 g portions of the well-mixed homogenate

were weighed out into screw-capped polyethylene plastic bottles, sealed and stored in a freezer at -20°C prior to the shipment.

The grapes used for the production of the blank test item were organically grown in the same field as the test item. A homogenate was prepared in the same way as the treated test item described above, but without addition of pesticides.

5.2 Homogeneity and stability study

Homogeneity and stability studies were performed by the European Union Reference Laboratory for Pesticide Residues in Fruit and Vegetables (EURL-FV) in Almeria, Spain. Ten bottles of the treated test item were randomly chosen from those stored in the freezer and analyses were performed on duplicate portions taken from each bottle. The injection sequence of the twenty extracts that were analysed by GC and LC was determined using a table of randomly-generated numbers. The quantification by GC and LC was performed using calibration curves constructed with matrix-matched standards prepared from the 'blank' grape test item.

Homogeneity was evaluated according to the test proposed by IUPAC [7]. Of the twenty pesticides, one (tebuconazole) failed for this test (Annex 8). Nevertheless it was decided to include an uncertainty contribution related to homogeneity, u_{bb}, in the uncertainty associated to the assigned value (u_{ref}) as recommended by ISO 13528 [8], not only for tebuconazole but for all the measurands.

The stability study was conducted by analysing the test item at two different time intervals. The material proved to be adequately stable for the twenty pesticides during the six weeks that elapsed between the dispatch of the samples and the deadline for reporting (Annex 8).

The contribution from homogeneity (u_{bb}) and stability (u_{st}) to the uncertainty of the reference value (u_{ref}) was calculated using softCRM [9].

6 Reference values, uncertainties and $\hat{\sigma}$

6.1 Assigned value X_{ref}

The assigned values for the twenty measurands were determined by the following five expert laboratories, which were selected based on their good performance in past PTs on the determination of pesticides in food matrices organised by the EURL-FV of Almeria:

- Austrian Agency for Health and Food Safety (Ages), Austria

- Laboratoire du SCL de Montpellier (SCL), France

- European Union Reference Laboratory for Pesticide Residues in Fruit and Vegetables (EURL-FV), Almeria, Spain

- European Union Reference Laboratory for Pesticide Residues in Fruit and Vegetables (EURL-FV) - Laboratorio Agroalimentario de Valencia, Spain

- National Food Agency (NFA), Sweden

Expert laboratories were asked to analyse two bottles of the test item on two different days (one bottle/day) performing three independent replicates per bottle (six replicates/measurand), using the method of their choice. Experts were also required to report their results together with the associated expanded uncertainty and with a clear and detailed description on how the uncertainty was estimated.

The mean of the independent means provided by the expert laboratories was used to derive the assigned value (X_{ref}) for this PT according to ISO Guide 35:2006 [10].

Ages and SCL analysed the measurands with the QuEChERS method (NF EN 15662), which uses a single extraction with acetonitrile followed by liquid chromatography coupled to triple quadrupole mass spectrometry (LC-MS/MS) and gas chromatography coupled to triple quadrupole mass spectrometry (GC-MS/MS).

The EURL-FV used two different extraction techniques, one extraction with acetonitrile followed by LC-MS/MS and one extraction with ethyl acetate followed by GC-MS/MS.

The EURL-FV Laboratorio Agroalimentario de Valencia used the QuEChERS method with an extraction with acetonitrile followed by LC-MS/MS.

NFA used an extraction with ethyl acetate and determination with GC-MS/MS and LC-MS/MS.

Details about the methods used by the expert laboratories are given in Annex 9. The mean results together with their associated expanded uncertainties reported by the expert laboratories are shown in Annex 10.

6.2 Associated uncertainty u_{ref}

The associated uncertainties (u_{ref}) of the assigned values were calculated combining the uncertainty of the characterization (u_{char}) with the contributions for homogeneity (u_{bb}) and stability (u_{st}) in compliance with ISO/IEC Guide 98 (GUM) [11] using Eq.1:

$$u_{ref} = \sqrt{u_{char}^2 + u_{bb}^2 + u_{st}^2} \qquad \text{Eq. 1}$$

The experts reported values non-overlapping within their respective expanded uncertainties for some of the measurands (Annex 10). Therefore u_{char} was calculated according to ISO Guide 35 [9]:

$$u_{char} = \frac{s}{\sqrt{p}} \qquad \text{Eq. 2}$$

Where: *s* refers to the standard deviation of the mean values obtained by the expert laboratories and *p* refers to the number of expert laboratories.

Table 1 presents the reference values (X_{ref}, u_{ref} and U_{ref}) for all measurands, the standard uncertainty contributions related to characterization, homogeneity and stability and the standard deviation for the PT assessment, $\hat{\sigma}$, expressed in mg kg^{-1}.

Table 1. Assigned values (X_{ref}), associated uncertainties (u_{ref}), uncertainty contributions (u_{char}, u_{bb}, u_{st}) and the standard deviation for the PT assessment ($\hat{\sigma}$). All values are expressed in mg kg^{-1}. The expanded uncertainty (U_{ref}) is calculated with a coverage factor k=2 corresponding to a level of confidence of about 95%. $\hat{\sigma}$ is set to 25%.

	X_{ref}	u_{char}	u_{bb}	u_{st}	u_{ref}	U_{ref} (k=2)	$\hat{\sigma}$
Azoxystrobin	**0.092**	0.0087	0.0091	0.0053	0.014	**0.027**	0.023
Carbendazim	**0.096**	0.0061	0.0050	0.0037	0.009	**0.017**	0.024
Chlorpyrifos	**0.055**	0.0065	0.0033	0.0025	0.008	**0.015**	0.014
Cyprodinil	**0.176**	0.0090	0.0125	0.0051	0.016	**0.032**	0.044
Difenoconazole	**0.332**	0.0262	0.0070	0.0119	0.030	**0.059**	0.083
Fenhexamid	**0.203**	0.0209	0.0148	0.0069	0.027	**0.053**	0.051
Fludioxonil	**0.095**	0.0106	0.0083	0.0049	0.014	**0.029**	0.024
Imidacloprid	**0.266**	0.0169	0.0160	0.0085	0.025	**0.050**	0.067
Indoxacarb	**0.284**	0.0215	0.0238	0.0159	0.036	**0.072**	0.071
Iprodione	**0.118**	0.0177	0.0095	0.0059	0.021	**0.042**	0.029
Kresoxim methyl	**0.189**	0.0296	0.0140	0.0104	0.034	**0.069**	0.047
Lambda-cyhalothrin	**0.031**	0.0034	0.0025	0.0010	0.004	**0.009**	0.008
Methoxyfenozide	**0.285**	0.0364	0.0083	0.0120	0.039	**0.078**	0.071
Myclobutanil	**0.169**	0.0151	0.0161	0.0083	0.024	**0.047**	0.042
Penconazole	**0.045**	0.0030	0.0049	0.0021	0.006	**0.012**	0.011
Pyraclostrobin	**0.131**	0.0145	0.0116	0.0068	0.020	**0.040**	0.033
Pyrimethanil	**0.057**	0.0052	0.0065	0.0026	0.009	**0.017**	0.014
Quinoxyfen	**0.060**	0.0045	0.0040	0.0028	0.007	**0.013**	0.015
Tebuconazole	**0.227**	0.0236	0.0256	0.0127	0.037	**0.074**	0.057
Triadimenol	**0.231**	0.0568	0.0183	0.0053	0.060	**0.120**	0.058

6.3 Standard deviation for the proficiency assessment $\hat{\sigma}$

On the basis of previous experience for this type of analysis acquired by the EURL-FV the standard deviation for proficiency assessment, $\hat{\sigma}$ (also called target standard deviation), was set to 25% of the respective assigned values (Table 1).

As shown in Table 1 $u_{ref} > \hat{\sigma}$ for triadimenol indicating that even the expert laboratories have problems to agree on a value for that measurand within the 25% target standard deviation fixed for IMEP-37. For this reason no scorings were given to the participants to benchmark the quality of their results for triadimenol.

7 Evaluation of results

7.1 Scores and evaluation criteria

Individual laboratory performance was expressed in terms of z- and ζ-scores in accordance with ISO 13528:2005 [8]:

$$z = \frac{x_{lab} - x_{ref}}{\hat{\sigma}} \qquad \text{Eq. 3}$$

$$\zeta = \frac{x_{lab} - x_{ref}}{\sqrt{u_{ref}^2 + u_{lab}^2}} \qquad \text{Eq. 4}$$

where:
- x_{lab} is the measurement result reported by a participant;
- u_{lab} is the standard uncertainty reported by a participant;
- X_{ref} is the reference value (assigned value);
- u_{ref} is the standard uncertainty of the reference value; and
- $\hat{\sigma}$ is the standard deviation for proficiency assessment

The interpretation of the z- and ζ-score is done according ISO 17043:2010 [6]:

|score| ≤ 2	satisfactory result	(green in annexes 11 to 30)
2 < |score| < 3	questionable result	(yellow in annexes 11 to 30)
|score| ≥ 3	unsatisfactory result	(red in annexes 11 to 30)

The z-score compares the participant's deviation from the reference value with the target standard deviation for proficiency assessment ($\hat{\sigma}$) used as common quality criterion. $\hat{\sigma}$ is defined by the PT organizer as the maximum acceptable standard uncertainty.

The ζ-score states whether the laboratory's result agrees with the assigned value within the respective uncertainty. The denominator is the combined uncertainty of the assigned value and the measurement uncertainty as stated by the laboratory. The ζ-score is therefore the most relevant evaluation parameter, as it includes all parts of a measurement result, namely the expected value (assigned value), its uncertainty and the unit of the result as well as the uncertainty of the reported values. An unsatisfactory ζ-score can either be caused by an inappropriate estimation of the concentration or of its uncertainty, or both.

The standard uncertainty of the laboratory (u_{lab}) was estimated by dividing the reported expanded uncertainty by the reported coverage factor, *k*. When no uncertainty was reported, it was set to zero ($u_{lab} = 0$).

Uncertainty estimation is not trivial, therefore an additional assessment was provided to each laboratory reporting uncertainty, indicating how reasonable their uncertainty estimate is. The standard uncertainty from the laboratory (u_{lab}) is most likely to fall in a range between a minimum uncertainty (u_{min}), and a maximum allowed (u_{max}), i.e. case "a". u_{min} is set to the standard uncertainty of the reference value. It is unlikely that a laboratory carrying out the analysis on a routine basis would measure the measurand with a smaller uncertainty than the expert laboratories chosen to establish the assigned value. u_{max} is set to the target standard deviation ($\hat{\sigma}$) accepted for the PT. If u_{lab} is smaller than u_{min}, (case "b") the laboratory may have underestimated its uncertainty. Such a statement has to be taken with care as each laboratory reported only measurement uncertainty, whereas the uncertainty of the reference value also includes

contributions of homogeneity and stability. If those are large, measurement uncertainties smaller than u_{min} are possible and plausible. If $u_{lab} > u_{max}$, (case "c") the laboratory may have overestimated the uncertainty. An evaluation of this statement can be made when looking at the difference of the reported value and the assigned value: if the difference is small and the uncertainty is large, then overestimation is likely. If, however, the deviation is large but is covered by the uncertainty, then the uncertainty is properly assessed but large. It should be pointed out that u_{max} is only a normative criterion if set down by legislation.

7.2 Laboratory results and scoring

From the 87 laboratories registered, 81 laboratories submitted results and 74 answered the associated questionnaire. From the 81 reporting laboratories, 40 were from EU countries while 41 were from outside EU (Australia, Brazil, Canada, China, Egypt, FYR of Macedonia, Hong Kong, Iceland, Israel, Norway, Peru, Serbia, Switzerland, Taiwan, Turkey, Uganda, United States, Uruguay). Not all labs reported results for all measurands. The total number of results received for the individual pesticides ranged from 57 (methoxyfenozide) to 74 (chlorpyrifos).

Those laboratories reporting "less than" and "0" values were not included in the evaluation. However, reported "less than" values were compared with the corresponding X_{ref} - U_{ref} values. If the reported limit value is lower than the corresponding X_{ref} - U_{ref}, this statement is considered incorrect, since the laboratory should have detected the respective element. In this exercise, L067 reported incorrectly "less than" 0.2 mg kg^{-1} for carbendazim, difenoconazole, fenhexamid, imidacloprid, methoxyfenozide, pyraclostrobin, pyrimethanil, quinoxyfen and triadimenol, L076 reported incorrectly "less than" 0.1 mg kg^{-1} for chlorpyrifos and lambda-cyhalothrin, L078 reported incorrectly "less than" 0.1 mg kg^{-1} for difenoconazole while it reported correctly "less than" 0.1 mg kg^{-1} for chlorpyrifos, lambda-cyhalothrin and penconazole.

The overall performance of the participants regarding the z- and ζ-scores is summarized in Figure 1: for the determination of the 19 scored target pesticides a range of 81 % (carbendazim) to 97 % (azoxystrobin, penconazole, pyrimethanil) of satisfactory z-scores were obtained by the participants in this exercise. Regarding ζ-scores satisfactory ζ-scores were obtained by 71 % (carbendazim) to 96 % (penconazole) of the participants.

The same calculations were done for the group of 41 non-EU participants. Results are presented in Figure 2 and show that these are very similar to the ones obtained for all participants together, with satisfactory z-scores ranging from 83% (fludioxonil) to 100% (kresoxim methyl) and satisfactory ζ-scores ranging from 60% (carbendazim) to 97% (kresoxim methyl and penconazole).

Even though the overall performance in this exercise is good, it has to be remarked that the $\hat{\sigma}$ in this exercise was taken as 25%, which is rather generous. At the same time the results of the expert laboratories led to a large uncertainty on the characterisation, u_{char}.

Figure 1. Number of evaluated laboratories with satisfactory, questionable and unsatisfactory z and ζ-scores. (The numbers on the bars correspond to the exact number of laboratories in a certain scoring category).

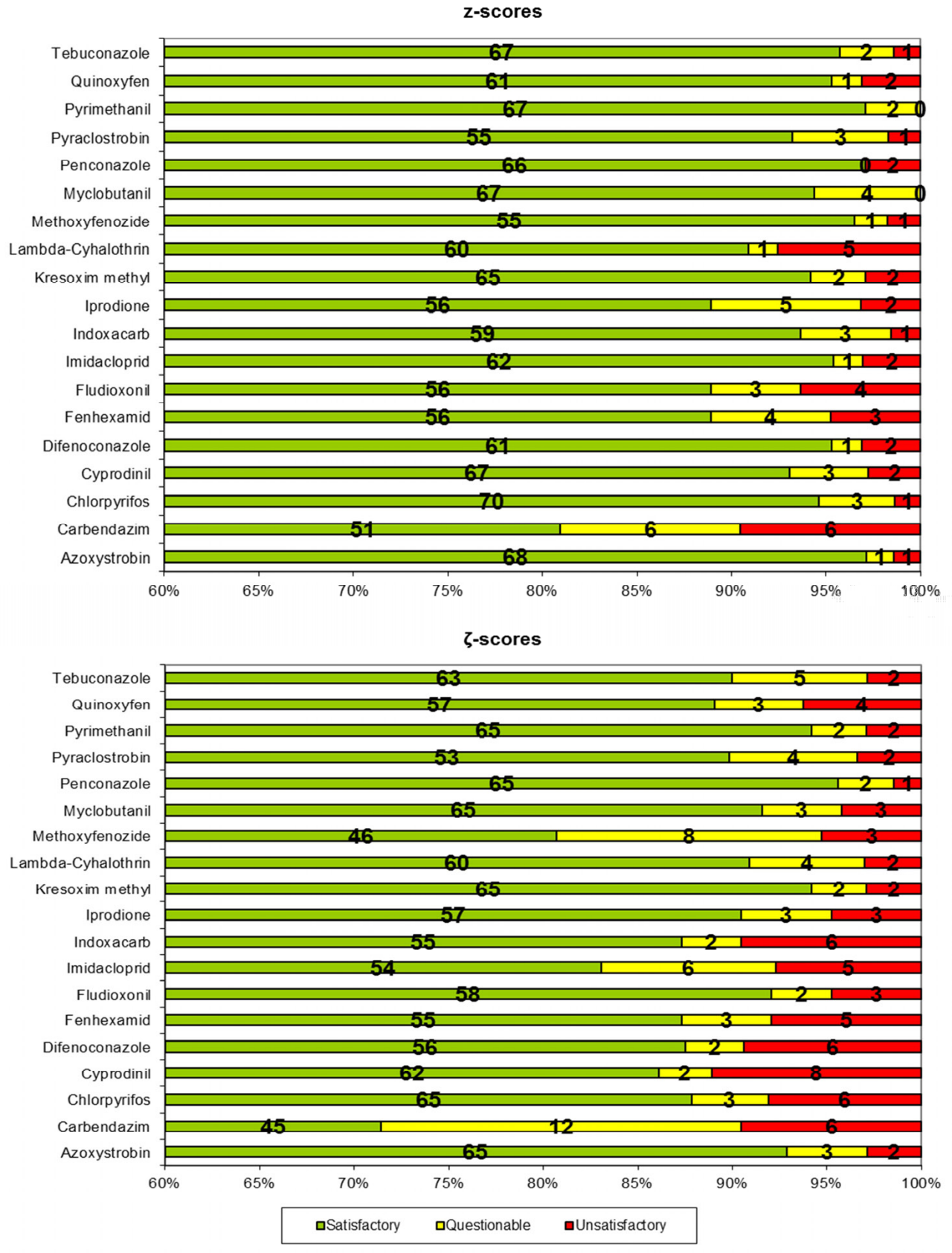
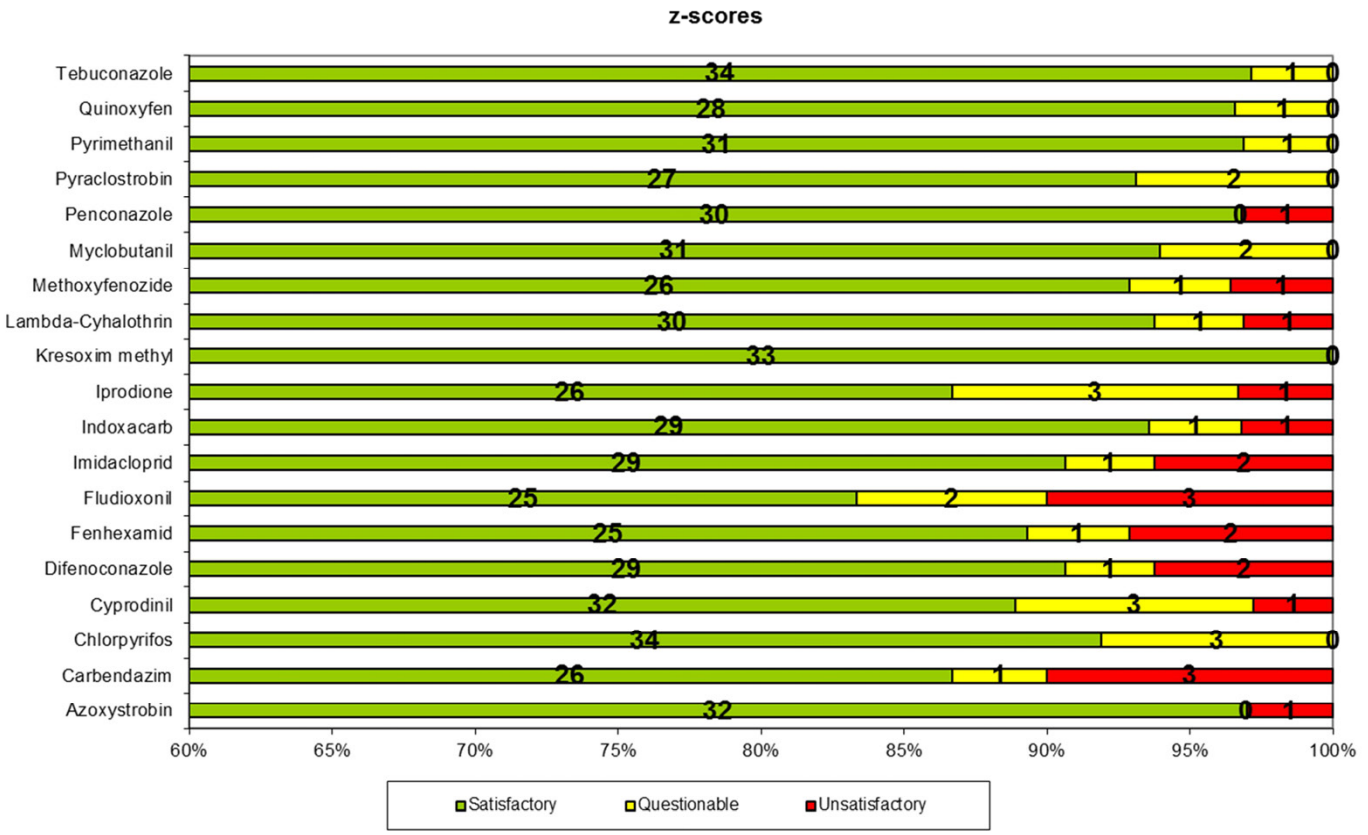
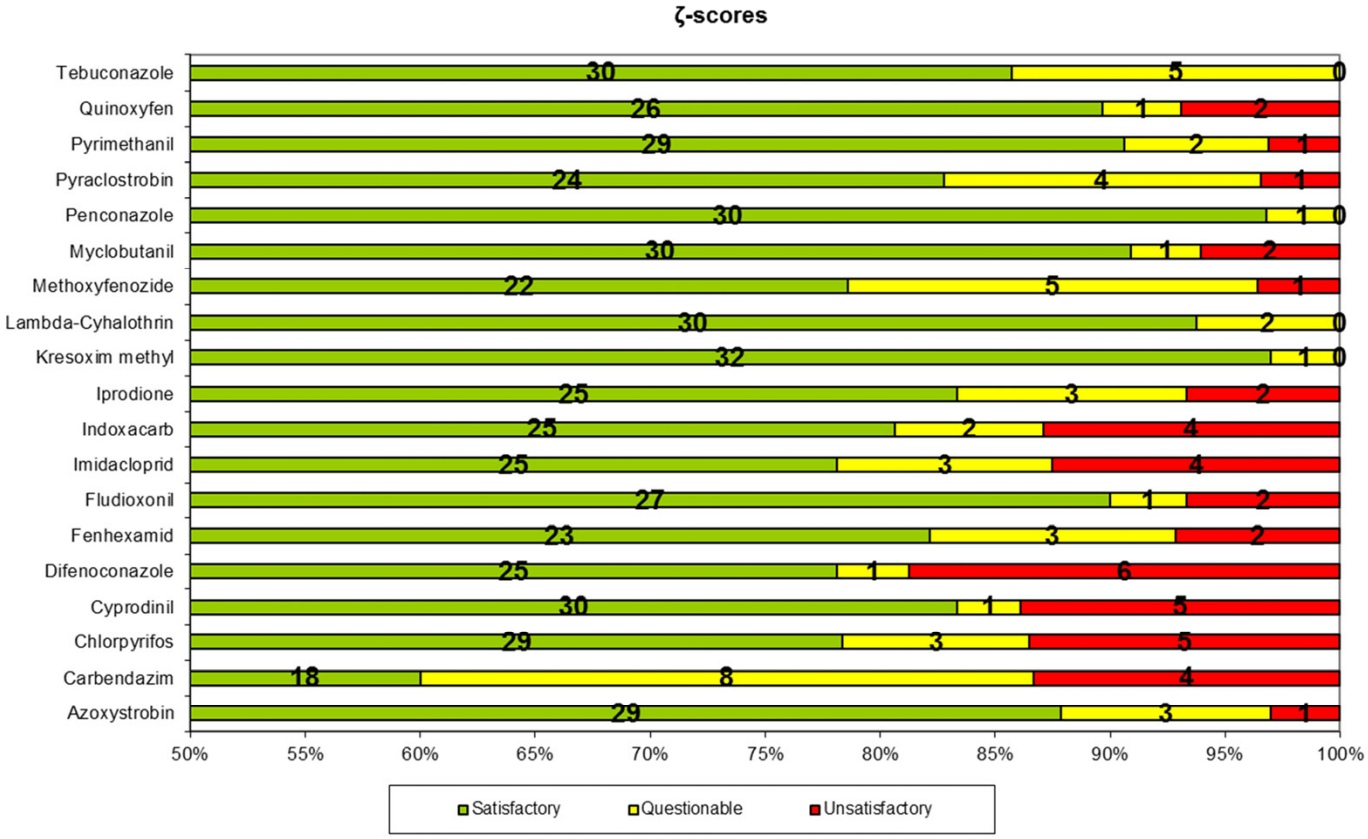


Figure 2. Number of evaluated non-EU laboratories with satisfactory, questionable and unsatisfactory z and ζ-scores. (The numbers on the bars correspond to the exact number of laboratories in a certain scoring category).





The latter aspect may suggest that this is the best possible performance at the moment in these kinds of multi-residue analyses of pesticides and that there is some room for further improvement.

The reported results for the individual pesticides are presented in Annexes 11 to 30 in the form of a table and a graph. The table shows the reported x_{lab}, U_{lab} and k of the participants, the technique used by each participant, the obtained z and ζ-scores of each participant and an uncertainty assessment. The graph displays the measurement results and associated uncertainties of the participants, the reference value X_{ref} with a reference interval and a target interval. In the graph σ_p stands for $\hat{\sigma}$. Furthermore, it includes a Kernel density plot which gives the probability density function of the reported measurement results together with the reference value X_{ref}. The Kernel density plot is used to check if there is a distribution different from normal of the measurement results (> 1 major peak). In this exercise no bimodal distribution was found for any of the measurands.

For the pesticide triadimenol, the variability on the results of the expert laboratories was very large leading to $u_{ref} > \hat{\sigma}$. Therefore laboratories were not scored for this measurand (Annex 30).

The uncertainty assessment ("a", "b" and "c") is also presented in Annexes 11 to 30. Remarkable is the low percentage of "a", standing for a reasonable uncertainty estimate, which is ranging from 15% (kresoxim methyl) to 49% (imidacloprid) and the high percentage of "b", ranging from 28% (quinoxyfen) to 54% (kresoxim methyl, tebuconazole) and meaning an underestimation of the uncertainty. This high percentage of "b" can partly be explained by the high standard uncertainty of the reference value. The five expert laboratories showed a variability in their results similar to the one found among the eighty-one participating laboratories. This variability was taken in u_{ref} via the u_{char} which was calculated according to ISO Guide 35 (Eq. 2 and Table 1). This may indicate that a high variability on the results of this type of multi-residue analyses is normal and therefore a relatively high uncertainty on these measurement results can be expected, reflecting the complexity inherent to pesticide analyses in food of vegetable origin.

7.3 Discussion on the reported results and on the additional information extracted from the questionnaire

The associated questionnaire was answered by 74 participating laboratories. According to those responses, 43 participants used an official method while 31 did not (Table 2). The official method which was used the most (30 labs) was the "QuEChERS", also known as the EN15662 or the AOAC 2007.01 method. "QuEChERS" stands for Quick, Easy, Cheap, Effective, Rugged and Safe. This technique involves an extraction with acetonitrile and a purification step using dispersive solid-phase extraction (d-SPE).

Most laboratories used a combination of liquid chromatography coupled to triple quadrupole mass spectrometry (LC-MS/MS) and gas chromatography coupled to triple quadrupole mass spectrometry (GC-MS/MS) to analyse all the pesticides. Annexes 11-30 show that in many cases the same pesticide is analysed using different techniques. When

evaluating these results, no correlation could be found between the use of a technique (like LC-MS or GC-MS) and the performance in the PT study.

Table 2. Summary of answers received in the questionnaire related to methodology, uncertainty estimation and quality system.

	Did you use an official method?	Do you usually provide an uncertainty statement to your customers for this type of analysis?	Does your laboratory have a quality system in place?
YES	**43**	**32**	**73**
NO	**31**	**42**	**1**
Detailed responses	**Methods used:** - Quechers, EN15662 or AOAC 2007.01: 30 labs - mini Luke: 3 labs - Analytical Methods for Pesticide Residues in Foodstuffs, 6th Ed, Ministry of Public Health, Welfare and Sport, Rijswijk, The Netherlands: 2 labs - Taiwan Food and Drug Administration Pesticides: Method for Multiresidue Analysis: 2 labs	**Basis of uncertainty estimate in this PT*:** a) uncertainty budget (ISO GUM): 15 labs b) known uncertainty from the standard method: 2 labs c) uncertainty of the method (in-house validation): 42 labs d) measurement of replicates: 27 labs e) estimation based on judgment: 6 labs f) use of intercomparison data: 7 labs g) other: 15 labs *combinations of 2 or more options per laboratory are possible	**Quality systems in place:** ISO 17025: 65 labs ISO 9001: 1 lab ISO 17025 + ISO 9001: 6 labs ISO 17025 + ISO 9001 + GLP: 1 lab

Acetonitrile was the extraction solvent used by most participants (44 labs, Table 3). Other solvents used were ethylacetate, acetone, methanol, dichloromethane and petroleumether. One observation was made with the use of ethylacetate as an extraction solvent: when analysing the results of the 6 participants using ethylacetate as only extraction solvent, it was observed that 88% of their results led to negative z-scores or non-detected analytes, meaning an underestimation of the amount present. However, this effect was not observed for the expert laboratory which used ethylacetate as an extraction solvent (Annex 10, expert laboratory 3).

Sample clean-up was done mostly by d-SPE (27 labs) or solid-phase extraction (SPE, 12 labs). At the same time 15 participants did not carry out a sample clean-up. This could not be linked to more questionable or unsatisfactory z-scores.

Correction for recovery was done by 40 participants. Other laboratories did not correct for recovery to be in line with the SANCO Guideline SANCO/12495/2011 which states that residue data do not have to be adjusted for recovery when the mean recovery is in the range of 70-120% [12]. No correlation was found between the correction for recovery and the performance in the exercise.

On the question whether the participants usually provide an uncertainty statement to their customers, 42 out of 74 replied they did not (Table 2). In this study, all participants provided an uncertainty estimation on their results. Table 2 summarises in detail the way in which uncertainty estimates have been calculated. Many different approaches were applied, but in many cases the uncertainty estimation was based on the uncertainty of the method (in-house validation) or based on the measurement of replicates.

Table 3. Extraction solvents used by the participants

What extraction solvents did you use?	
1 solvent	- acetonitrile: 44 - ethyl acetate: 6 - acetone: 1
2 solvents	- acetonitrile / ethyl acetate: 6 - methanol / ethyl acetate: 2 - acetonitrile / aceton: 4 - 1% acetic acid in acetonitrile: 1
3 solvents	- acetone / dichloromethane / petroleumether: 6 - acetone / dichloromethane / hexane: 1 - acetone / dichloromethane / ethylacetate: 1 - acetone / cyclohexane / ethylacetate: 1 - acetonitrile / acetone / dichloromethane: 1

8 Conclusion

According to the results obtained in the frame of the IMEP-37 study, the participants performed satisfactorily for the 19 scored pesticides. When analysing the results of the group of non-EU countries separately, similar results were obtained. It can be concluded that the performance in this PT is satisfactory for the laboratories world-wide.

Most of the participants used the QuEChERS methodology to analyse the pesticides and most used acetonitrile alone as an extraction solvent. Results in this study showed a systematic underestimation of the values reported by the laboratories using only ethyl acetate as an extraction solvent.

The results also show the need for some extra effort in the evaluation of uncertainties associated to the results, since the number of questionable and unsatisfactory ζ-scores was in most cases higher than those of the z-scores. Moreover the number of "a" scores (reasonable uncertainty estimate) in the uncertainty assessment was relatively low. This may be related to the fact that many labs do not have the experience to report measurement uncertainty for this type of analyses and that u_{ref} was high for some pesticides.

9 Acknowledgements

The laboratories participating in this exercise, listed below in Table 4, are kindly acknowledged. T. Linsinger and G. Kerckhove from the Standards for Innovation and Sustainable Development (SID) Unit of the IRMM are acknowledged for their support in

the storage and dispatch of the samples. F. Ulberth (IRMM) is acknowledged for reviewing the manuscript.

Table 4. Laboratories that participated in IMEP-37 and their respective country of origin.

Organisation	Country
Agrisearch Analytical Pty Ltd	AUSTRALIA
BIUTEC F & E GmbH, staatl. akkreditierte Prüf- und Inspektionsstelle	AUSTRIA
MA 38 - Lebensmitteluntersuchungsanstalt der Stadt Wien	AUSTRIA
Eurofins - ofi Lebensmittelanalytik GmbH	AUSTRIA
LOVAP	BELGIUM
Fytolab cvba	BELGIUM
Scientific Institute of Public Health	BELGIUM
Eurofins do Brasil Analises de Alimentos Ltda	BRAZIL
Laboratório Nacional Agropecuário - LANAGRO/MG	BRAZIL
Central laboratory for chemical testing and control- Bulgarian Food Safety Agency	BULGARIA
Euro Lab-Interpred Eurologistic Ltd.	BULGARIA
Regional Health Inspectorate Varna (appointed by EA BAS)	BULGARIA
Regional Health Inspectorate - Veliko Tarnovo	BULGARIA
Ministere agriculture pecherie et alimentation du Quebec	CANADA
University of Guelph	CANADA
University of Guelph	CANADA
Exova Canada Inc.	CANADA
Silliker JR Laboratories ULC	CANADA
China Center for Food Safety Risk Assessment	CHINA
EUROINSPEKT CROATIAKONTROLA d.o.o.	CROATIA
Central Lab of Residue analysis of pesticides and heavy metals in foods	EGYPT
University of Tartu	ESTONIA
MetropoliLab Oy	FINLAND
Finnish Customs Laboratory	FINLAND
Center of public health	FYR OF MACEDONIA
Center for public health Bitola	FYR OF MACEDONIA
LUFA-ITL	GERMANY
TeLA GmbH	GERMANY
Labor Lippert GmbH	GERMANY
AGENT LABS	GREECE
AGROLAB SA	GREECE
Agrolab SA	GREECE
Government Laboratory	HONG KONG
Enviro Labs Limited	HONG KONG
Matis	ICELAND
Katif Center Laboratories	ISRAEL
PPIS	ISRAEL

Bactochem Lab	ISRAEL
Aminolab Ltd	ISRAEL
Bioforsk, Plant Health and Plant Protection Division	NORWAY
Servio Nacional de Sanisas Agraria - Senasa. Centro de Control de Insumos y Residuos Toxicos	PERU
Institite of Plant Protection-National Research Institute; Department of Pesticide	POLAND
Agricultural and Food Quality Inspection	POLAND
Wojewodzka Stacja Sanitarno-Epidemiologiczna w Rzeszowie	POLAND
Institute of Plant Protection - National Research Institute	POLAND
Laboratório Regional de Veterinária e Segurança Alimentar	PORTUGAL
Instituto Nacional de Investigação Agrária e Veterinária, I.P.	PORTUGAL
Laboratory for Pesticides Residues Control in Plants and Vegetables	ROMANIA
Directia pentru Agricultura - Unitatea Fitosanitara Mures	ROMANIA
Sanitary Veterinary and Food Safety Directorate	ROMANIA
NATIONAL INSTITUTE OF PUBLIC HEALTH	ROMANIA
Sanitary Veterinary and Food Safety Laboratory IAIS	ROMANIA
SP LABORATORIJA	SERBIA
Enoloska stanica Vrsac doo Vrsac	SERBIA
A BIO TECH LAB	SERBIA
Center for Food Analysis	SERBIA
Public Health Institute of Belgrade	SERBIA
Kmetijski inštitut slovenije (Agricultural Institute of Slovenia)	SLOVENIA
Zavod za zdravstveno varstvo Maribor	SLOVENIA
Labs&Technological Services AGQ, S.L.	SPAIN
Laboratorio de producción y Sanidad Vegetal de Almería	SPAIN
LABORATORI AGENCIA DE SALUT PUBLICA DE BARCELONA	SPAIN
SICA AGRIQ, S.L.	SPAIN
Analytica Alimentaria GmbH, Branch Spain	SPAIN
COEXPHAL	SPAIN
Eurofins Food&Agro Testing Sweden Ab	SWEDEN
Labor Veritas AG	SWITZERLAND
LABORATORIO CANTONALE	SWITZERLAND
Swiss Quality Testing Services	SWITZERLAND
Coop Central Laboratory, NOMINATED BY SAS	SWITZERLAND
Cantonal Office of Consumer Protection Aargau (NOMINATED BY SAS)	SWITZERLAND
National PingTung University of Science & Technology, CAAPIC	TAIWAN
Food Industry Research and Development Institute(FIRDI)	TAIWAN
Tzu Chi University	TAIWAN
National Formosa University	TAIWAN
AGRICULTURAL CHEMICALS AND TOXIC SUBSTANCES RESEARCH INSTITUTE	TAIWAN

SGS SUPERVISE GOZETME ETUD KONTROL SERVISLERI A.S.	TURKEY
Chemiphar (U) LTD	UGANDA
Waters Agricultural Laboratories, Inc.	UNITED STATES
Columbia Food Laboratories, Inc	UNITED STATES
Facutlad de Quimica UdelaR	URUGUAY

Abbreviations

APLAC	Asian Pacific Laboratory Accreditation Cooperation
EA	European Cooperation for Accreditation
EU	European Union
EURL-FV	European Union Reference Laboratory for Pesticide Residues
IAAC	InterAmerican Accreditation Cooperation
ILC	Interlaboratory Comparison
IMEP	International Measurement Evaluation Programme
IRMM	Institute for Reference Materials and Measurements
JRC	Joint Research Centre
PCA	Polish Centre for Accreditation
PT	Proficiency Testing

References

[1] Commission Regulation (EC) 396/2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin, Official Journal of the European Union, L70/1 (2005).

[2] Fintschenko Y, Krynitsky J. A., Wong W. J. (2010) "Emerging pesticide residue issues and analytical approaches", J. Agric. Food Chem., 58, 5859-5861.

[3] Hollosi L., Mittendorf K., Senyuva Z. H. (2012) Coupled turbulent flow chromatography: LC-MS/MS method for the analysis of pesticide residues in grapes, baby food and wheat flour matrices, Chromatographia, 75, 1377-1393.

[4] Hernandez F, Cervera I. M., Portolés T., Beltrán J., Pitarch E. (2013) The role of GC-MS/MS with triple quadrupole in pesticide residue analysis in food and the environment, Anal. Methods, 5, 5875-5894.

[5] http://ec.europa.eu/sanco_pesticides/public/

[6] ISO/IEC 17043:2010 "Conformity assessment – General requirements for proficiency testing", issued by the International Organisation for Standardization, Geneva

[7] IUPAC, Thompson M, Ellison L.R. S., Wood R, The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories, 2006.

[8] ISO 13528:2005 – "Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons", issued by ISO-Geneva (CH), International Organisation for Standardization.

[9] http://www.eie.gr/iopc/softcrm/index.html

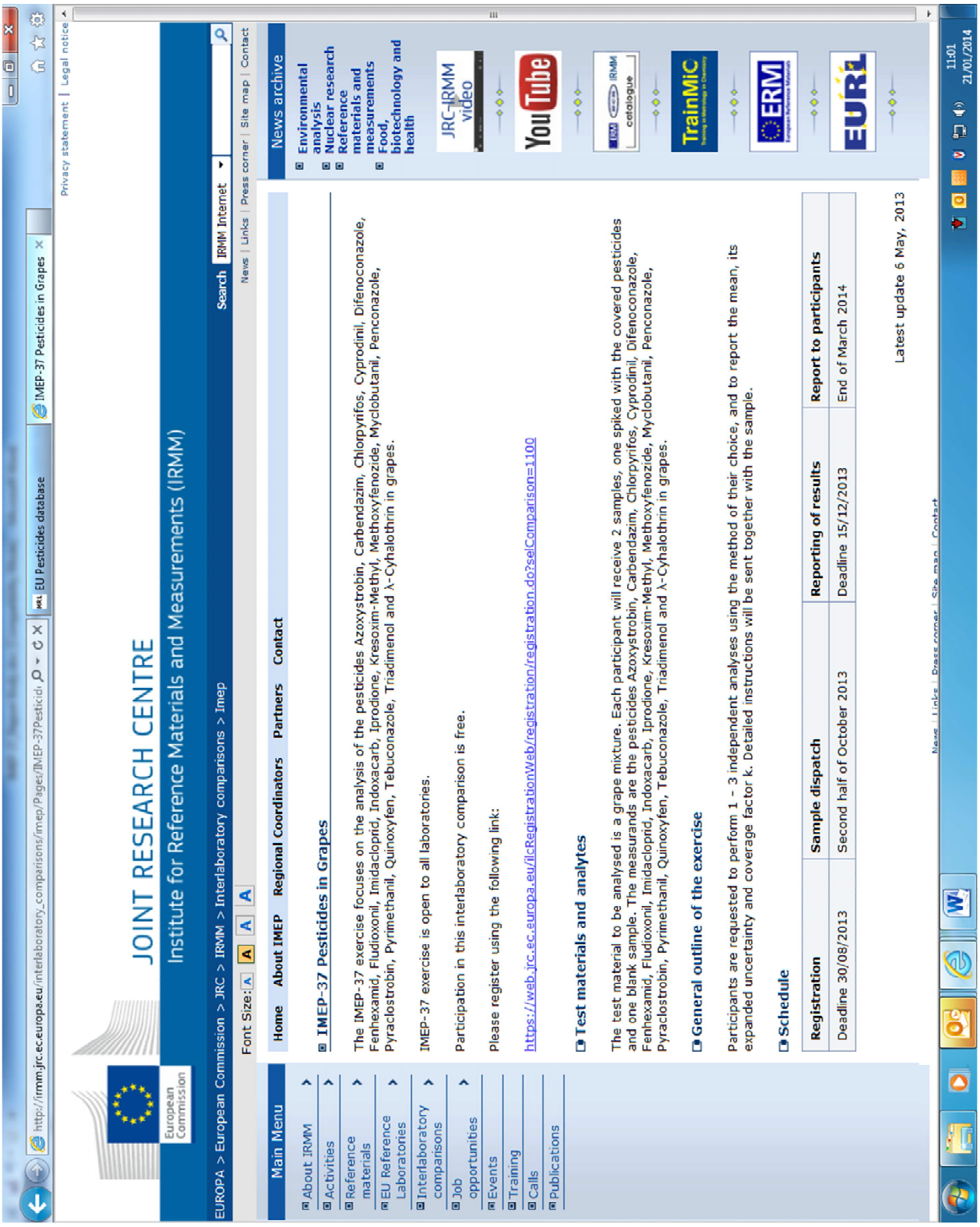
[10] ISO Guide 35 Reference Materials – general and statistical principles for certification (2006), issued by ISO-Geneva (CH), ISO-Geneva (CH).

[11] ISO/IEC Guide 98:2008, "Uncertainty of measurement – Part 3: Guide to the expression of uncertainty in measurement" (GUM 1995), issued by International Organisation for Standardisation, Geneva.

[12] SANCO/12495/2011, Method validation and quality control procedures for pesticide residues analysis in food and feed, 2012.

Annexes

Annex 1: IRMM – IMEP web announcement



Annex 2: Invitation letter to EA

Ref. Ares(2013)1010323 - 08/05/2013

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
International Measurement Evaluation Program

6 May 2013

PCA
Hanna Tugi
Ul. Szczotkarska 42,
01-382 Warszawa,
POLAND

IMEP-37: Interlaboratory comparison for the determination of pesticides in grapes

Dear Hanna,

The Institute for Reference Materials and Measurements (IRMM) organises IMEP-37, an interlaboratory comparison for the **"Determination of pesticides in grapes".**

In the frame of the EA-IRMM collaboration agreement, IRMM kindly invites EA to nominate laboratories for free participation. They should hold (or be in the process of obtaining) an accreditation for this type of measurement.

I suggest that you forward this invitation to the national EA accreditation bodies for its consideration. There is a limited number of samples at your disposal and the number of nominees should not exceed 5 laboratories per country.

Due to the special nature of this exercise, participation in IMEP-37 is free of charge for all participants under the condition though that **only laboratories with capacities for the determination of pesticides in vegetable food and fruit should register.**

Confidentiality of the participants and their results towards third parties is guaranteed. However, IMEP will disclose details of the participants that have been nominated by EA to the EA working group for ILCs in Testing coordinator for this exercise. The EA accreditation bodies may wish to inform the nominees of this disclosure.

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 767, Fax: (32-14) 571 865

E-mail: jrc-irmm-imep@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

The registration page for laboratories appointed by EA is open until **30 August 2013**. Distribution of the samples is foreseen for the second half of October 2013. The deadline for submission of results is **15 December 2013**.

In order to register, laboratories must:

1. **Enter** their details online:

https://web.jrc.ec.europa.eu/ilcRegistrationWeb/registration/registration.do?selComparison=1100

2. **Print** the completed form when the system asks to do so and clearly indicate on the printed form that they have been appointed by the European Cooperation for Accreditation to take part in this exercise.

3. **Send** the printout to both the IMEP-37 and the EA-IMEP-37 coordinators:

IMEP-37 coordinator	**EA-IMEP-37 coordinator**
Dr. Beatriz de la Calle	Hanna Tugi
Fax +32 14 571 252	
E-mail jrc-irmm-imep@ec.europa.eu	E-mail h.tugi@pca.gov.pl

Please contact me if you have any questions or comments. We are looking forward to our cooperation!

With kind regards

Beatriz de la Calle
IMEP-37 Coordinator

Annex 3: Invitation letter to APLAC

Ref. Ares(2013)1010360 - 06/05/2013

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
International Measurement Evaluation Program

Geel, 6 May 2013

To: Cynthia Chen
APLAC PT Committee

IMEP-37: Interlaboratory comparison for the determination of pesticides in grapes

Dear Mrs Chen,

The Institute for Reference Materials and Measurements (IRMM) organises IMEP-37, an interlaboratory comparison for the **"Determination of pesticides in grapes"**.

IRMM kindly invites APLAC to nominate laboratories for free participation. However, they should hold (or be in the process of obtaining) an accreditation for this type of measurement.

I suggest that you forward this invitation to a selection of specialised laboratories in this area. There is a limited number of samples at your disposal and the number of nominees should not exceed 5 laboratories per country.

Due to the special nature of this exercise, participation in IMEP-37 is free of charge for all participants under the condition though that only laboratories with capacities for the determination of pesticides in vegetable food and fruit should register.

Confidentiality of the participants and their results towards third parties is guaranteed.

The registration page is open until **30 August 2013**. Distribution of the samples is foreseen for the second half of October 2013. The deadline for submission of results is **15 December 2013.**

In order to register, laboratories must:

1. **Enter** their details online:

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 767, Fax: (32-14) 571 865

E-mail: jrc-irmm-imep@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

https://web.jrc.ec.europa.eu/ilcRegistrationWeb/registration/registration.do?selComparison=1100

2. **Print** the completed form when the system asks to do so and clearly indicate on the printed form that they have been appointed by APLAC to take part in this exercise.

3. **Send** the printout to both the IMEP-37 and the APLAC coordinators:

IMEP-37 coordinator	**APLAC coordinator**
Dr. Beatriz de la Calle	Cynthia Chen
Fax +32 14 571 252	
E-mail: jrc-imum-imep@ec.europa.eu	E.Mail: cynthia_chen@taftw.org

Please contact me if you have any questions or comments. We are looking forward to our cooperation!

With kind regards

Beatriz de la Calle

IMEP-37 Coordinator

Annex 4: Invitation letter to IAAC

Ref. Ares(2013)1010404 - 06/05/2013

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
International Measurement Evaluation Program

6 May 2013

To: Barbara Belzer
IAAC Lab Committee

IMEP-37: Interlaboratory comparison for the determination of pesticides in grapes

Dear Barbara,

The Institute for Reference Materials and Measurements (IRMM) organises IMEP-37, an interlaboratory comparison for the **"Determination of pesticides in grapes ".**

IRMM kindly invites IAAC to nominate laboratories for free participation. However, they should hold (or be in the process of obtaining) an accreditation for this type of measurement.

I suggest that you forward this invitation to a selection of specialised laboratories in this area. There is a limited number of samples at your disposal and the number of nominees should not exceed 5 laboratories per country.

Due to the special nature of this exercise, participation in IMEP-37 is free of charge for all participants under the condition though that only laboratories with capacities for the determination of pesticides in vegetable food and fruit should register.

Confidentiality of the participants and their results towards third parties is guaranteed.

The registration page is open until **30 August 2013**. Distribution of the samples is foreseen for the second half of October 2013. The deadline for submission of results is **15 December 2013**.

In order to register, laboratories must:

1. **Enter** their details online:

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211
Telephone: direct line (32-14) 571 767. Fax: (32-14) 571 865

E-mail: jrc-irmm-imep@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

https://web.jrc.ec.europa.eu/ilcRegistrationWeb/registration/registration.do?selComparison=1100

2. **Print** the completed form when the system asks to do so and clearly indicate on the printed form that they have been appointed by IAAC to take part in this exercise.

3. **Send** the printout to both the IMEP-37 and the IAAC coordinators:

IMEP-37 coordinator	**IAAC coordinator**
Dr. Beatriz de la Calle	Barbara Belzer
Fax +32 14 571 252	
E-mail: jrc-irmm-imep@ec.europa.eu	E.Mail: secretariat@iaac.org.mx

Please contact me if you have any questions or comments. We are looking forward to our cooperation!

With kind regards

Beatriz de la Calle
IMEP-37 Coordinator

Annex 5: "Confirmation of Receipt" form

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
International Measurement Evaluation Program

Annex to JRC.D5/PD/acs/
Ares(2013)3153044

«Title» «Firstname» «Surname»
«Organisation»
«Address»
«Address2»
«Zip» «Town»
«Country»

IMEP-37

Pesticides in Grapes

Confirmation of receipt of the samples

Please return this form at your earliest convenience.
This confirms that the sample package arrived.
In case the package is damaged,
please state this on the form and contact us immediately.

ANY REMARKS .....
.....

Date of package arrival .....

Signature .....

Please return this form to:

Beatriz De La Calle

IMEP-37 Coordinator
EC-JRC-IRMM
Retieseweg 111
B-2440 GEEL, Belgium

Fax : +32-14-571865

e-mail : JRC-IRMM-IMEP@ec.europa.eu

Annex 6: Accompanying letter

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
International Measurement Evaluation Program

Geel, 01 October 2013
JRC.D5/PD/acs/

«Title» «Firstname» «Surname»
«Organisation»
«Department»
«Address»
«Address2»
«Zip» «Town»
«Country»

Participation in IMEP-37, a proficiency test exercise for the determination of pesticides in grapes.

Dear «Title» «Surname»,

Thank you for participating in the IMEP-37 proficiency test for the determination of pesticides in grapes.

Please keep this letter. You need it to report your results.

This parcel contains:
a) One bottle containing approximately 220 g of the test item
b) One bottle containing approximately 220 g of blank material
b) A "Confirmation of Receipt" form
c) This accompanying letter.

Please check whether the bottles containing the test item and blank material remained undamaged during transport. Then, please send the "Confirmation of receipt" form back (fax: +32-14-571865, e-mail: jrc-irmm-imep@ec.europa.eu). You should store the sample in a freezer at preferably -20 °C.

The measurands are Azoxystrobin, Carbendazim, Chlorpyrifos, Cyprodinil, Difenoconazole, Fenhexamid, Fludioxonil, Imidacloprid, Indoxacarb, Iprodione, Kresoxim-Methyl, Methoxyfenozide, Myclobutanil, Penconazole, Pyraclostrobin, Pyrimethanil, Quinoxyfen, Tebuconazole, Triadimenol and λ-Cyhalothrin in grapes.

The procedure used for the analyses should resemble as closely as possible the one that you use in routine analyses.

Retieseweg 111, B-2440 Geel - Belgium. Telephone: +32-(0)14-571 211.
Telephone: direct line +32-(0)14-571 767, Fax: +32-(0)14-571 865.

E-mail: jrc-irmm-eurl-heavy-metals@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

Reporting of results

Please perform two or three independent measurements, correct the measurements results for recovery and report on the reporting website:

- the **mean** of your two or three measurement results (mg kg^{-1})
- the associated expanded **uncertainty** (mg kg^{-1}),
- the **coverage factor** and
- the **technique** you used.

The results should be reported in the same form (e.g. number of significant figures) as those normally reported to the customer.

The reporting website is https://irmm.jrc.ec.europa.eu/ilc/ilcReporting.do

To access the webpage you need a personal password key, which is: «**Part_key**». The system will guide you through the reporting procedure. After entering your results, please complete also the relating questionnaire.

Do not forget to submit and confirm always when required.

Directly after submitting your results and the questionnaire information online, you will be prompted to print the completed report form. Please do so, **sign the paper version and return it to IRMM by fax (at +32-14-571-865) or by e-mail**. Check your results carefully for any errors before submission, since this is your last definitive confirmation.

The **deadline** for submission of results is 16/12/2013**.**

Please keep in mind that collusion is contrary to professional scientific conduct and serves only to nullify the benefits of proficiency tests to customers, accreditation bodies and analysts alike.

Your participation in this project is greatly appreciated. If you have any remaining questions, please contact me by e-mail: jrc-irmm-imep@ec.europa.eu

With kind regards,

Cc: F. Ulberth (SFB HoU)

Retieseweg 111, B-2440 Geel - Belgium. Telephone: +32-(0)14-571 211.
Telephone: direct line +32-(0)14-571 767, Fax: +32-(0)14-571 865.

E-mail: jrc-irmm-eurl-heavy-metals@ec.europa.eu
Web site: http://irmm.jrc.ec.europa.eu

Annex 7: Questionnaire

1. **Experimental details about the analysis.**

1.1. What kind of techniques did you use to analyse the pesticides in the grapes sample?

1.1.1. What was the mode of operation of the MS used?

- ☐ a) Selective Ion Recording
- ☐ b) Selective Reaction Monitoring
- ☐ c) Product Ion
- ☐ d) Full Scan
- ☐ e) Other

1.1.2. If other, specify which one(s). If more than one, specify for which pesticides.

1.1.3. What calibration mode was used?

- ☐ a) External standard
- ☐ b) Standard addition
- ☐ c) Internal standard
- ☐ d) Isotope dilution
- ☐ e) other

1.1.4. If other, specify which one(s). If more than one, specify for which pesticides.

1.2. What extraction solvents did you use?

1.2.1. Specify the extraction solvent(s) that you used.

Questions/Response table	**Acetone**	**Acetonitrile**	**Cyclohexane**	**Dichloromethane**	**Ethyl acetate**	**Methanol**	**Other**	*Info*
Extraction solvent 1	☐	☐	☐	☐	☐	☐	☐	
Extraction solvent 2 (optional)	☐	☐	☐	☐	☐	☐	☐	
Extraction solvent 3 (optional)	☐	☐	☐	☐	☐	☐	☐	

1.2.2. If other, specify which one(s).

1.3. How did you carry out the clean-up of the sample?

- ☐ a) Solid phase extraction (SPE)
- ☐ b) Dispersive solid phase extraction (DSPE)
- ☐ c) Gel permeation chromatography (GPC)
- ☐ d) Liquid-liquid partitioning
- ☐ e) Freezing out
- ☐ f) None
- ☐ g) Other

1.3.1. If other, specify how.

1.4. Does your laboratory use reference material for this type of analysis?

- ○ No
- ○ Yes

1.4.1. If "yes", specify which one.

1.4.2. The reference material was used for:

- ☐ Calibration of instrument
- ☐ Validation of procedure

1.5. Did you use an official method?

- ○ No
- ○ Yes

1.5.1. If "yes", specify which one.

1.6. Did you correct your results for recovery?

- ○ No
- ○ Yes

1.6.1. If "no", why not?

2. **What is the basis of your uncertainty estimate (multiple answers are possible)?**

- ☐ a) Uncertainty budget (ISO GUM)
- ☐ b) Known uncertainty of the standard method (ISO 21748)
- ☐ c) Uncertainty of the method (in-house validation)
- ☐ d) Measurement of replicates (precision)
- ☐ e) Estimation based on judgemnt
- ☐ f) Use of intercomparison data
- ☐ g) Other

2.1. If other, specify.

3. **What is the level of confidence (in %) reflected by the coverage (k) assigned to your reported uncertainty?**

4. **Do you usually provide an uncertainty statement to your customers for this type of analysis?**

- ○ No
- ○ Yes

5. **Does your laboratory have a quality system in place?**

- ○ No
- ○ Yes

5.1. If "yes", specify which one.

- ☐ ISO 17025
- ☐ ISO 9001
- ☐ Other

6. **Does your laboratory take part in inter-laboratory comparison scheme for this type of analysis?**

- ○ No
- ○ Yes

6.1. If "yes", specify which one.

Annex 8: Homogeneity and stability studies

8.1 Homogeneity

	azoxystrobin		carbendazim		chlorpyrifos		cyprodinil	
Bottle	R1	R2	R1	R2	R1	R2	R1	R2
1	0.073	0.076	0.092	0.093	0.053	0.055	0.235	0.220
2	0.072	0.073	0.091	0.091	0.056	0.057	0.219	0.215
3	0.062	0.061	0.087	0.081	0.049	0.049	0.193	0.186
4	0.087	0.081	0.084	0.084	0.053	0.06	0.235	0.247
5	0.075	0.073	0.081	0.091	0.05	0.057	0.204	0.205
6	0.085	0.083	0.087	0.084	0.055	0.058	0.216	0.208
7	0.068	0.073	0.092	0.111	0.048	0.05	0.215	0.198
8	0.064	0.065	0.096	0.092	0.048	0.044	0.195	0.196
9	0.081	0.073	0.100	0.096	0.048	0.056	0.217	0.225
10	0.082	0.081	0.091	0.097	0.067	0.054	0.226	0.233
Mean	0.074		0.091		0.053		0.214	
$\hat{\sigma}$	0.019		0.023		0.013		0.054	
0.3*$\hat{\sigma}$	0.006		0.007		0.004		0.016	
Critical value	0.000066		0.000117		0.000049		0.000532	
s_x	0.008		0.006		0.004		0.016	
s_w	0.003		0.005		0.004		0.007	
s_s	0.007		0.005		0.003		0.015	
s_s^2< critical	Pass		Pass		Pass		Pass	

	difenoconazole		fenhexamid		fludioxonil		imidacloprid	
Bottle	R1	R2	R1	R2	R1	R2	R1	R2
1	0.232	0.225	0.153	0.147	0.078	0.079	0.245	0.253
2	0.221	0.218	0.146	0.148	0.079	0.076	0.254	0.256
3	0.224	0.216	0.137	0.138	0.067	0.064	0.216	0.229
4	0.204	0.211	0.17	0.164	0.089	0.090	0.244	0.237
5	0.226	0.221	0.123	0.127	0.077	0.076	0.211	0.216
6	0.238	0.226	0.142	0.140	0.078	0.077	0.208	0.217
7	0.228	0.236	0.143	0.133	0.073	0.073	0.224	0.213
8	0.219	0.230	0.144	0.141	0.068	0.065	0.231	0.226
9	0.224	0.237	0.148	0.153	0.077	0.079	0.231	0.229
10	0.213	0.238	0.146	0.142	0.081	0.077	0.234	0.227
Mean	0.224		0.144		0.076		0.230	
$\hat{\sigma}$	0.056		0.036		0.019		0.058	
0.3*$\hat{\sigma}$	0.017		0.011		0.006		0.017	
Critical value	0.000599		0.000233		0.000064		0.000589	
s_x	0.007		0.011		0.007		0.014	
s_w	0.008		0.004		0.002		0.005	
s_s	0.005		0.011		0.007		0.014	
s_s^2< critical	Pass		Pass		Pass		Pass	

	indoxacarb		iprodione		kresoxim methyl		lambda-cyhalothrin	
Bottle	R1	R2	R1	R2	R1	R2	R1	R2
1	0.273	0.268	0.099	0.101	0.128	0.129	0.040	0.041
2	0.272	0.255	0.101	0.093	0.130	0.120	0.040	0.038
3	0.228	0.234	0.086	0.087	0.109	0.111	0.036	0.036
4	0.276	0.308	0.106	0.120	0.133	0.145	0.035	0.036
5	0.241	0.267	0.096	0.096	0.116	0.121	0.031	0.034
6	0.256	0.265	0.098	0.103	0.121	0.128	0.034	0.035
7	0.234	0.227	0.095	0.094	0.114	0.110	0.033	0.033
8	0.213	0.216	0.086	0.083	0.105	0.105	0.030	0.031
9	0.226	0.255	0.093	0.105	0.119	0.128	0.032	0.036
10	0.243	0.240	0.100	0.099	0.131	0.130	0.036	0.035
Mean	0.250		0.097		0.122		0.035	
$\hat{\sigma}$	0.062		0.024		0.030		0.009	
0.3*$\hat{\sigma}$	0.019		0.007		0.009		0.003	
Critical value	0.000814		0.000122		0.000178		0.000015	
s_x	0.023		0.008		0.010		0.003	
s_w	0.012		0.005		0.005		0.001	
s_s	0.021		0.007		0.010		0.003	
s_s^2< critical	Pass		Pass		Pass		Pass	

	methoxyfenozide		myclobutanil		penconazole		pyraclostrobin	
Bottle	R1	R2	R1	R2	R1	R2	R1	R2
1	0.207	0.214	0.160	0.161	0.051	0.053	0.113	0.113
2	0.201	0.218	0.161	0.151	0.052	0.045	0.114	0.111
3	0.245	0.202	0.138	0.142	0.043	0.043	0.097	0.095
4	0.238	0.219	0.153	0.165	0.046	0.050	0.117	0.128
5	0.205	0.203	0.137	0.139	0.041	0.041	0.092	0.114
6	0.227	0.207	0.138	0.144	0.041	0.045	0.104	0.106
7	0.226	0.211	0.129	0.122	0.040	0.037	0.094	0.095
8	0.214	0.207	0.117	0.118	0.037	0.035	0.089	0.08
9	0.205	0.216	0.135	0.146	0.037	0.041	0.094	0.111
10	0.223	0.215	0.149	0.150	0.044	0.041	0.121	0.1
Mean	0.215		0.143		0.043		0.104	
$\hat{\sigma}$	0.054		0.036		0.011		0.026	
0.3*$\hat{\sigma}$	0.016		0.011		0.003		0.008	
Critical value	0.000662		0.000239		0.000026		0.000188	
s_x	0.007		0.014		0.005		0.011	
s_w	0.013		0.005		0.002		0.008	
s_s			0.014		0.005		0.009	
s_s^2< critical	Pass		Pass		Pass		Pass	

	pyrimethanil		quinoxyfen		tebuconazole		triadimenol	
Bottle	R1	R2	R1	R2	R1	R2	R1	R2
1	0.042	0.042	0.056	0.059	0.186	0.190	0.121	0.114
2	0.035	0.037	0.045	0.048	0.189	0.176	0.138	0.120
3	0.031	0.036	0.059	0.050	0.153	0.153	0.123	0.135
4	0.048	0.051	0.064	0.046	0.178	0.191	0.098	0.111
5	0.042	0.044	0.055	0.057	0.143	0.149	0.096	0.105
6	0.043	0.044	0.052	0.052	0.148	0.154	0.120	0.118
7	0.038	0.044	0.046	0.043	0.145	0.143	0.123	0.099
8	0.033	0.035	0.053	0.056	0.134	0.135	0.124	0.114
9	0.039	0.040	0.048	0.049	0.152	0.170	0.103	0.096
10	0.040	0.042	0.048	0.042	0.167	0.167	0.107	0.105
Mean	0.040		0.051		0.161		0.114	
$\hat{\sigma}$	0.010		0.013		0.040		0.028	
0.3*$\hat{\sigma}$	0.003		0.004		0.012		0.009	
Critical value	0.000022		0.000052		0.000313		0.000212	
s_x	0.005		0.005		0.019		0.011	
s_w	0.002		0.005		0.006		0.009	
s_s	0.005		0.003		0.018		0.009	
s_s^2< critical	Pass		Pass		Failed		Pass	

8.1 Stability

	Time in weeks		u_{st}
	0 weeks	6 weeks	
Azoxystrobin	0.068	0.077	0.0053
Carbendazim	0.095	0.101	0.0037
Chlorpyrifos	0.046	0.047	0.0025
Cyprodinil	0.210	0.216	0.0051
Difenoconazole	0.291	0.301	0.0119
Fenhexamid	0.143	0.147	0.0069
Fludioxonil	0.072	0.076	0.0049
Imidacloprid	0.249	0.262	0.0085
Indoxacarb	0.237	0.246	0.0159
Iprodione	0.091	0.098	0.0059
Kresoxim methyl	0.113	0.121	0.0104
Lambda-cyhalothrin	0.035	0.034	0.0010
Methoxyfenozide	0.209	0.226	0.0120
Myclobutanil	0.139	0.139	0.0083
Penconazole	0.044	0.042	0.0021
Pyraclostrobin	0.102	0.099	0.0068
Pyrimethanil	0.041	0.041	0.0026
Quinoxyfen	0.056	0.053	0.0028
Tebuconazole	0.154	0.154	0.0127
Triadimenol	0.116	0.113	0.0053

Annex 9: Methods used by the certifiers

Certifier	Method used
Austrian Agency for Health and Food Safety (Ages), Austria	Sample extraction for determination of mass fraction of the indicated measureands has been carried out according to the "QuEChERs method" (EN ISO 15662) followed by LC-MS/MS and GC-MS/MS. 10g of sample were weighed into an 50ml PP-tube and spiked with the ISTD (Triphenylphosphate). After addition of 10ml Acetonitrile and shaking by hands (1 min) QuEChERs salt 1 (4 g MgSO4, 1 g NaCl, 1 g TSCD, 0.5 g DHS per sample) was added and the sample was again shaken for another minute. Afterwards, the extract was centrifuged (5min at 4000 rpm). An aliquot of this extract has been used for injection into LC-MS/MS (dilution of the extract 1/10 with pure water and 20µl injection). For GC-MS/MS the extract was cleaned-up with QuEChERs salt 2 (150 mg MgSO4 and 25 mg PSA per ml extract), stabilized using 5% formic acid and 12.5µl injected (in LVI). Abbreviations: TSCD—trisodium citrate dehydrate, DHS—disodium hydrogen citrate sesquihydrate
Laboratoire du SCL de Montpellier (SCL), France	The test samples were analysed performing three independent replicates per bottle using the "QueChERS" method (NF EN 15662). The all process was achieved twice for GC-MS/MS analysis and three time for LC-MS/MS analysis except for fludioxonil, so the independent results are the means. Method description: In a 50 ml centrifuge tube: - Sample intake: 10g - Sample extraction: add 10ml acetonitrile, 300µl NaOH and 50µl internal standard - shake for 1 mn - add 4g MgSO4, 1 g NaCl, 1g trisodium citrate dihydrate, 0.5 g disodium hydrogen citrate sesquihydrate. - shake for 1 mn - Centrifuge 3 mn at 5000 rpm - Clean-up procedure: transfer an aliquot of acetonitrile extract on a purification cartridge of 50mg PSA + 150mg MgSO4. - Centrifuge 3 mn at 5000 rpm - Filtration The acetonitrile purified extract is diluted with water for LC-MS/MS analysis. The acetonitrile extract are evaporated to dryness at 40°C. and taken up with hexane for GC-MS/MS. The measurands: Fludioxonil was analysed without the clean-up procedure and indoxacarb without filtration.
European Union Reference Laboratory for Pesticide Residues in Fruit and Vegetables (EURL-FV), Alemeria, Spain	**1.1.LC-MS/MS extraction method.** 1. Weigh 10 g ± 0.1 g of sample in 50 mL PTFE centrifuge tube. 2. Add 10 mL of acetonitrile and 50 µL of 10 mg/L triphenyl phosphate (TPP) and malathion-d10 (internal surrogate standards). 3. Shake in automatic axial extractor for 7 minutes. 4. Add 4 g of magnesium sulphate, 1 g of sodium chloride, 1 g of trisodiumcitrate dehydrate and 0.5 g of disodium hydrogencitrate sesquihydrate. 5. Shake in automatic axial extractor for 7 minutes. 6. Centrifuge for 5 min at 3700 rpm. 7. Transfer 5 mL of supernatant into 15 mL PTFE centrifuge tube containing 750 mg of magnesium sulphate, 125 mg of primary-secondary amine (PSA) and 125 mg of C18 and shake in a vortex 30 s. 8. Centrifuge for 5 min at 3700 rpm. 9. Add to the extract 40 µL of 5% formic acid in acetonitrile. 10.Filter the sample thorough 0.45 µm PTFE filter. 11.Add 4 µL of 2.5 mg/L dimethoate-d6 (injection standard) to 200 µL of filtered extract and dilute it 5 times with milliQ water for the LC analysis. **1.2.GC-MS/MS extraction method.** 1. Weigh 10 g ± 0.1 g of sample in 50 mL PTFE centrifuge tube. 2. Add 10 mL of ethyl acetate and 50 µL of 10 mg/L triphenyl phosphate (TPP) and dichlorvos-d6 (internal surrogate standards). 3. Shake 3 second by hand. 4. Add 8 g of magnesium sulphate and 1.5 g of sodium chloride.

	5. Shake in automatic axial extractor for 15 minutes. 6. Add 2 µL of 1.25 mg/L lindane-d6 (injection standard) to 50 µL of extract. **1.3. Measurement** Both LC and GC systems were operated in multiple reaction monitoring mode (MRM). Selected reaction monitoring (SRM) experiments were carried out to obtain the maximum sensitivity for the detection of the target molecules. For confirmation of the studied compounds, two SRM transitions and a correct ratio between the abundances of the two optimised SRM transitions (SRM2/SRM1) were used, along with retention time matching. The mass transitions used are presented in Appendix I. **1.4. Instrumentation and analytical conditions for the LC- MS/MS system** 1.4.1. HPLC Agilent 1200 • Column: Agilent Zorbax SB, C8, 4.6 mm x 150 mm, 5 µm • Mobile phase A: 0.1% formic acid in acetonitrile • Mobile phase B: 0.1% formic acid in ultra-pure water • Flow rate: 0.6 mL/min • Injection volume: 10 µL Mobile phase gradient for pesticides Time [min] Mobile phase A Mobile phase B 0 20% 80% 2 20% 80% 18 100% 0% 21 100% 0% Re-equilibration with initial mobile phase: 6 minutes. 1.4.2. QqQ MS/MS Agilent 6490 • Ionisation mode: positive • ESI source gas temperature: 120 °C • Gas flow: 15 L/min • Nebuliser gas: nitrogen • Nebuliser gas pressure: 35 psi • Sheath gas temperature: 375 ºC • Sheath gas flow: 12 L/min • Capillary voltage in positive mode: 3500 V • Collision gas: nitrogen • Nozzle voltage: 300V **1.5. Instrumentation and analytical conditions for the GC- MS/MS system** 1.5.1. Gas chromatograph Agilent 7890 • Column: HP-5MS UI 15 m × 0.25 mm x 0.25 µm • Retention Time Locking compound: trifluralin (retention time 5.81 min) • Injection mode: splitless • Ultra inert inlet liner, with a glass wool frit from Agilent • Injection volume: 2 µl • Injector temperature: Time [min] Temperature 0 80 °C 0.1 80 °C 0.6 300 °C 20 300 °C • Carrier gas: helium • Carrier gas purity: 99.999% • Carrier gas pressure: constant, 14.194 psi • Oven temperature: 70°C for 1 min, programmed to 150°C at 50°C/min, then to 200°C at 6°C/min and finally to 280°C at 16°C/min (4.07 min). The total run time was 20 minutes with 3 additional minutes for backflushing at 280°C. 1.5.2. QqQ MS/MS Agilent 7000 • Ionisation mode: electron impact ionisation • Temperature of the transfer line: 280 °C • Temperature of ion source: 280 °C • Temperature of quadrupole 1 and 2: 150 °C • Quenching gas: helium • Collision gas: nitrogen • Collision gas purity: 99.999% • Solvent delay: 2 minutes 2. Quantification The quantification by GC and LC was performed using five point calibration curves constructed from matrix-matched standards prepared from the 'blank' grape test item in bracketing mode covering the range from 0.020 to 0.400 mg/kg.

European Union Reference Laboratory for Pesticide Residues in Fruit and Vegetables (EURL-FV) – Laboratorio Agroalimentario de Valencia, Spain	**1. Short Description** The analysis of pesticide residues was performed by using QuEChERS Method. The homogeneous sample is extracted with acetonitrile. After salts addition the mixture is shaken intensively and centrifuged for phase separation. An aliquot of the organic phase is taken for the clean up with bulk sorbents (PSA) and MgSO4 anhydrous to remove the residual water. Extracts are shaken by vortex and a small aliquot is diluted with acetonitrile. **2. Apparatus and Consumables** _ Sample processing equipment, e.g. Dito Sama-K55 Food Processor. _ Automatic pipettes, suitable for handling volumes of 10 to 20 µL, 100 to 1000 µL, 0.5 to 5 mL and 1 to 10 mL. _ 50 ml centrifuge tubes with screw caps, for example 50 mL centrifuge tubes with screw cabs (e.g Sharlab S. L, Spain, article-no 027 – 409926). _ 10 mL centrifuge tubes with screw caps. _ 10 mL solvent-dispenser for acetonitrile. _ Test tubes, e.g. 10 mL. _ Centrifuge, suitable for the centrifuge tubes employed in the procedure and capable of achieving at least 4000 rpm. _ Syringes, e.g. 2 mL disposable syringes. _ Syrengies filters, 0.45 µm pore size. _ Injection vials, 1.5 ml, suitable for LC auto-sampler. _ Concentration Workstation, e.g. TurboVap LV, Zymark **3. Chemicals** _ Acetonitrile, HPLC quality _ NaCl pa. _ Magnesium sulphate, anhydrous, grit, for example MERCK 1.06067. Phthalates can be removed in a muffle furnace by heating to 550ºC. _ Disodium hydrogencitratesesquihydrate (e.g. Fluka 71635) _ Trisodium citrate dehydrate (e.g. Sigma S4641) _ Magnesium sulphate anhydrous coarsely grained. _ PSA, for example UCT CUMPS2CT _ Pesticides Standards, e.g. Dr. Ehrenstorfe, Scharlab. _ Cyclohexane, for GC residue analysis _ Acetone, for GC residue analysis **4. Procedure** 4.1 Sample preparation Samples were prepared according to the "Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed" (Document No. SANCO/10684/2009).. Sample was frozen for its storage immediatelyafter its arrival.. 4.2 Recovery Experiment The commodity used for fortification was grape. The commodity employed should not contain any of the pesticides analyzed. Organically grown samples are recommended for the analysis. A fortified sample at a level of 0.01 mg/Kg was prepared for this analysis 4.3 Extraction Pesticides analysed by HPLC-MS/MS 1. Weigh 10 g ± 0.1g sample in 50 mL centrifuge tube 2. Sample fortification: 3. Shake vigorously for 1 min to allow pesticides distribution 4. Add 10 ml of acetonitrile 5. Shake vigorously by hand or vortex for 1 min 6. Salt-mixtures addition for the Partitioning Step: _ 4 g ± 0.2 g Magnesium sulphate anhydrous _ 1 g ± 0.05 g Sodium chloride _ 1 g ± 0.05 g Trisodium citrate dihydrate _ 0.5 g ± 0.03 g Disodium hydrogencitrate sesquihydrate 7. Shake vigorously by hand or vortex for 1 min 8. Centrifuge for 5 min at 4000 rpm (Extract I) 9. Clean-up: 4 mL Extract I is transferred into a PP – single centrifuge tube which contains 100 mg PSA and 600 mg magnesium sulphate anhydrous (25 mg PSA and 150 mg magnesium sulphate per mL extract). Shake vigorously by hand or vortex for 1 min 10. Centrifuge for 2 min at 6000 rpm (Extract II) 11. Transfer 1mL Extract II into a test tube. Add 220 µL of acetonitrile 12. Vortex sample to mix it properly 13. Filter Extract III into a injection vial suitable for LC 4.5 Instrumentation and Analytical Conditions for the LC/QqQ (MS/MS) System LC-MS/MS System 3200 Q TRAP, Applied Biosystem:

	- Column: Atlantis T3 3 µm 2.1x100 mm - Column temperature: 40 ºC - Mobile phase A: H2O, 2 mM ammonia formiate, 0.1 1% formic acid. - Mobile phase B: methanol - Injection volume: 5µL - Autosampler temperature: 10 ºC - Analysis time: 18 min. **5. Calibration Curves** A calibration curve was calculated for each pesticide at four calibration levels; 0.01 µg/mL, 0.02 µg/mL, 0.05 µg/mL , 0.1 µg/mL and 0.2 µg/mL. The calibration curves were best fitted to a linear curve.
National Food Agency (NFA), Sweden	The analytical multi residue method: The method used for analysis of pesticide residues in the present study is based on extraction with ethyl acetate and determination with GC-MS/MS and LC-MS/MS. The homogenized sample of fruit and vegetable is extracted with ethyl acetate after addition of NaHCO3. At the end of the extraction, Na2SO4 is added. Sample extract is centrifuged and filtered prior to injection to GC-MS/MS and LC-MS/MS. No clean up step is needed. The method validation has been performed according to the guidelines in SANCO document "Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed", SANCO/12495/2011 taking account the selected commodity groups. The Limit of Quantification (LOQ) of the method is 0.01 mg/kg for most of the analytes.

Annex 10: Results by the certifiers

(Mean result X with the associated expanded uncertainty U)

	Cert1		Cert2		Cert3		Cert4		Cert5	
	X_1	U_1 (k=2)	X_2	U_2	X_3	U_3	X_4	U_4	X_5	U_5
Azoxystrobin	0.067	0.016	0.097	0.01	0.0883	0.011	0.121	0.033	0.0877	0.0073
Carbendazim	0.086	0.008	0.087	0.006	0.104	0.012	0.116	0.032	0.0856	0.0076
Chlorpyrifos	0.043	0.01	0.051	0.003	0.057	0.007	0.079	0.022	0.0445	0.0054
Cyprodinil	0.179	0.035	0.185	0.013	0.171	0.021	0.199	0.055	0.1446	0.0149
Difenoconazole	0.261	0.023	0.345	0.025	0.385	0.046	0.387	0.107	0.2801	0.0422
Fenhexamid	0.151	0.035	0.228	0.018	0.236	0.028	0.245	0.068	0.1525	0.0105
Fludioxonil	0.063	0.013	0.101	0.01	0.1	0.012	0.127	0.035	0.083	0.0076
Imidacloprid	0.213	0.015	0.288	0.019	0.283	0.034	0.305	0.084	0.2415	0.0238
Indoxacarb	0.23	0.064	0.298	0.031	0.272	0.033	0.358	0.099	0.2616	0.0235
Iprodione	0.086	0.021	0.12	0.009	0.12	0.014	0.181	0.05	0.082	0.0091
Kresoxim methyl	0.108	0.026	0.21	0.014	0.21	0.025	0.277	0.076	0.1412	0.0154
Lambda-cyhalothrin	0.03	0.004	0.033	0.003	0.03	0.004	0.042	0.011	0.0208	0.0028
Methoxyfenozide	0.21	0.016	0.276	0.025	0.422	0.051	0.275	0.076	0.2417	0.0198
Myclobutanil	0.126	0.028	0.184	0.012	0.171	0.02	0.215	0.059	0.1493	0.0134
Penconazole	0.035	0.008	0.052	0.003	0.047	0.006	0.049	0.013	0.0418	0.0036
Pyraclostrobin	0.096	0.023	0.135	0.01	0.146	0.018	0.176	0.049	0.104	0.015
Pyrimethanil	0.044	0.005	0.063	0.005	0.055	0.007	0.074	0.02	0.0503	0.0045
Quinoxyfen	0.049	0.009	0.06	0.005	0.066	0.008	0.073	0.02	0.0515	0.0068
Tebuconazole	0.154	0.037	0.243	0.017	0.235	0.028	0.298	0.082	0.2049	0.0153
Triadimenol	0.109	0.013	0.242	0.017	0.21	0.025	0.439	0.121	0.1554	0.0161

Annex 11-30: Results for the different pesticides

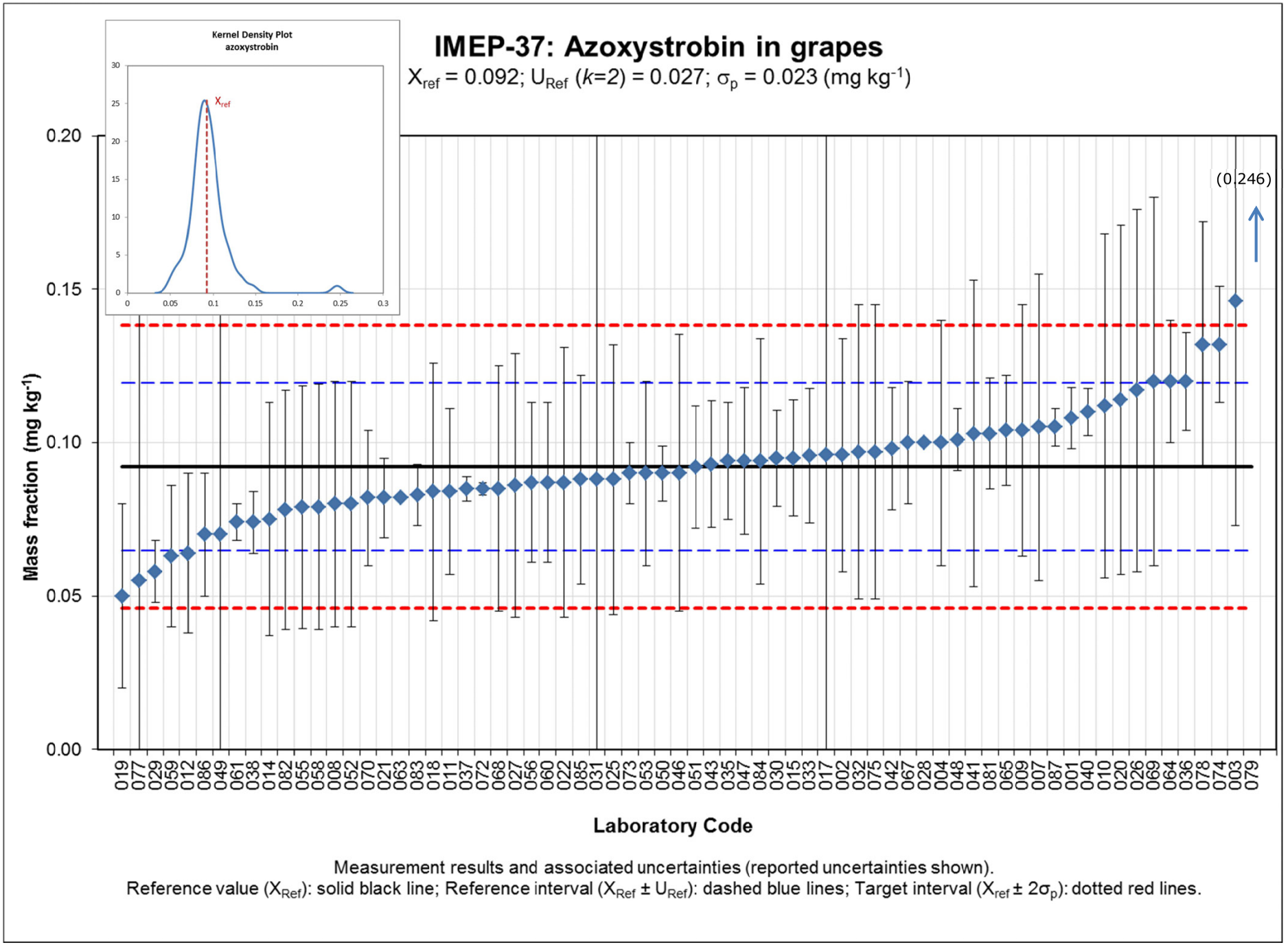
The table shows the reported x_{lab}, U_{lab} and k of the participants, the technique used by each participant, the obtained z and ζ-scores of each participant and an uncertainty assessment. A satisfactory result is green, a questionable result is yellow and an unsatisfactory result is red in annexes 11 to 30.
a: $u_{min}\ (u_{ref}) \leq u_{lab} \leq u_{max}\ (\hat{\sigma})$; b: $u_{lab} < u_{min}$; c: $u_{lab} > u_{max}\ (\hat{\sigma})$

The graph shows the measurement results and associated uncertainties of the participants, the reference value X_{ref} with a reference interval and a target interval. In the graph σ_p stands for $\hat{\sigma}$.

Annex 11: Results for Azoxystrobin

X_{ref} = 0.092; U_{Ref} (k=2) = 0.027; $\hat{\sigma}$ = 0.023 (mg kg^{-1})

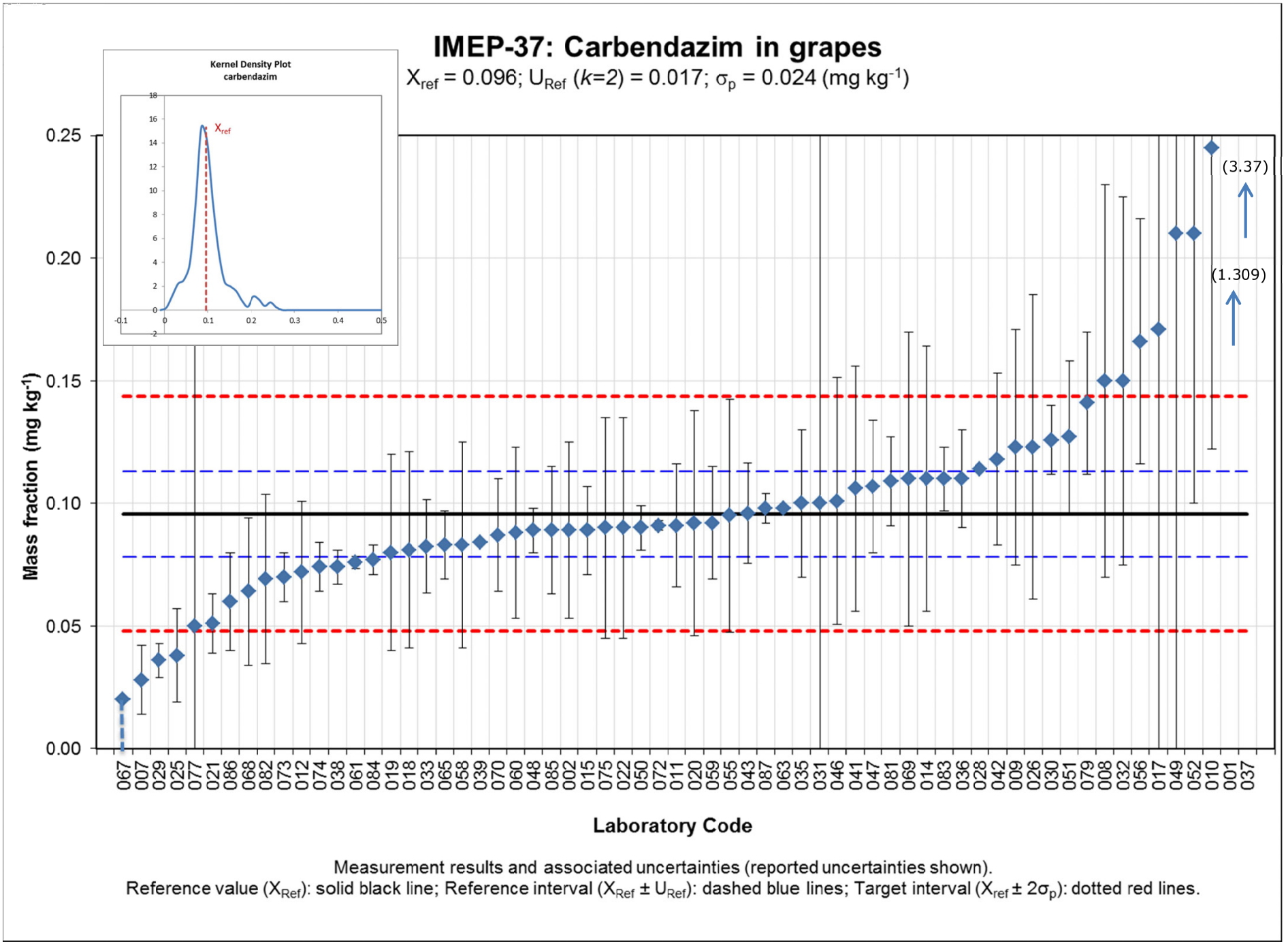
Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	0.108	0.010	2	GC-MS (QqQ)	0.005	0.69	1.08	b
002	0.096	0.038	0.022	LC-MS (QqQ)	1.727273	0.16	0.00	c
003	0.146	0.073	83.5	LC-MS (QqQ)	0.000874	2.33	3.93	b
004	0.10	0.040	2	GC-MS (QqQ)	0.02	0.34	0.32	a
007	0.105	0.05	1	LC-MS (QqQ)	0.05	0.56	0.25	c
008	0.08	0.04	2	LC-MS (QqQ)	0.02	-0.53	-0.50	a
009	0.104	0.041	2	LC-MS (QqQ)	0.0205	0.51	0.48	a
010	0.112	0.056	2	LC-MS (QqQ)	0.028	0.86	0.64	c
011	0.084	0.027	98	LC-MS (QqQ)	0.000276	-0.36	-0.60	b
012	0.064	0.026	2	LC-MS (QqQ)	0.013	-1.22	-1.49	b
014	0.075	0.038	2	LC-MS (QqQ)	0.019	-0.75	-0.73	a
015	0.095	0.019	2	GC-MS (Q)	0.0095	0.12	0.17	b
017	0.0960	30	2.0	GC-MS (Q)	15	0.16	0.00	c
018	0.084	0.042	2	LC-MS (IT)	0.021	-0.36	-0.33	a
019	0.05	0.03	2	LC-MS (QqQ)	0.015	-1.83	-2.08	a
020	0.114	0.057	2	LC-MS (QqQ)	0.0285	0.95	0.69	c
021	0.082	0.013	2	LC-MS (QqQ)	0.0065	-0.44	-0.67	b
022	0.087	0.044	2	LC-MS (QqQ)	0.022	-0.23	-0.20	a
025	0.088	0.044	2	LC-MS (QqQ)	0.022	-0.18	-0.16	a
026	0.117	0.059	2	GC-MS (IT)	0.0295	1.08	0.76	c
027	0.086	0.043	2	LC-MS (QqQ)	0.0215	-0.27	-0.24	a
028	0.10	0	0	LC-MS (QqQ)	0	0.34	0.57	b
029	0.058	0.01	2	LC-MS (QqQ)	0.005	-1.48	-2.35	b
030	0.0949	0.0157	2	LC-MS (QqQ)	0.00785	0.12	0.17	b
031	0.088	25	2	GC-MS (QqQ)	12.5	-0.18	0.00	c
032	0.097	0.048	2	LC-MS (QqQ)	0.024	0.21	0.17	c
033	0.0958	0.022	1	GC-MS (QqQ)	0.022	0.16	0.14	a
035	0.094	0.019	2	LC-MS (QqQ)	0.0095	0.08	0.11	b
036	0.120	0.016	2	LC-MS (QqQ)	0.008	1.21	1.75	b
037	0.085	0.004	2	GC/ECD	0.002	-0.31	-0.52	b
038	0.074	0.010	2	LC-MS (QqQ)	0.005	-0.79	-1.25	b
040	0.110	0.0078	2	GC-MS (Q)	0.0039	0.77	1.25	b
041	0.103	0.05	2	LC-MS (QqQ)	0.025	0.47	0.38	c
042	0.098	0.020	2	LC-MS (QqQ)	0.01	0.25	0.34	b
043	0.093	0.02062	2	LC-MS (QqQ)	0.01031	0.03	0.05	b
046	0.0901	0.0451	2	LC-MS (QqQ)	0.02255	-0.09	-0.08	a
047	0.094	0.024	0.99	GC-MS (Q)	0.024242	0.08	0.06	c
048	0.101	0.010	97	LC-MS (QqQ)	0.000103	0.38	0.64	b
049	0.07	20	1.10	GC-MS (Q)	18.18182	-0.96	0.00	c
050	0.090	0.009	2	GC-MS (Q)	0.0045	-0.10	-0.15	b
051	0.092	0.020	2.3	LC-MS (QqQ)	0.008696	-0.01	-0.01	b
052	0.08	0.04	2	LC-MS (QqQ)	0.02	-0.53	-0.50	a
053	0.09	0.03	2	GC-MS (TOF)	0.015	-0.10	-0.11	a
055	0.079	0.0395	2	LC-MS (QqQ)	0.01975	-0.57	-0.55	a
056	0.087	0.026	2	LC-MS (QqQ)	0.013	-0.23	-0.28	b
058	0.079	0.040	2	LC-MS (QqQ)	0.02	-0.57	-0.54	a
059	0.063	0.023	2	GC-ECD/NPD	0.0115	-1.27	-1.63	b
060	0.087	0.026	2	LC-MS (QqQ)	0.013	-0.23	-0.28	b
061	0.074	0.00598	2	LC-MS (QqQ)	0.00299	-0.79	-1.30	b
063	0.082	0	0	LC-MS (QqQ)	0	-0.44	-0.75	b
064	0.12	0.02	2	GC-MS (IT)	0.01	1.21	1.64	b
065	0.104	0.018	2	GC-MS (Q)	0.009	0.51	0.72	b
067	0.100	0.02	2	LC-MS (QqQ)	0.01	0.34	0.46	b
068	0.085	0.04	2	LC-MS (QqQ)	0.02	-0.31	-0.30	a
069	0.12	0.06	2	GC-MS (Q)	0.03	1.21	0.84	c
070	0.082	0.022	2	LC-MS (QqQ)	0.011	-0.44	-0.58	b
072	0.085	0.002	2	LC-MS (QqQ)	0.001	-0.31	-0.52	b
073	0.09	0.01	2		0.005	-0.10	-0.15	b
074	0.132	0.019	2	UPLC-MS/MS	0.0095	1.73	2.39	b
075	0.097	0.048	2	GC-MS (Q)	0.024	0.21	0.17	c
077	0.055	0.5	2	LC-MS (QqQ)	0.25	-1.61	-0.15	c
078	0.132	0.04	2	GC-MS (Q)	0.02	1.73	1.64	a
079	0.246	0.018	2	GC-MS (Q)	0.009	6.67	9.39	b
081	0.103	0.018	2	GC-MS (Q)	0.009	0.47	0.66	b
082	0.078	0.039	2	LC-MS (QqQ)	0.0195	-0.62	-0.60	a
083	0.083	0.010	2	GC-MS (QqQ)	0.005	-0.40	-0.63	b
084	0.094	0.040	2	GC-ECD	0.02	0.08	0.07	a
085	0.088	0.034	2	GC-MS (QqQ)	0.017	-0.18	-0.19	a
086	0.07	0.02	2	LC-MS (Q)	0.01	-0.96	-1.31	b
087	0.105	0.006	2	LC-MS(Q ; QqQ)	0.003	0.56	0.91	b


IMEP-37: Azoxystrobin in grapes
X_{ref} = 0.092; U_{Ref} (k=2) = 0.027; σ_p = 0.023 (mg kg^{-1})
Kernel Density Plot
azoxystrobin
X_{ref}
(0.246)
Mass fraction (mg kg^{-1})
0.00
0.05
0.10
0.15
0.20
019 077 029 059 012 086 049 061 038 014 082 055 058 008 052 070 021 063 083 018 011 037 072 068 027 056 060 022 085 031 025 073 053 050 046 051 043 035 047 084 030 015 033 017 002 032 075 042 067 028 004 048 041 081 065 009 007 087 001 040 010 020 026 069 064 036 078 074 003 079
Laboratory Code
Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 12: Results for Carbendazim

X_{ref} = 0.096; U_{Ref} (*k=2*) = 0.017; $\hat{\sigma}$ = 0.024 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	1.309	0.014	2	LC-MS (QqQ)	0.007	50.70	108.37	b
002	0.089	0.036	0.016	LC-MS (QqQ)	2.25	-0.28	0.00	c
007	0.028	0.014	1	LC-MS (QqQ)	0.014	-2.83	-4.10	a
008	0.15	0.08	2	LC-MS (QqQ)	0.04	2.27	1.33	c
009	0.123	0.048	2	LC-MS (QqQ)	0.024	1.14	1.07	c
010	0.245	0.123	2	LC-MS (QqQ)	0.0615	6.24	2.40	c
011	0.091	0.025	98	LC-MS (QqQ)	0.000255	-0.20	-0.54	b
012	0.072	0.029	2	LC-MS (QqQ)	0.0145	-0.99	-1.40	a
014	0.11	0.054	2	LC-MS (QqQ)	0.027	0.60	0.50	c
015	0.089	0.018	2	LC-FLD	0.009	-0.28	-0.54	a
017	0.171	30	2	LC-MS (Q)	15	3.15	0.01	c
018	0.081	0.04	2	LC-MS (IT)	0.02	-0.62	-0.67	a
019	0.08	0.04	2	LC-MS (QqQ)	0.02	-0.66	-0.72	a
020	0.092	0.046	2	LC-MS (QqQ)	0.023	-0.16	-0.15	a
021	0.051	0.012	2	LC-MS (QqQ)	0.006	-1.87	-4.22	b
022	0.09	0.045	2	LC-MS (QqQ)	0.0225	-0.24	-0.24	a
025	0.038	0.019	2	LC-MS (QqQ)	0.0095	-2.41	-4.47	a
026	0.123	0.062	2	LC-MS (QqQ)	0.031	1.14	0.85	c
028	0.114	0	0	LC-MS (QqQ)	0	0.76	2.09	b
029	0.036	0.007	2	LC-MS (QqQ)	0.0035	-2.50	-6.34	b
030	0.1259	0.0142	2	LC-MS (QqQ)	0.0071	1.26	2.68	b
031	0.1	25	2	LC-MS (QqQ)	12.5	0.18	0.00	c
032	0.15	0.075	2	LC-MS (QqQ)	0.0375	2.27	1.41	c
033	0.0824	0.019	1	LC-MS (QqQ)	0.019	-0.56	-0.64	a
035	0.1	0.03	2	LC-MS (QqQ)	0.015	0.18	0.25	a
036	0.11	0.02	2	LC-MS (QqQ)	0.01	0.60	1.08	a
037	3.37	0.325	2	HPLC/UV	0.1625	136.83	20.12	c
038	0.074	0.007	2	LC-MS (QqQ)	0.0035	-0.91	-2.31	b
039	0.084	0	0	LC-MS (QqQ)	0	-0.49	-1.34	b
041	0.106	0.05	2	LC-MS (QqQ)	0.025	0.43	0.39	c
042	0.118	0.035	2	LC-MS (QqQ)	0.0175	0.93	1.14	a
043	0.096	0.02033	2	LC-MS (QqQ)	0.010165	0.01	0.02	a
046	0.101	0.0505	2	LC-MS (QqQ)	0.02525	0.22	0.20	c
047	0.107	0.027	1.33	LC-MS (QqQ)	0.020301	0.47	0.51	a
048	0.089	0.009	91	LC-MS (QqQ)	9.89E-05	-0.28	-0.77	b
049	0.21	14	1.23	LC-MS (QqQ)	11.38211	4.78	0.01	c
050	0.09	0.009	2	LC-MS (QqQ)	0.0045	-0.24	-0.58	b
051	0.127	0.031	2.3	LC-MS (QqQ)	0.013478	1.31	1.95	a
052	0.21	0.11	2	LC-MS (QqQ)	0.055	4.78	2.05	c
055	0.095	0.0475	2	LC-MS (QqQ)	0.02375	-0.03	-0.03	a
056	0.166	0.05	2	LC-MS (QqQ)	0.025	2.94	2.65	c
058	0.083	0.042	2	LC-MS (QqQ)	0.021	-0.53	-0.56	a
059	0.092	0.023	2	UPLC/DAD	0.0115	-0.16	-0.26	a
060	0.088	0.035	2	LC-MS (QqQ)	0.0175	-0.32	-0.39	a
061	0.076	0.00256	2	LC-MS (QqQ)	0.00128	-0.82	-2.23	b
063	0.098	0	0	LC-MS (QqQ)	0	0.10	0.26	b
065	0.083	0.014	2	HPLC-UV	0.007	-0.53	-1.14	b
067	< 0.02			GC-MS (QqQ)				
068	0.064	0.03	2	LC-MS (QqQ)	0.015	-1.33	-1.83	a
069	0.11	0.06	2	LC-MS (QqQ)	0.03	0.60	0.46	c
070	0.087	0.023	2	LC-MS (QqQ)	0.0115	-0.36	-0.60	a
072	0.091	0.002	2	LC-MS (QqQ)	0.001	-0.20	-0.54	b
073	0.07	0.01	2		0.005	-1.07	-2.55	b
074	0.074	0.01	2	UPLC-MS/MS	0.005	-0.91	-2.16	b
075	0.09	0.045	2	LC-MS (QqQ)	0.0225	-0.24	-0.24	a
077	0.05	0.5	2	LC-MS (QqQ)	0.25	-1.91	-0.18	c
079	0.141	0.029	2	LC-MS (QqQ)	0.0145	1.89	2.67	a
081	0.109	0.018	2	LC-MS (QqQ)	0.009	0.55	1.06	a
082	0.069	0.0345	2	LC-MS (QqQ)	0.01725	-1.12	-1.38	a
083	0.11	0.013	2	LC-MS (QqQ)	0.0065	0.60	1.31	b
084	0.077	0.006	2	HPLC-UV vis	0.003	-0.78	-2.03	b
085	0.089	0.026	2	LC-MS (QqQ)	0.013	-0.28	-0.43	a
086	0.06	0.02	2	LC-MS (Q)	0.01	-1.49	-2.69	a
087	0.098	0.006	2	LC-MS(Q ; QqQ)	0.003	0.10	0.25	b

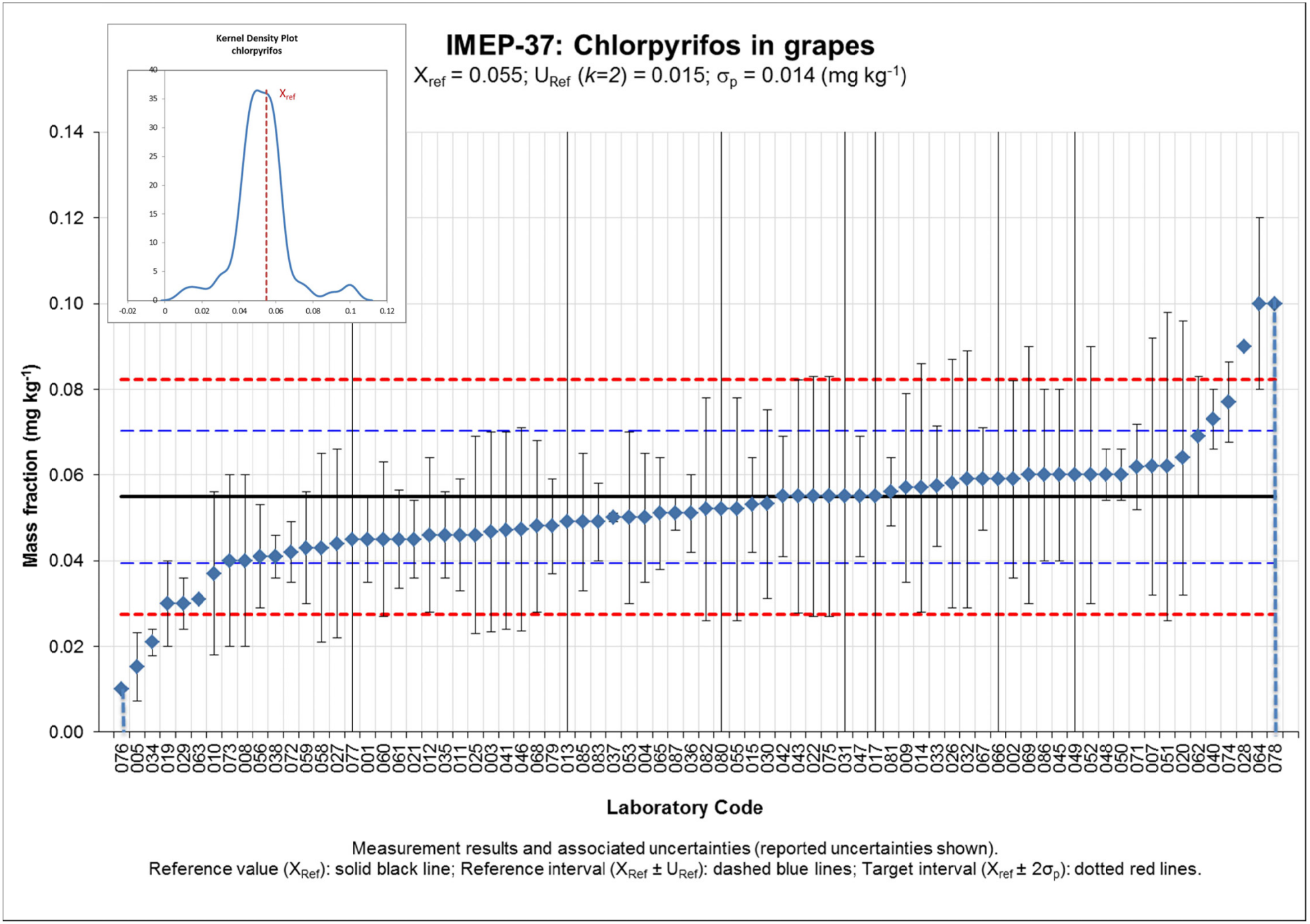


Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 13: Results for Chlorpyrifos

X_{ref} = 0.055; U_{Ref} (k=2) = 0.015; $\hat{\sigma}$ = 0.014 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	0.045	0.01	2	GC-MS (QqQ)	0.005	-0.72	-1.08	b
002	0.059	0.023	0.036	GC-MS (QqQ)	0.638889	0.30	0.01	c
003	0.0467	0.02335	91.5	LC-MS (QqQ)	0.000255	-0.60	-1.06	b
004	0.05	0.015	2	GC-MS (QqQ)	0.0075	-0.36	-0.45	b
005	0.01515	0.008	2	GC-NPD,quechers	0.004	-2.90	-4.57	b
007	0.062	0.03	1	GC-MS (QqQ)	0.03	0.52	0.23	c
008	0.04	0.02	2	GC-MS (QqQ)	0.01	-1.09	-1.18	a
009	0.057	0.022	2	GC-MS (Q)	0.011	0.15	0.16	a
010	0.037	0.019	2	GC-MS (QqQ)	0.0095	-1.30	-1.46	a
011	0.046	0.013	71	GC-MS (QqQ)	0.000183	-0.65	-1.15	b
012	0.046	0.018	2	LC-MS (QqQ)	0.009	-0.65	-0.75	a
013	0.049	21	2	GC-MS (Q)	10.5	-0.43	0.00	c
014	0.057	0.029	2	GC-MS (QqQ)	0.0145	0.15	0.13	c
015	0.053	0.011	2	GC-MS (Q)	0.0055	-0.14	-0.20	b
017	0.055	30	2	GC-MS (Q)	15	0.01	0.00	c
019	0.03	0.01	2	LC-MS (QqQ)	0.005	-1.81	-2.70	b
020	0.064	0.032	2	LC-MS (QqQ)	0.016	0.66	0.51	c
021	0.045	0.009	2	LC-MS (QqQ)	0.0045	-0.72	-1.11	b
022	0.055	0.028	2	LC-MS (QqQ)	0.014	0.01	0.01	c
025	0.046	0.023	2	GC-MS (Q)	0.0115	-0.65	-0.64	a
026	0.058	0.029	2	GC-MS (IT)	0.0145	0.23	0.19	c
027	0.044	0.022	2	GC-MS (QqQ)	0.011	-0.79	-0.81	a
028	0.09	0	0	LC-MS (QqQ)	0	2.56	4.54	b
029	0.03	0.006	2	GC-MS (QqQ)	0.003	-1.81	-3.00	b
030	0.0532	0.022	2	LC-MS (QqQ)	0.011	-0.12	-0.13	a
031	0.055	25	2	GC-MS (QqQ)	12.5	0.01	0.00	c
032	0.059	0.03	2	LC-MS (QqQ)	0.015	0.30	0.24	c
033	0.0574	0.014	1	GC-MS (QqQ)	0.014	0.18	0.16	c
034	0.0209	0.003	2	GC-NPD,quechers	0.0015	-2.48	-4.32	b
035	0.046	0.01	2	GC-MS (QqQ)	0.005	-0.65	-0.97	b
036	0.051	0.009	2	LC-MS (QqQ)	0.0045	-0.28	-0.44	b
037	0.05	0.001	2	GC/ECD	0.0005	-0.36	-0.63	b
038	0.041	0.005	2	GC-MS (Q)	0.0025	-1.01	-1.71	b
040	0.073	0.007	2	GC-MS (Q)	0.0035	1.32	2.13	b
041	0.047	0.023	2	GC-MS (QqQ)	0.0115	-0.58	-0.57	a
042	0.055	0.014	2	GC-MS (QqQ)	0.007	0.01	0.01	b
043	0.055	0.02723	2	GC-MS (TOF)	0.013615	0.01	0.01	a
045	0.06	0.02	2	GC-MS (El Quadrapole)	0.01	0.37	0.40	a
046	0.0473	0.0237	2	LC-MS (QqQ)	0.01185	-0.55	-0.54	a
047	0.055	0.014	0.9	GC-MS (Q)	0.015556	0.01	0.01	c
048	0.06	0.006	89	LC-MS (QqQ)	6.74E-05	0.37	0.66	b
049	0.06	20	1.03	GC-MS (Q)	19.41748	0.37	0.00	c
050	0.06	0.006	2	GC-MS (Q)	0.003	0.37	0.62	b
051	0.062	0.036	2.3	GC-NPD	0.015652	0.52	0.41	c
052	0.06	0.03	2	GC-MS (QqQ)	0.015	0.37	0.30	c
053	0.05	0.02	2	GC-MS (TOF)	0.01	-0.36	-0.39	a
055	0.052	0.026	2	GC-MS (QqQ)	0.013	-0.21	-0.19	a
056	0.041	0.012	2	GC-MS (Q)	0.006	-1.01	-1.42	b
058	0.043	0.022	2	GC-MS (QqQ)	0.011	-0.87	-0.89	a
059	0.043	0.013	2	GC-ECD/NPD	0.0065	-0.87	-1.18	b
060	0.045	0.018	2	GC-MS (QqQ)	0.009	-0.72	-0.83	a
061	0.045	0.01151	2	LC-MS (QqQ)	0.005755	-0.72	-1.03	b
062	0.069	0.014	2	GC	0.007	1.03	1.35	b
063	0.031	0	0	LC-MS (QqQ)	0	-1.74	-3.09	b
064	0.1	0.02	2	GC-MS (IT)	0.01	3.29	3.57	a
065	0.051	0.013	2	GC-MS (Q)	0.0065	-0.28	-0.39	b
066	0.059	50	2	GC-MS (QqQ)	25	0.30	0.00	c
067	0.059	0.012	2	GC-MS (QqQ)	0.006	0.30	0.42	b
068	0.048	0.02	2	GC-MS (Q)	0.01	-0.50	-0.55	a
069	0.06	0.03	2	GC-MS (Q)	0.015	0.37	0.30	c
071	0.0618	0.01	2	LC-MS (Q)	0.005	0.50	0.75	b
072	0.042	0.007	2	GC-MS (QqQ)	0.0035	-0.94	-1.52	b
073	0.04	0.02	2		0.01	-1.09	-1.18	a
074	0.077	0.0093	2	UPLC-MS/MS	0.00465	1.61	2.45	b
075	0.055	0.028	2	GC-MS (Q)	0.014	0.01	0.01	c
076	< 0.01			GC-MS (Q)				
077	0.045	0.5	2	LC-MS (QqQ)	0.25	-0.72	-0.04	c
078	< 0.1			GC-MS (Q)				
079	0.048	0.011	2	GC-MS (Q)	0.0055	-0.50	-0.73	b
080	0.052	0.356	2	GC-MS	0.178	-0.21	-0.02	c
081	0.056	0.008	2	GC-MS (Q)	0.004	0.08	0.13	b
082	0.052	0.026	2	GC-MS (QqQ)	0.013	-0.21	-0.19	a
083	0.049	0.009	2	GC-MS (QqQ)	0.0045	-0.43	-0.66	b
085	0.049	0.016	2	GC-MS (QqQ)	0.008	-0.43	-0.53	a
086	0.06	0.02	2	GC-MS (Q)	0.01	0.37	0.40	a
087	0.051	0.004	2	LC-MS(Q ; QqQ)	0.002	-0.28	-0.49	b

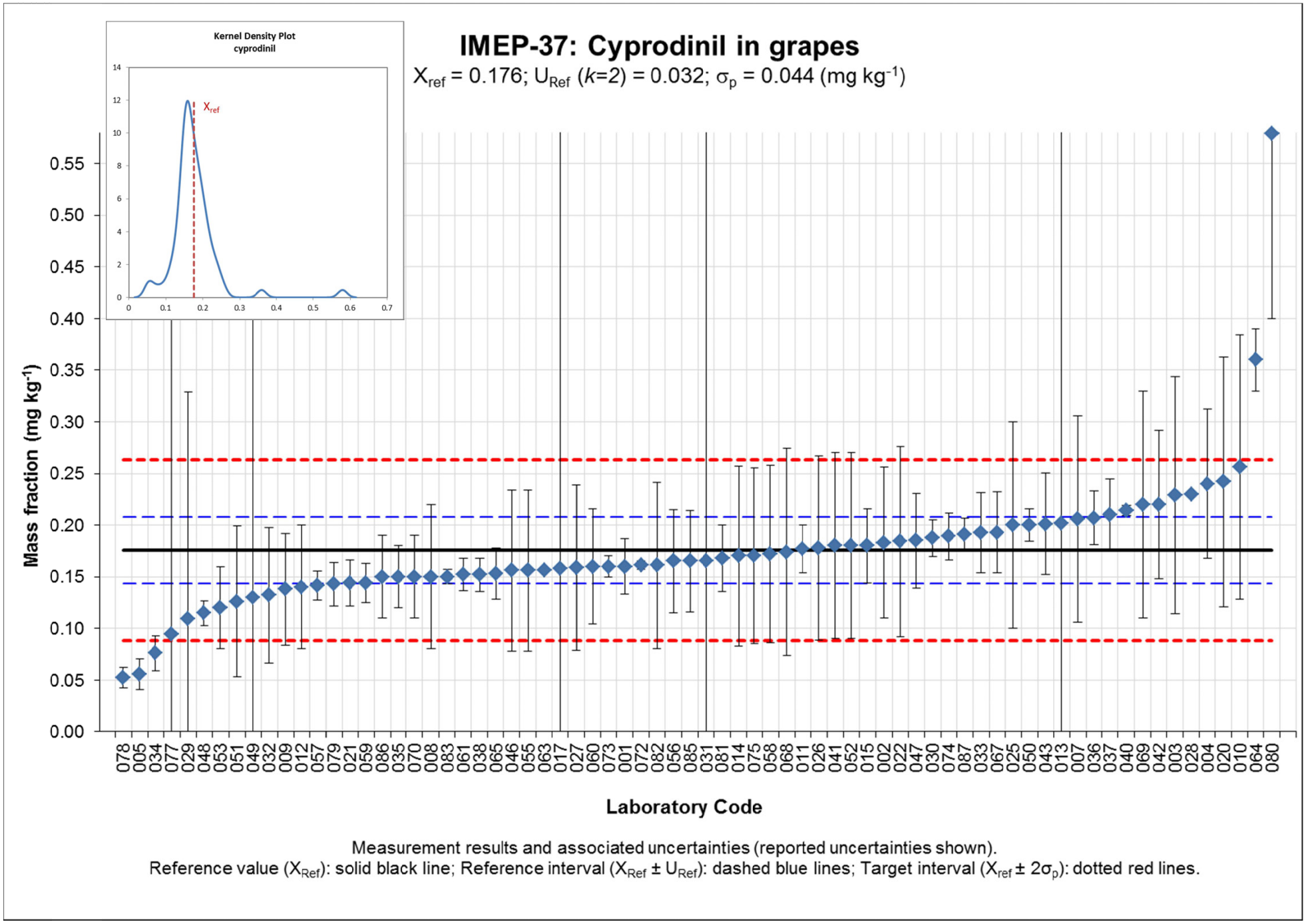


Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 14: Results for Cyprodinil

X_{ref} = 0.176; U_{Ref} (*k=2*) = 0.032; $\hat{\sigma}$ = 0.044 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	0.16	0.027	2	GC-MS (QqQ)	0.0135	-0.36	-0.74	b
002	0.183	0.073	0.023	GC-MS (QqQ)	3.173913	0.17	0.00	c
003	0.229	0.1145	82	LC-MS (QqQ)	0.001396	1.21	3.27	b
004	0.24	0.072	2	GC-MS (QqQ)	0.036	1.46	1.63	a
005	0.055741	0.015	2	GC-NPD,quechers	0.0075	-2.73	-6.71	b
007	0.206	0.1	1	LC-MS (QqQ)	0.1	0.69	0.30	c
008	0.15	0.07	2	GC-MS (QqQ)	0.035	-0.59	-0.67	a
009	0.138	0.054	2	GC-MS (Q)	0.027	-0.86	-1.20	a
010	0.256	0.128	2	LC-MS (QqQ)	0.064	1.83	1.22	c
011	0.177	0.023	100	LC-MS (QqQ)	0.00023	0.03	0.08	b
012	0.14	0.06	2	LC-MS (QqQ)	0.03	-0.81	-1.05	a
013	0.202	20	2	GC-MS (Q)	10	0.60	0.00	c
014	0.17	0.087	2	GC-MS (QqQ)	0.0435	-0.13	-0.12	a
015	0.18	0.036	2	GC-MS (Q)	0.018	0.10	0.18	a
017	0.158	30	2	GC-MS (Q)	15	-0.40	0.00	c
020	0.242	0.121	2	LC-MS (QqQ)	0.0605	1.51	1.06	c
021	0.144	0.022	2	LC-MS (QqQ)	0.011	-0.72	-1.62	b
022	0.184	0.092	2	LC-MS (QqQ)	0.046	0.19	0.17	c
025	0.2	0.1	2	LC-MS (QqQ)	0.05	0.55	0.46	c
026	0.178	0.089	2	GC-MS (IT)	0.0445	0.05	0.05	c
027	0.159	0.08	2	LC-MS (QqQ)	0.04	-0.38	-0.39	a
028	0.23	0	0	LC-MS (QqQ)	0	1.24	3.35	b
029	0.109	0.22	2	LC-MS (QqQ)	0.11	-1.52	-0.60	c
030	0.1873	0.0174	2	LC-MS (QqQ)	0.0087	0.26	0.63	b
031	0.165	25	2	GC-MS (QqQ)	12.5	-0.24	0.00	c
032	0.132	0.066	2	LC-MS (QqQ)	0.033	-1.00	-1.19	a
033	0.1927	0.039	1	GC-MS (QqQ)	0.039	0.39	0.40	a
034	0.07594	0.017	2	GC-NPD,quechers	0.0085	-2.27	-5.45	b
035	0.15	0.03	2	GC-MS (QqQ)	0.015	-0.59	-1.16	b
036	0.207	0.026	2	LC-MS (QqQ)	0.013	0.71	1.50	b
037	0.21	0.035	2	GC-MS (Q)	0.0175	0.78	1.44	a
038	0.152	0.016	2	LC-MS (QqQ)	0.008	-0.54	-1.31	b
040	0.214	0.0049	2	GC-MS (Q)	0.00245	0.87	2.33	b
041	0.18	0.09	2	GC-MS (QqQ)	0.045	0.10	0.09	c
042	0.22	0.072	2	GC-MS (QqQ)	0.036	1.01	1.12	a
043	0.201	0.04919	2	GC-MS (TOF)	0.024595	0.58	0.86	a
046	0.156	0.078	2	LC-MS (QqQ)	0.039	-0.45	-0.47	a
047	0.185	0.046	0.97	GC-MS (Q)	0.047423	0.21	0.19	c
048	0.115	0.012	90	GC-MS (Q)	0.000133	-1.38	-3.74	b
049	0.13	8	1.12	GC-MS (Q)	7.142857	-1.04	-0.01	c
050	0.2	0.016	2	GC-MS (Q)	0.008	0.55	1.34	b
051	0.126	0.073	2.3	GC-NPD	0.031739	-1.13	-1.39	a
052	0.18	0.09	2	GC-MS (QqQ)	0.045	0.10	0.09	c
053	0.12	0.04	2	GC-MS (TOF)	0.02	-1.27	-2.16	a
055	0.156	0.078	2	GC-MS (QqQ)	0.039	-0.45	-0.47	a
056	0.165	0.05	2	LC-MS (QqQ)	0.025	-0.24	-0.36	a
057	0.1418	0.014	2	GC-MS	0.007	-0.77	-1.92	b
058	0.172	0.086	2	LC-MS (QqQ)	0.043	-0.08	-0.08	a
059	0.144	0.019	2	GC-NPD	0.0095	-0.72	-1.69	b
060	0.16	0.056	2	GC-MS (QqQ)	0.028	-0.36	-0.49	a
061	0.152	0.01583	2	LC-MS (QqQ)	0.007915	-0.54	-1.31	b
063	0.156	0	0	LC-MS (QqQ)	0	-0.45	-1.22	b
064	0.36	0.03	2	GC-MS (IT)	0.015	4.19	8.34	b
065	0.153	0.025	2	GC-MS (Q)	0.0125	-0.52	-1.11	b
067	0.193	0.039	2	GC-MS (QqQ)	0.0195	0.39	0.68	a
068	0.174	0.1	2	GC-MS (Q)	0.05	-0.04	-0.03	c
069	0.22	0.11	2	GC-MS (Q)	0.055	1.01	0.77	c
070	0.15	0.04	2	LC-MS (QqQ)	0.02	-0.59	-1.00	a
072	0.161	0.004	2	LC-MS (QqQ)	0.002	-0.34	-0.90	b
073	0.16	0.01	2		0.005	-0.36	-0.93	b
074	0.189	0.023	2	UPLC-MS/MS	0.0115	0.30	0.67	b
075	0.17	0.085	2	GC-MS (Q)	0.0425	-0.13	-0.13	a
077	0.094	0.5	2	LC-MS (QqQ)	0.25	-1.86	-0.33	c
078	0.052	0.01	2	GC-MS (Q)	0.005	-2.82	-7.29	b
079	0.143	0.021	2	GC-MS (Q)	0.0105	-0.74	-1.69	b
080	0.579	0.179	2	GC-MS	0.0895	9.18	4.43	c
081	0.168	0.032	2	GC-MS (Q)	0.016	-0.18	-0.34	b
082	0.161	0.0805	2	LC-MS (QqQ)	0.04025	-0.34	-0.34	a
083	0.15	0.007	2	GC-MS (QqQ)	0.0035	-0.59	-1.55	b
085	0.165	0.049	2	GC-MS (QqQ)	0.0245	-0.24	-0.36	a
086	0.15	0.04	2	GC-MS (Q)	0.02	-0.59	-1.00	a
087	0.191	0.016	2	LC-MS(Q ; QqQ)	0.008	0.35	0.84	b

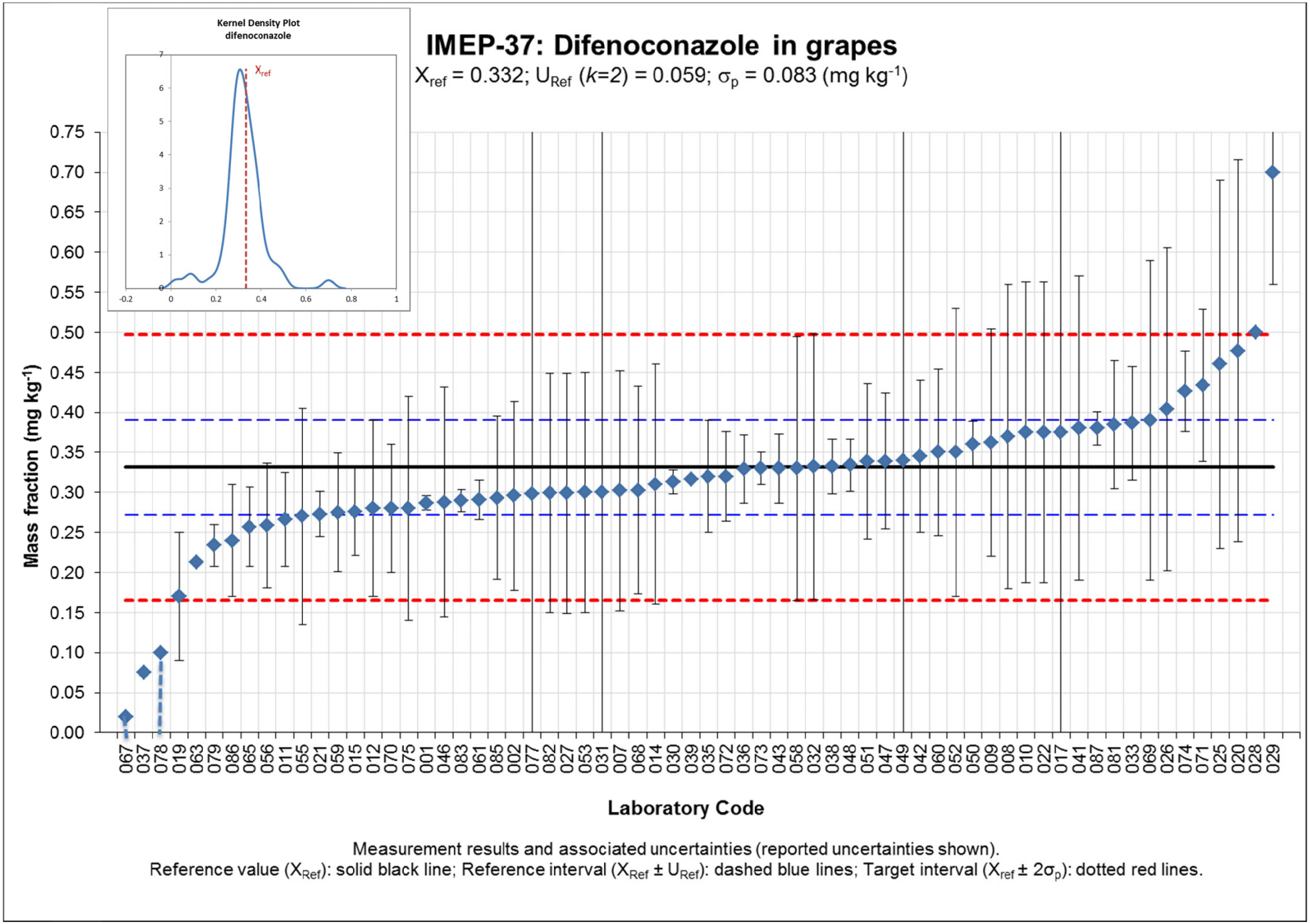


Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 15: Results for Difenoconazole

X_{ref} = 0.332; U_{Ref} (k=2) = 0.059; $\hat{\sigma}$ = 0.083 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	0.287	0.009	2	LC-MS (QqQ)	0.0045	-0.54	-1.49	b
002	0.296	0.118	0.014	GC-MS (QqQ)	8.428571	-0.43	0.00	c
007	0.302	0.15	1	LC-MS (QqQ)	0.15	-0.36	-0.19	c
008	0.37	0.19	2	LC-MS (QqQ)	0.095	0.46	0.39	c
009	0.362	0.142	2	LC-MS (QqQ)	0.071	0.37	0.39	a
010	0.375	0.188	2	GC-MS (QqQ)	0.094	0.52	0.44	c
011	0.266	0.059	73	GC-MS (QqQ)	0.000808	-0.79	-2.21	b
012	0.28	0.11	2	GC-MS (QqQ)	0.055	-0.62	-0.83	a
014	0.31	0.15	2	LC-MS (QqQ)	0.075	-0.26	-0.27	a
015	0.276	0.055	2	GC-MS (Q)	0.0275	-0.67	-1.38	b
017	0.375	30	2	GC-MS (Q)	15	0.52	0.00	c
019	0.17	0.08	2	LC-MS (QqQ)	0.04	-1.95	-3.25	a
020	0.477	0.239	2	LC-MS (QqQ)	0.1195	1.75	1.18	c
021	0.273	0.028	2	LC-MS (QqQ)	0.014	-0.71	-1.79	b
022	0.375	0.188	2	LC-MS (QqQ)	0.094	0.52	0.44	c
025	0.46	0.23	2	LC-MS (QqQ)	0.115	1.55	1.08	c
026	0.404	0.202	2	GC-MS (IT)	0.101	0.87	0.69	c
027	0.299	0.15	2	LC-MS (QqQ)	0.075	-0.39	-0.40	a
028	0.5	0	0	LC-MS (QqQ)	0	2.03	5.68	b
029	0.7	0.14	2	GC-MS (QqQ)	0.07	4.44	4.85	a
030	0.3131	0.0148	2	LC-MS (QqQ)	0.0074	-0.22	-0.61	b
031	0.3	25	2	GC-MS (QqQ)	12.5	-0.38	0.00	c
032	0.332	0.166	2	LC-MS (QqQ)	0.083	0.00	0.00	c
033	0.3864	0.071	1	GC-MS (QqQ)	0.071	0.66	0.71	a
035	0.32	0.07	2	GC-MS (QqQ)	0.035	-0.14	-0.25	a
036	0.329	0.043	2	LC-MS (QqQ)	0.0215	-0.03	-0.07	b
037	0.075	0.004	2	GC/ECD	0.002	-3.10	-8.64	b
038	0.332	0.034	2	LC-MS (QqQ)	0.017	0.00	0.01	b
039	0.316	0	0	LC-MS (QqQ)	0	-0.19	-0.53	b
041	0.38	0.19	2	LC-MS (QqQ)	0.095	0.58	0.49	c
042	0.345	0.095	2	GC-MS (QqQ)	0.0475	0.16	0.24	a
043	0.33	0.04329	2	GC-MS (TOF)	0.021645	-0.02	-0.04	b
046	0.288	0.144	2	LC-MS (QqQ)	0.072	-0.53	-0.56	a
047	0.339	0.085	1.04	GC-MS (Q)	0.081731	0.09	0.08	a
048	0.334	0.033	99	LC-MS (QqQ)	0.000333	0.03	0.08	b
049	0.34	6	1.19	GC-MS (Q)	5.042017	0.10	0.00	c
050	0.36	0.029	2	GC-MS (Q)	0.0145	0.34	0.86	b
051	0.339	0.097	2.3	LC-MS (QqQ)	0.042174	0.09	0.14	a
052	0.35	0.18	2	GC-MS (QqQ)	0.09	0.22	0.19	c
053	0.3	0.15	2	GC-MS (TOF)	0.075	-0.38	-0.39	a
055	0.27	0.135	2	LC-MS (QqQ)	0.0675	-0.74	-0.84	a
056	0.259	0.078	2	LC-MS (QqQ)	0.039	-0.88	-1.48	a
058	0.33	0.165	2	LC-MS (QqQ)	0.0825	-0.02	-0.02	a
059	0.275	0.074	2	GC-ECD/NPD	0.037	-0.68	-1.19	a
060	0.35	0.104	2	LC-MS (QqQ)	0.052	0.22	0.31	a
061	0.291	0.0243	2	LC-MS (QqQ)	0.01215	-0.49	-1.27	b
063	0.213	0	0	LC-MS (QqQ)	0	-1.43	-4.00	b
065	0.257	0.05	2	GC-MS (Q)	0.025	-0.90	-1.92	b
067	< 0.02			GC-MS (QqQ)				
068	0.303	0.13	2	LC-MS (QqQ)	0.065	-0.35	-0.40	a
069	0.39	0.2	2	LC-MS (QqQ)	0.1	0.70	0.56	c
070	0.28	0.08	2	LC-MS (QqQ)	0.04	-0.62264	-1.037	a
071	0.434	0.095	2	LC-MS (Q)	0.0475	1.23	1.83	a
072	0.32	0.056	2	GC-MS (QqQ)	0.028	-0.14	-0.29	b
073	0.33	0.02	2		0.01	-0.02	-0.05	b
074	0.426	0.05	2	UPLC-MS/MS	0.025	1.14	2.43	b
075	0.28	0.14	2	GC-MS (Q)	0.07	-0.62264	-0.6791	a
077	0.298	0.5	2	LC-MS (QqQ)	0.25	-0.41	-0.13	c
078	< 0.1			GC-MS (Q)				
079	0.234	0.026	2	GC-MS (Q)	0.013	-1.18	-3.02	b
081	0.385	0.08	2	GC-MS (Q)	0.04	0.64	1.07	a
082	0.299	0.1495	2	LC-MS (QqQ)	0.07475	-0.39	-0.41	a
083	0.29	0.014	2	LC-MS (QqQ)	0.007	-0.50	-1.37	b
085	0.293	0.102	2	LC-MS (QqQ)	0.051	-0.47	-0.65	a
086	0.24	0.07	2	LC-MS (Q)	0.035	-1.11	-2.00	a
087	0.38	0.021	2	LC-MS(Q ; QqQ)	0.0105	0.58	1.54	b

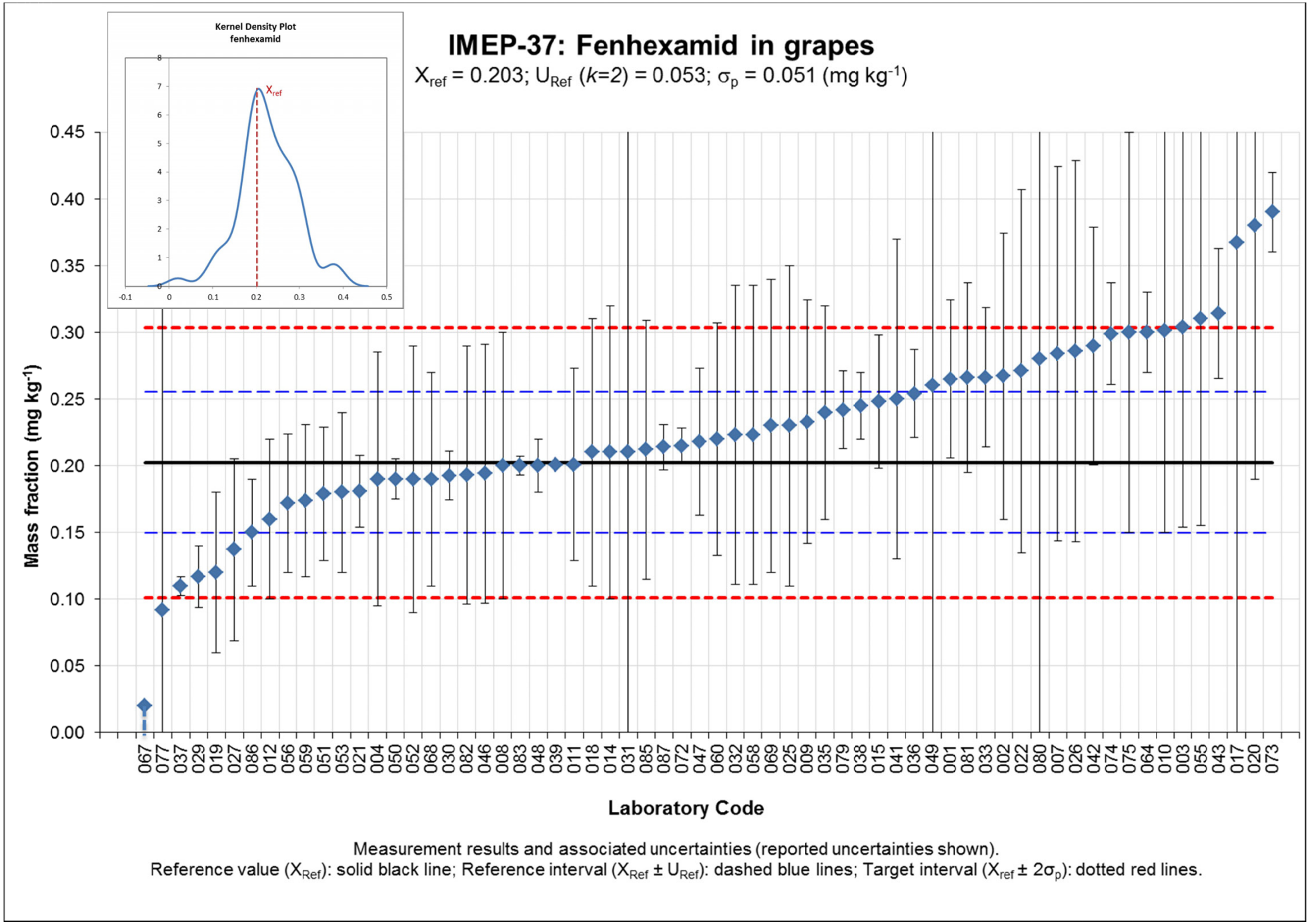


Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 16: Results for Fenhexamid

X_{ref} = 0.203; U_{Ref} (k=2) = 0.053; $\hat{\sigma}$ = 0.051 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	0.265	0.059	2	GC-MS (QqQ)	0.0295	1.23	1.58	a
002	0.267	0.107	0.008	LC-MS (QqQ)	13.375	1.27	0.00	c
003	0.304	0.1502	78.5	LC-MS (QqQ)	0.001913	2.00	3.82	b
004	0.19	0.095	2	GC-MS (QqQ)	0.0475	-0.24691	-0.2298	a
007	0.284	0.14	1	LC-MS (QqQ)	0.14	1.61	0.57	c
008	0.2	0.1	2	LC-MS (QqQ)	0.05	-0.05	-0.04	a
009	0.233	0.091	2	LC-MS (QqQ)	0.0455	0.60	0.58	a
010	0.301	0.151	2	LC-MS (QqQ)	0.0755	1.95	1.23	c
011	0.201	0.072	101	LC-MS (QqQ)	0.000713	-0.03	-0.06	b
012	0.16	0.06	2	LC-MS (QqQ)	0.03	-0.84	-1.06	a
014	0.21	0.11	2	LC-MS (QqQ)	0.055	0.15	0.12	c
015	0.248	0.05	2	GC-MS (Q)	0.025	0.90	1.25	b
017	0.367	30	2	GC-MS (Q)	15	3.25	0.01	c
018	0.21	0.1	2	LC-MS (IT)	0.05	0.15	0.13	a
019	0.12	0.06	2	LC-MS (QqQ)	0.03	-1.63	-2.06	a
020	0.38	0.19	2	LC-MS (QqQ)	0.095	3.51	1.80	c
021	0.181	0.027	2	LC-MS (QqQ)	0.0135	-0.42	-0.72	b
022	0.271	0.136	2	LC-MS (QqQ)	0.068	1.35	0.94	c
025	0.23	0.12	2	LC-MS (QqQ)	0.06	0.54	0.42	c
026	0.286	0.143	2	GC-MS (IT)	0.0715	1.65	1.10	c
027	0.137	0.068	2	LC-MS (QqQ)	0.034	-1.29	-1.52	a
029	0.117	0.023	2	LC-MS (QqQ)	0.0115	-1.69	-2.96	b
030	0.1926	0.0183	2	LC-MS (QqQ)	0.00915	-0.20	-0.35	b
031	0.21	25	2	LC-MS (QqQ)	12.5	0.15	0.00	c
032	0.223	0.112	2	LC-MS (QqQ)	0.056	0.40	0.33	c
033	0.2663	0.052	1	LC-MS (QqQ)	0.052	1.26	1.09	c
035	0.24	0.08	2	LC-MS (QqQ)	0.04	0.74	0.78	a
036	0.254	0.033	2	LC-MS (QqQ)	0.0165	1.02	1.65	b
037	0.11	0.007	2	GC-MS (Q)	0.0035	-1.83	-3.46	b
038	0.245	0.025	2	LC-MS (QqQ)	0.0125	0.84	1.45	b
039	0.201	0	0	LC-MS (QqQ)	0	-0.03	-0.06	b
041	0.25	0.12	2	LC-MS (QqQ)	0.06	0.94	0.72	c
042	0.29	0.089	2	GC-MS (QqQ)	0.0445	1.73	1.69	a
043	0.314	0.04853	2	GC-MS (TOF)	0.024265	2.20	3.10	b
046	0.194	0.097	2	LC-MS (QqQ)	0.0485	-0.17	-0.15	a
047	0.218	0.055	1.02	GC-MS (Q)	0.053922	0.31	0.26	c
048	0.2	0.02	98	LC-MS (QqQ)	0.000204	-0.05	-0.09	b
049	0.26	14	0.84	LC-MS (QqQ)	16.66667	1.14	0.00	c
050	0.19	0.015	2	GC-MS (Q)	0.0075	-0.24691	-0.4538	b
051	0.179	0.05	2.4	LC-MS (QqQ)	0.020833	-0.46	-0.70	b
052	0.19	0.1	2	LC-MS (QqQ)	0.05	-0.25	-0.22	a
053	0.18	0.06	2	GC-MS (TOF)	0.03	-0.44	-0.56	a
055	0.31	0.155	2	LC-MS (QqQ)	0.0775	2.12	1.31	c
056	0.172	0.052	2	LC-MS (QqQ)	0.026	-0.60	-0.82	b
058	0.223	0.112	2	LC-MS (QqQ)	0.056	0.40	0.33	c
059	0.174	0.057	2	GC-ECD/NPD	0.0285	-0.56	-0.73	a
060	0.22	0.087	2	LC-MS (QqQ)	0.0435	0.35	0.34	a
064	0.3	0.03	2	GC-MS (IT)	0.015	1.93	3.20	b
067	< 0.02			GC-MS (QqQ)				
068	0.19	0.08	2	LC-MS (QqQ)	0.04	-0.25	-0.26	a
069	0.23	0.11	2	LC-MS (QqQ)	0.055	0.54	0.45	c
072	0.215	0.013	2	LC-MS (QqQ)	0.0065	0.25	0.46	b
073	0.39	0.03	2		0.015	3.70	6.16	b
074	0.299	0.038	2	UPLC-MS/MS	0.019	1.91	2.96	b
075	0.3	0.15	2	LC-MS (QqQ)	0.075	1.93	1.23	c
077	0.092	0.5	2	LC-MS (QqQ)	0.25	-2.18	-0.44	c
079	0.242	0.029	2	GC-MS (Q)	0.0145	0.78	1.31	b
080	0.28	0.405	2	GC-MS	0.2025	1.53	0.38	c
081	0.266	0.071	2	GC-MS (Q)	0.0355	1.25	1.43	a
082	0.193	0.0965	2	LC-MS (QqQ)	0.04825	-0.19	-0.17	a
083	0.2	0.007	2	LC-MS (QqQ)	0.0035	-0.05	-0.09	b
085	0.212	0.097	2	LC-MS (QqQ)	0.0485	0.19	0.17	a
086	0.15	0.04	2	LC-MS (Q)	0.02	-1.04	-1.58	b
087	0.214	0.017	2	LC-MS(Q ; QqQ)	0.0085	0.23	0.41	b

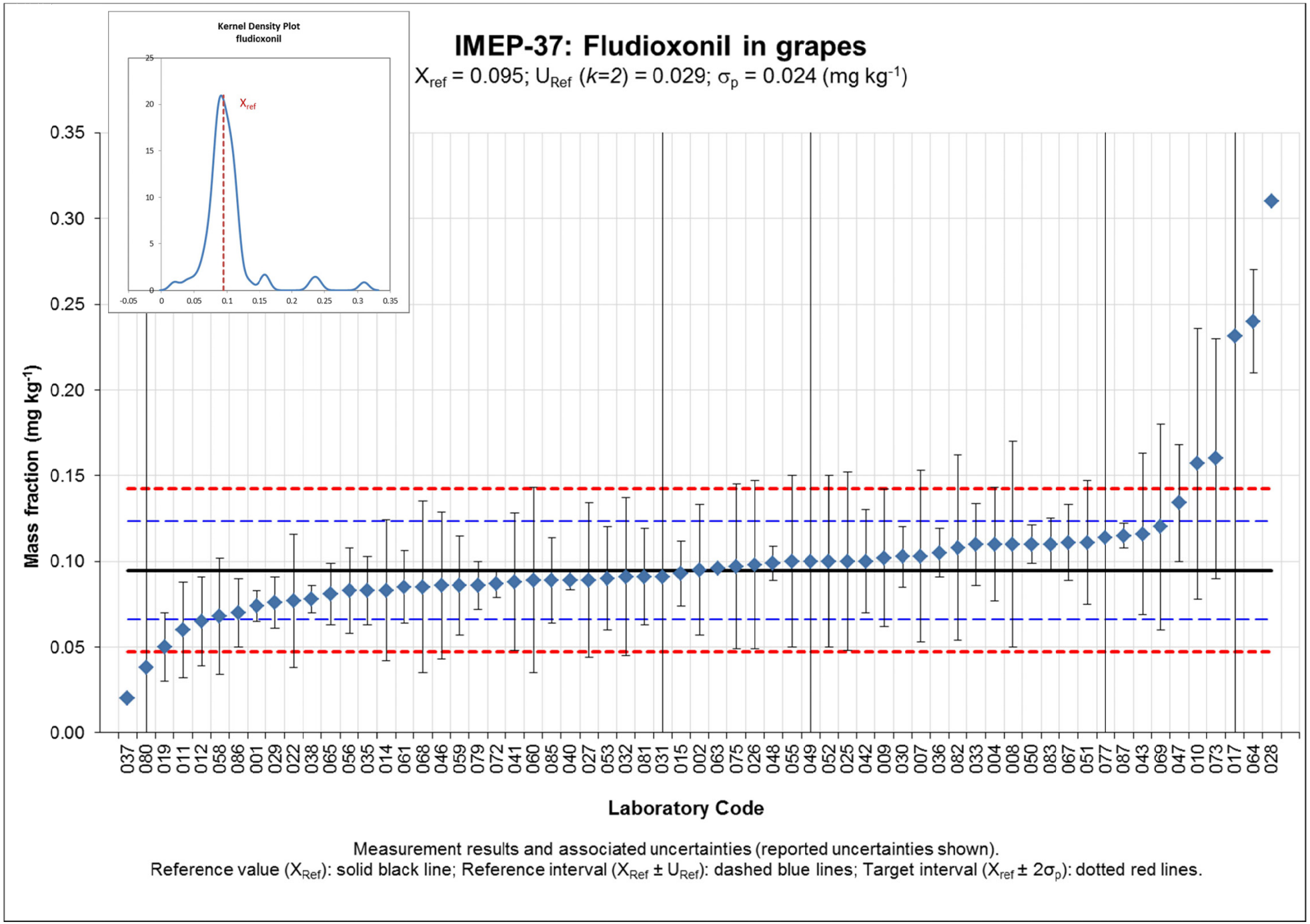


Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 17: Results for Fludioxonil

X_{ref} = 0.095; U_{Ref} (k=2) = 0.029; $\hat{\sigma}$ = 0.024 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	0.074	0.009	2	GC-MS (QqQ)	0.0045	-0.88	-1.38	b
002	0.095	0.038	0.007	GC-MS (QqQ)	5.428571	0.01	0.00	c
004	0.11	0.033	2	GC-MS (QqQ)	0.0165	0.64	0.69	a
007	0.103	0.05	1	LC-MS (QqQ)	0.05	0.35	0.16	c
008	0.11	0.06	2	GC-MS (QqQ)	0.03	0.64	0.46	c
009	0.102	0.04	2	GC-MS (Q)	0.02	0.30	0.29	a
010	0.157	0.079	2	GC-MS (QqQ)	0.0395	2.62	1.48	c
011	0.06	0.028	78	GC-MS (QqQ)	0.000359	-1.46835	-2.42072	b
012	0.065	0.026	2	LC-MS (QqQ)	0.013	-1.26	-1.54	b
014	0.083	0.041	2	LC-MS (QqQ)	0.0205	-0.50	-0.47	a
015	0.093	0.019	2	GC-MS (Q)	0.0095	-0.08	-0.10	b
017	0.2315	30	2	GC-MS (Q)	15	5.77	0.01	c
019	0.05	0.02	2	LC-MS (QqQ)	0.01	-1.89	-2.56	b
022	0.077	0.039	2	LC-MS (QqQ)	0.0195	-0.75	-0.73	a
025	0.1	0.052	2	LC-MS (QqQ)	0.026	0.22	0.18	c
026	0.098	0.049	2	GC-MS (IT)	0.0245	0.14	0.11	c
027	0.089	0.045	2	LC-MS (QqQ)	0.0225	-0.24	-0.22	a
028	0.31	0	0	LC-MS (QqQ)	0	9.08	14.97	b
029	0.076	0.015	2	GC-MS (QqQ)	0.0075	-0.79	-1.16	b
030	0.1027	0.0177	2	LC-MS (QqQ)	0.00885	0.33	0.47	b
031	0.091	25	2	GC-MS (QqQ)	12.5	-0.16	0.00	c
032	0.091	0.046	2	LC-MS (QqQ)	0.023	-0.16	-0.14	a
033	0.1099	0.024	1	GC-MS (QqQ)	0.024	0.64	0.54	c
035	0.083	0.02	2	GC-MS (QqQ)	0.01	-0.50	-0.67	b
036	0.105	0.014	2	LC-MS (QqQ)	0.007	0.43038	0.638078	b
037	0.02	0.001	2	GC-MS (Q)	0.0005	-3.16	-5.20	b
038	0.078	0.008	2	GC-MS (Q)	0.004	-0.71	-1.13	b
040	0.089	0.0056	2	GC-MS (Q)	0.0028	-0.24	-0.40	b
041	0.088	0.04	2	GC-MS (QqQ)	0.02	-0.29	-0.28	a
042	0.1	0.03	2	GC-MS (QqQ)	0.015	0.22	0.25	a
043	0.116	0.04718	2	GC-MS (TOF)	0.02359	0.89	0.77	a
046	0.0858	0.0429	2	LC-MS (QqQ)	0.02145	-0.38	-0.35	a
047	0.134	0.034	0.88	LC-MS (QqQ)	0.038636	1.65	0.95	c
048	0.099	0.01	99	LC-MS (QqQ)	0.000101	0.18	0.29	b
049	0.10	8	1.15	GC-MS (Q)	6.956522	0.22	0.00	c
050	0.11	0.011	2	LC-MS (QqQ)	0.0055	0.64	0.99	b
051	0.111	0.036	2.3	LC-MS (QqQ)	0.015652	0.68	0.76	a
052	0.1	0.05	2	GC-MS (QqQ)	0.025	0.22	0.18	c
053	0.09	0.03	2	HPLC-DAD	0.015	-0.20	-0.23	a
055	0.1	0.05	2	LC-MS (QqQ)	0.025	0.22	0.18	c
056	0.083	0.025	2	LC-MS (QqQ)	0.0125	-0.50	-0.62	b
058	0.068	0.034	2	GC-MS (QqQ)	0.017	-1.13	-1.20	a
059	0.086	0.029	2	GC-NPD	0.0145	-0.37	-0.43	a
060	0.089	0.054	2	LC-MS (QqQ)	0.027	-0.24	-0.19	c
061	0.085	0.0212	2	LC-MS (QqQ)	0.0106	-0.41	-0.55	b
063	0.096	0	0	LC-MS (QqQ)	0	0.05	0.08	b
064	0.24	0.03	2	GC-MS (IT)	0.015	6.13	6.99	a
065	0.081	0.018	2	GC-MS (Q)	0.009	-0.58	-0.81	b
067	0.111	0.022	2	GC-MS (QqQ)	0.011	0.68	0.90	b
068	0.085	0.05	2	LC-MS (QqQ)	0.025	-0.41	-0.34	c
069	0.12	0.06	2	GC-MS (Q)	0.03	1.06	0.76	c
072	0.087	0.008	2	LC-MS (QqQ)	0.004	-0.33	-0.52	b
073	0.16	0.07	2		0.035	2.75	1.72	c
075	0.097	0.048	2	GC-MS (Q)	0.024	0.09	0.08	c
077	0.114	0.5	2	GC-MS (QqQ)	0.25	0.81	0.08	c
079	0.086	0.014	2	GC-MS (Q)	0.007	-0.37	-0.55	b
080	0.038	0.356	2	GC-MS	0.178	-2.40	-0.32	c
081	0.091	0.028	2	GC-MS (Q)	0.014	-0.16	-0.19	b
082	0.108	0.054	2	LC-MS (QqQ)	0.027	0.56	0.43	c
083	0.11	0.015	2	GC-MS (QqQ)	0.0075	0.64	0.94	b
085	0.089	0.025	2	GC-MS (QqQ)	0.0125	-0.24	-0.30	b
086	0.07	0.02	2	GC-MS (Q)	0.01	-1.05	-1.42	b
087	0.115	0.007	2	LC-MS(Q ; QqQ)	0.0035	0.85	1.37	b

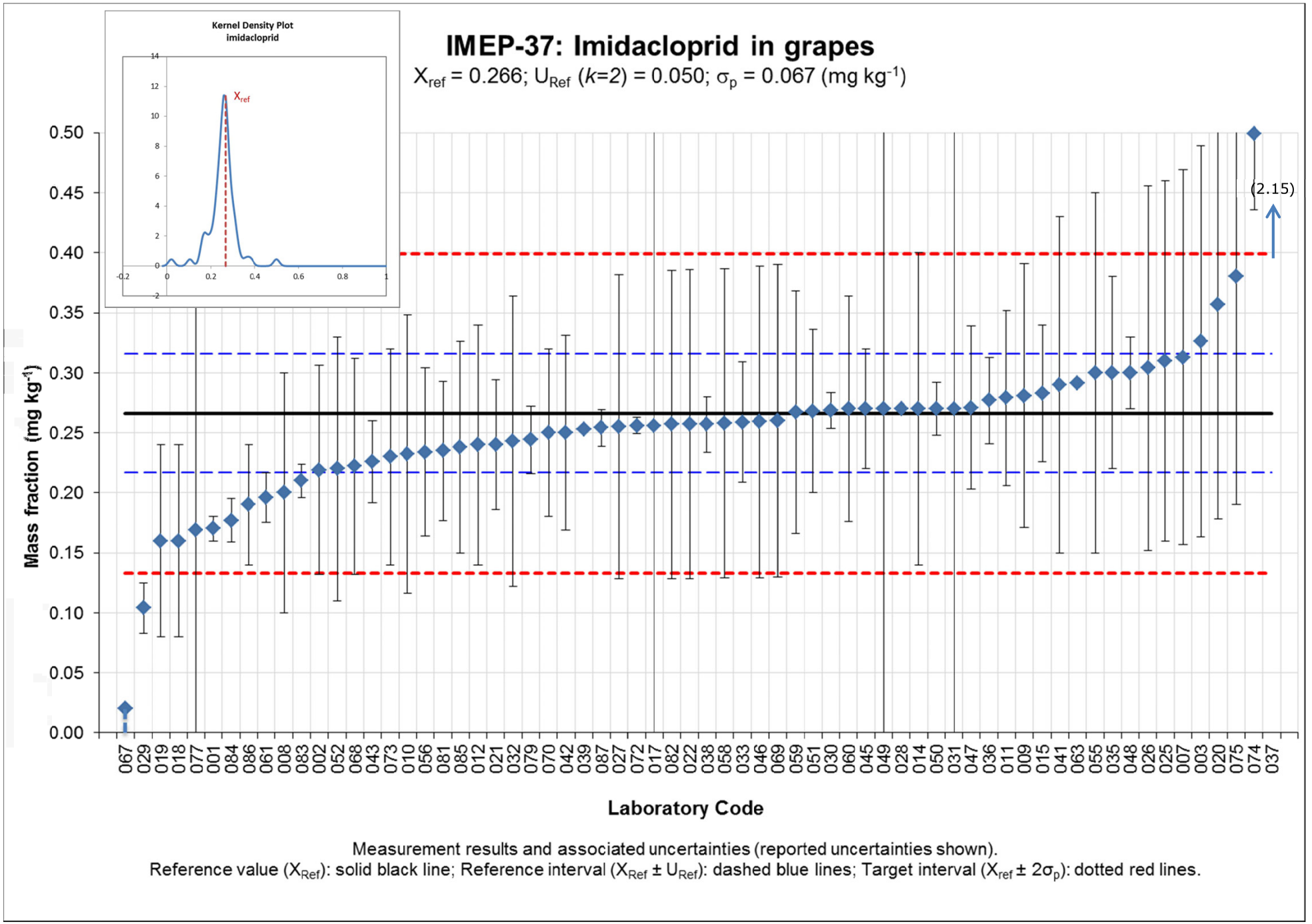


Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 18: Results for Imidacloprid

X_{ref} = 0.266; U_{Ref} (*k=2*) = 0.050; $\hat{\sigma}$ = 0.067 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	0.17	0.01	2	LC-MS (QqQ)	0.005	-1.44	-3.81	b
002	0.219	0.087	0.01	LC-MS (QqQ)	8.7	-0.71	-0.01	c
003	0.326	0.163	77.5	LC-MS (QqQ)	0.002103	0.90	2.41	b
007	0.313	0.156	1	LC-MS (QqQ)	0.156	0.70	0.30	c
008	0.2	0.1	2	LC-MS (QqQ)	0.05	-0.99	-1.18	a
009	0.281	0.11	2	LC-MS (QqQ)	0.055	0.22	0.25	a
010	0.232	0.116	2	LC-MS (QqQ)	0.058	-0.51	-0.54	a
011	0.279	0.073	103	LC-MS (QqQ)	0.000709	0.19	0.52	b
012	0.24	0.1	2	LC-MS (QqQ)	0.05	-0.39	-0.47	a
014	0.27	0.13	2	LC-MS (QqQ)	0.065	0.06	0.06	a
015	0.283	0.057	2	LC-MS (IT)	0.0285	0.25	0.45	a
017	0.256	30	2	LC-MS (Q)	15	-0.15	0.00	c
018	0.16	0.08	2	LC-MS (IT)	0.04	-1.59	-2.26	a
019	0.16	0.08	2	LC-MS (QqQ)	0.04	-1.59489	-2.25562	a
020	0.357	0.179	2	LC-MS (QqQ)	0.0895	1.37	0.98	c
021	0.24	0.054	2	LC-MS (QqQ)	0.027	-0.39	-0.71	a
022	0.257	0.129	2	LC-MS (QqQ)	0.0645	-0.14	-0.13	a
025	0.31	0.15	2	LC-MS (QqQ)	0.075	0.66	0.56	c
026	0.304	0.152	2	LC-MS (QqQ)	0.076	0.57	0.47	c
027	0.255	0.127	2	LC-MS (QqQ)	0.0635	-0.17	-0.16	a
028	0.27	0	0	LC-MS (QqQ)	0	0.06	0.16	b
029	0.104	0.021	2	LC-MS (QqQ)	0.0105	-2.44	-6.03	b
030	0.2685	0.0151	2	LC-MS (QqQ)	0.00755	0.04	0.09	b
031	0.27	25	2	LC-MS (QqQ)	12.5	0.06	0.00	c
032	0.243	0.121	2	LC-MS (QqQ)	0.0605	-0.35	-0.35	a
033	0.2588	0.05	1	LC-MS (QqQ)	0.05	-0.11	-0.13	a
035	0.3	0.08	2	LC-MS (QqQ)	0.04	0.51	0.72	a
036	0.277	0.036	2	LC-MS (QqQ)	0.018	0.16	0.36	b
037	2.15	0.198	2	HPLC/UV	0.099	28.32	18.46	c
038	0.257	0.023	2	LC-MS (QqQ)	0.0115	-0.14	-0.33	b
039	0.253	0	0	LC-MS (QqQ)	0	-0.20	-0.53	b
041	0.29	0.14	2	LC-MS (QqQ)	0.07	0.36	0.32	c
042	0.25	0.081	2	LC-MS (QqQ)	0.0405	-0.24	-0.34	a
043	0.226	0.03418	2	LC-MS (QqQ)	0.01709	-0.60	-1.33	b
045	0.27	0.05	2	LC-MS (ESI Quadrapole)	0.025	0.06	0.11	a
046	0.259	0.13	2	LC-MS (QqQ)	0.065	-0.11	-0.10	a
047	0.271	0.068	1	GC-MS (QqQ)	0.068	0.07	0.07	c
048	0.3	0.03	99	LC-MS (QqQ)	0.000303	0.51	1.37	b
049	0.27	8	0.74	LC-MS (QqQ)	10.81081	0.058625	0.000361	c
050	0.27	0.022	2	LC-MS (QqQ)	0.011	0.06	0.14	b
051	0.268	0.068	2.2	LC-MS (QqQ)	0.030909	0.03	0.05	a
052	0.22	0.11	2	LC-MS (QqQ)	0.055	-0.69	-0.76	a
055	0.3	0.15	2	LC-MS (QqQ)	0.075	0.51	0.43	c
056	0.234	0.07	2	LC-MS (QqQ)	0.035	-0.48	-0.75	a
058	0.258	0.129	2	LC-MS (QqQ)	0.0645	-0.12	-0.12	a
059	0.267	0.101	2	UPLC/DAD	0.0505	0.01	0.02	a
060	0.27	0.094	2	LC-MS (QqQ)	0.047	0.06	0.07	a
061	0.196	0.02036	2	LC-MS (QqQ)	0.01018	-1.05	-2.62	b
063	0.291	0	0	LC-MS (QqQ)	0	0.37	1.01	b
067	< 0.02			GC-MS (QqQ)				
068	0.222	0.09	2	LC-MS (QqQ)	0.045	-0.66	-0.86	a
069	0.26	0.13	2	LC-MS (QqQ)	0.065	-0.09	-0.09	a
070	0.25	0.07	2	LC-MS (QqQ)	0.035	-0.24	-0.38	a
072	0.256	0.007	2	LC-MS (QqQ)	0.0035	-0.15	-0.40	b
073	0.23	0.09	2		0.045	-0.54	-0.70	a
074	0.499	0.063	2	UPLC-MS/MS	0.0315	3.50	5.81	a
075	0.38	0.19	2	LC-MS (QqQ)	0.095	1.71	1.16	c
077	0.169	0.5	2	LC-MS (QqQ)	0.25	-1.46	-0.39	c
079	0.244	0.028	2	LC-MS (QqQ)	0.014	-0.33	-0.78	b
081	0.235	0.058	2	LC-MS (QqQ)	0.029	-0.47	-0.82	a
082	0.257	0.1285	2	LC-MS (QqQ)	0.06425	-0.14	-0.13	a
083	0.21	0.014	2	LC-MS (QqQ)	0.007	-0.84	-2.18	b
084	0.177	0.018	2	HPLC-UV vis	0.009	-1.34	-3.38	b
085	0.238	0.088	2	LC-MS (QqQ)	0.044	-0.42	-0.56	a
086	0.19	0.05	2	LC-MS (Q)	0.025	-1.14	-2.16	a
087	0.254	0.015	2	LC-MS(Q ; QqQ)	0.0075	-0.18	-0.47	b

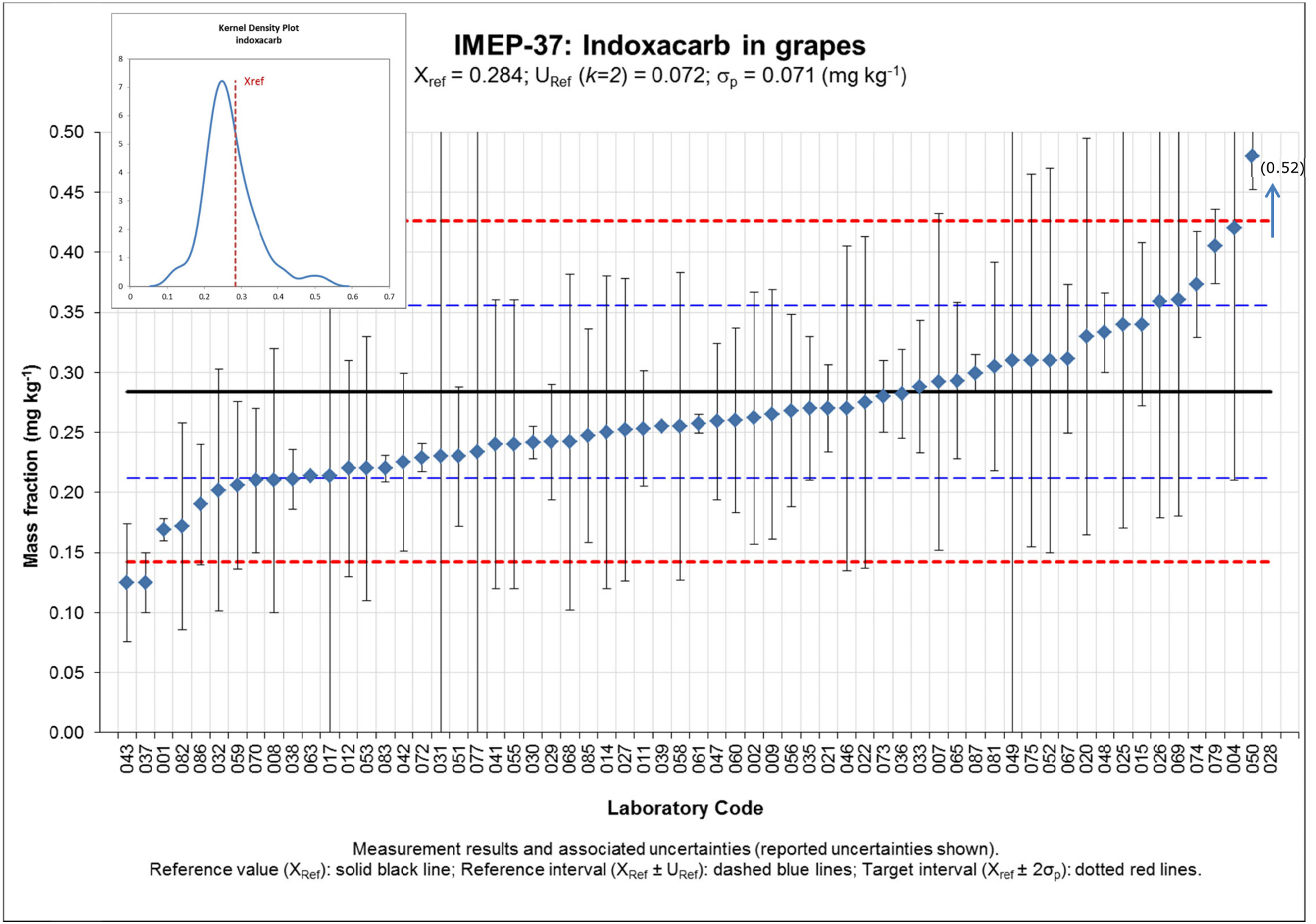


Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 19: Results for Indoxacarb

X_{ref} = 0.284; U_{Ref} (*k=2*) = 0.072; $\hat{\sigma}$ = 0.071 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	0.169	0.009	2	LC-MS (QqQ)	0.0045	-1.62	-3.18	b
002	0.262	0.105	0.011	LC-MS (QqQ)	9.545455	-0.31	0.00	c
004	0.42	0.21	2	GC-MS (QqQ)	0.105	1.92	1.23	c
007	0.292	0.14	1	LC-MS (QqQ)	0.14	0.113835	0.055913	c
008	0.21	0.11	2	GC-MS (QqQ)	0.055	-1.04	-1.13	a
009	0.265	0.104	2	LC-MS (QqQ)	0.052	-0.27	-0.30	a
011	0.253	0.048	108	LC-MS (QqQ)	0.000444	-0.44	-0.86	b
012	0.22	0.09	2	LC-MS (QqQ)	0.045	-0.90	-1.11	a
014	0.25	0.13	2	LC-MS (QqQ)	0.065	-0.48	-0.46	a
015	0.34	0.068	2	GC-MS (Q)	0.034	0.79	1.14	b
017	0.214	30	2	LC-MS (Q)	15	-0.99	0.00	c
020	0.33	0.165	2	LC-MS (QqQ)	0.0825	0.65	0.51	c
021	0.27	0.036	2	LC-MS (QqQ)	0.018	-0.20	-0.35	b
022	0.275	0.138	2	LC-MS (QqQ)	0.069	-0.13	-0.11	a
025	0.34	0.17	2	LC-MS (QqQ)	0.085	0.79	0.61	c
026	0.359	0.18	2	LC-MS (QqQ)	0.09	1.06	0.78	c
027	0.252	0.126	2	LC-MS (QqQ)	0.063	-0.45	-0.44	a
028	0.52	0	0	LC-MS (QqQ)	0	3.33	6.59	b
029	0.242	0.048	2	GC-MS (QqQ)	0.024	-0.59	-0.97	b
030	0.2415	0.0135	2	LC-MS (QqQ)	0.00675	-0.60	-1.16	b
031	0.23	25	2	LC-MS (QqQ)	12.5	-0.76	0.00	c
032	0.202	0.101	2	LC-MS (QqQ)	0.0505	-1.15	-1.32	a
033	0.288	0.055	1	LC-MS (QqQ)	0.055	0.06	0.06	a
035	0.27	0.06	2	GC-MS (QqQ)	0.03	-0.20	-0.30	b
036	0.282	0.037	2	LC-MS (QqQ)	0.0185	-0.03	-0.05	b
037	0.125	0.025	2	GC/ECD	0.0125	-2.24	-4.19	b
038	0.211	0.025	2	GC-MS (Q)	0.0125	-1.03	-1.92	b
039	0.255	0	0	LC-MS (QqQ)	0	-0.41	-0.81	b
041	0.24	0.12	2	GC-MS (QqQ)	0.06	-0.62	-0.63	a
042	0.225	0.074	2	LC-MS (QqQ)	0.037	-0.83	-1.14	a
043	0.125	0.04924	2	LC-MS (QqQ)	0.02462	-2.24	-3.66	b
046	0.27	0.135	2	GC-MS (Q)	0.0675	-0.20	-0.18	a
047	0.259	0.065	1.07	GC-MS (Q)	0.060748	-0.35	-0.35	a
048	0.333	0.033	99	LC-MS (QqQ)	0.000333	0.69	1.37	b
049	0.31	6	0.81	LC-MS (QqQ)	7.407407	0.37	0.00	c
050	0.48	0.028	2	LC-MS (QqQ)	0.014	2.76	5.10	b
051	0.23	0.058	2.3	LC-MS (QqQ)	0.025217	-0.76	-1.23	b
052	0.31	0.16	2	LC-MS (QqQ)	0.08	0.37	0.30	c
053	0.22	0.11	2	GC-MS (TOF)	0.055	-0.90	-0.97	a
055	0.24	0.12	2	LC-MS (QqQ)	0.06	-0.62	-0.63	a
056	0.268	0.08	2	LC-MS (QqQ)	0.04	-0.22	-0.30	a
058	0.255	0.128	2	LC-MS (QqQ)	0.064	-0.41	-0.39	a
059	0.206	0.07	2	GC-ECD/NPD	0.035	-1.10	-1.56	b
060	0.26	0.077	2	LC-MS (QqQ)	0.0385	-0.34	-0.45	a
061	0.257	0.00766	2	LC-MS (QqQ)	0.00383	-0.38	-0.75	b
063	0.214	0	0	LC-MS (QqQ)	0	-0.99	-1.95	b
065	0.293	0.065	2	GC-MS (Q)	0.0325	0.13	0.19	b
067	0.311	0.062	2	LC-MS (QqQ)	0.031	0.38	0.57	b
068	0.242	0.14	2	GC-MS (Q)	0.07	-0.59	-0.53	a
069	0.36	0.18	2	GC-MS (Q)	0.09	1.07	0.79	c
070	0.21	0.06	2	LC-MS (QqQ)	0.03	-1.04	-1.58	b
072	0.229	0.012	2	LC-MS (QqQ)	0.006	-0.77	-1.51	b
073	0.28	0.03	2		0.015	-0.06	-0.10	b
074	0.373	0.044	2	UPLC-MS/MS	0.022	1.26	2.12	b
075	0.31	0.155	2	GC-MS (Q)	0.0775	0.37	0.31	c
077	0.234	0.5	2	LC-MS (QqQ)	0.25	-0.70	-0.20	c
079	0.405	0.031	2	LC-MS (QqQ)	0.0155	1.71	3.10	b
081	0.305	0.087	2	LC-MS (QqQ)	0.0435	0.30	0.37	a
082	0.172	0.086	2	LC-MS (QqQ)	0.043	-1.57678	-1.99976	a
083	0.22	0.011	2	LC-MS (QqQ)	0.0055	-0.90	-1.76	b
085	0.247	0.089	2	GC-MS (QqQ)	0.0445	-0.52	-0.65	a
086	0.19	0.05	2	LC-MS (Q)	0.025	-1.32	-2.15	b
087	0.299	0.016	2	LC-MS(Q ; QqQ)	0.008	0.21	0.41	b

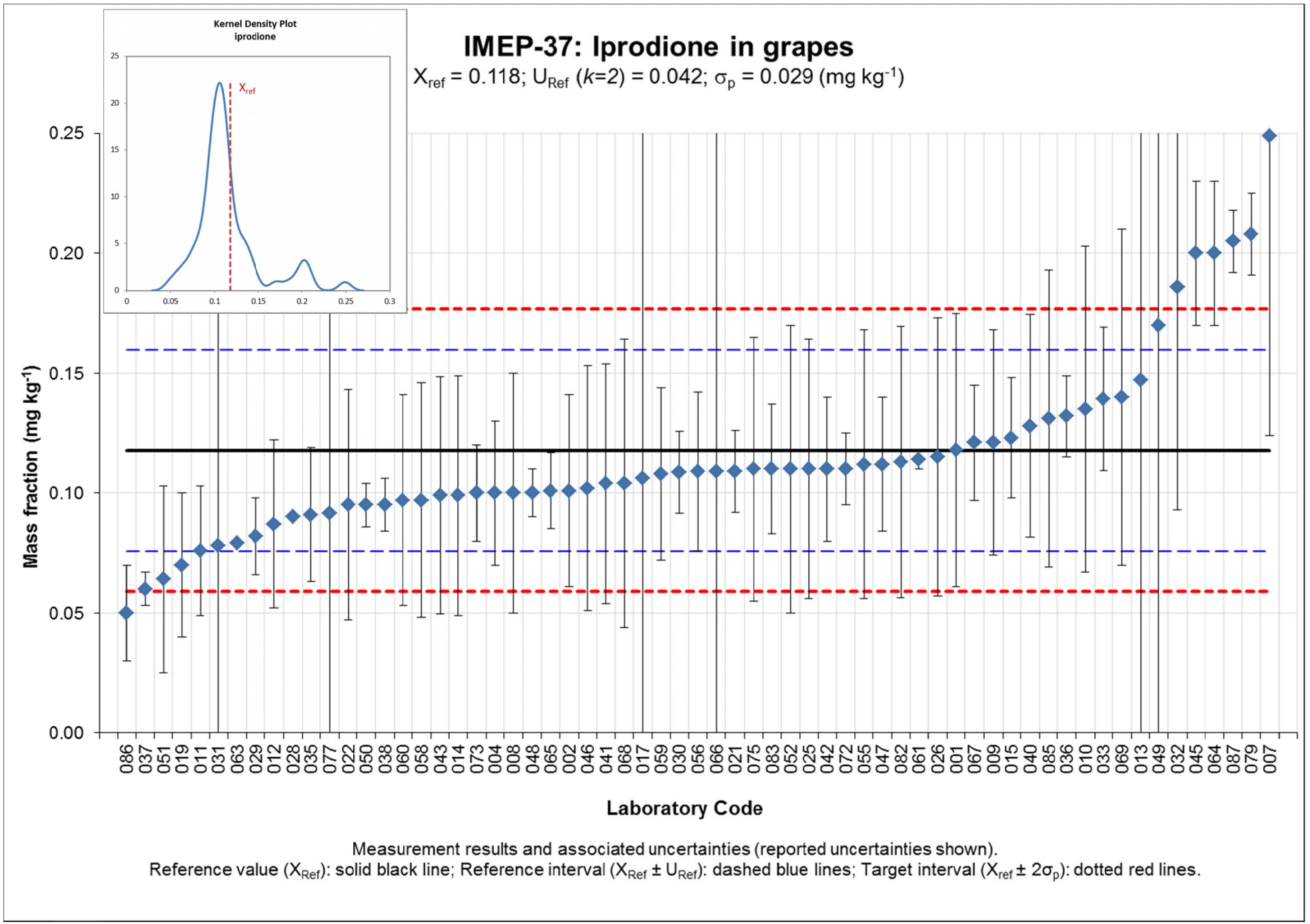


Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 20: Results for Iprodione

X_{ref} = 0.118; U_{Ref} (k=2) = 0.042; $\hat{\sigma}$ = 0.029 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	0.118	0.057	2	GC-MS (QqQ)	0.0285	0.01	0.01	a
002	0.101	0.04	0.021	GC-MS (QqQ)	1.904762	-0.57	-0.01	c
004	0.1	0.03	2	GC-MS (QqQ)	0.015	-0.60	-0.69	b
007	0.249	0.125	1	GC-MS (QqQ)	0.125	4.46	1.04	c
008	0.1	0.05	2	GC-MS (QqQ)	0.025	-0.60	-0.55	a
009	0.121	0.047	2	GC-MS (Q)	0.0235	0.11	0.10	a
010	0.135	0.068	2	GC-MS (QqQ)	0.034	0.58	0.43	c
011	0.076	0.027	76	GC-MS (QqQ)	0.000355	-1.41935	-1.99114	b
012	0.087	0.035	2	GC-MS (QqQ)	0.0175	-1.05	-1.13	b
013	0.147	20	2	GC-MS (Q)	10	0.99	0.00	c
014	0.099	0.05	2	GC-MS (QqQ)	0.025	-0.64	-0.58	a
015	0.123	0.025	2	GC-MS (Q)	0.0125	0.18	0.21	b
017	0.106	30	2	GC-MS (Q)	15	-0.40	0.00	c
019	0.07	0.03	2	LC-MS (QqQ)	0.015	-1.62	-1.85	b
021	0.109	0.017	2	LC-MS (QqQ)	0.0085	-0.30	-0.39	b
022	0.095	0.048	2	LC-MS (QqQ)	0.024	-0.77	-0.72	a
025	0.11	0.054	2	LC-MS (QqQ)	0.027	-0.26	-0.23	a
026	0.115	0.058	2	GC-MS (IT)	0.029	-0.10	-0.08	a
028	0.09	0	0	LC-MS (QqQ)	0	-0.94	-1.32	b
029	0.082	0.016	2	GC-MS (QqQ)	0.008	-1.22	-1.59	b
030	0.1086	0.0172	2	LC-MS (QqQ)	0.0086	-0.31	-0.41	b
031	0.078	25	2	GC-MS (QqQ)	12.5	-1.35	0.00	c
032	0.186	0.093	2	GC-MS (QqQ)	0.0465	2.32	1.34	c
033	0.1393	0.03	1	LC-MS (QqQ)	0.03	0.73	0.59	c
035	0.091	0.028	2	GC-MS (QqQ)	0.014	-0.91	-1.06	b
036	0.132	0.017	2	GC-MS (QqQ)	0.0085	0.48	0.63	b
037	0.06	0.007	2	GC-MS (Q)	0.0035	-1.96	-2.72	b
038	0.095	0.011	2	GC-MS (Q)	0.0055	-0.77	-1.05	b
040	0.128	0.0464	2	GC-MS (Q)	0.0232	0.35	0.33	a
041	0.104	0.05	2	GC-MS (QqQ)	0.025	-0.47	-0.42	a
042	0.11	0.03	2	GC-MS (QqQ)	0.015	-0.26	-0.30	b
043	0.099	0.04938	2	GC-MS (TOF)	0.02469	-0.64	-0.58	a
045	0.2	0.03	1	GC-MS (EI Quadrapole)	0.03	2.79	2.25	c
046	0.102	0.051	2	LC-MS (QqQ)	0.0255	-0.54	-0.48	a
047	0.112	0.028	0.99	GC-MS (Q)	0.028283	-0.20	-0.16	a
048	0.1	0.01	87	GC-MS (Q)	0.000115	-0.60	-0.85	b
049	0.17	29	0.73	LC-MS (QqQ)	39.72603	1.77	0.00	c
050	0.095	0.009	2	GC-MS (Q)	0.0045	-0.77	-1.06	b
051	0.064	0.039	2.2	GC-ECD	0.017727	-1.83	-1.96	b
052	0.11	0.06	2	GC-MS (QqQ)	0.03	-0.26	-0.21	c
055	0.112	0.056	2	GC-MS (QqQ)	0.028	-0.20	-0.17	a
056	0.109	0.033	2	LC-MS (QqQ)	0.0165	-0.30	-0.33	b
057								
058	0.097	0.049	2	GC-MS (QqQ)	0.0245	-0.71	-0.64	a
059	0.108	0.036	2	GC-ECD/NPD	0.018	-0.33	-0.35	b
060	0.097	0.044	2	LC-MS (QqQ)	0.022	-0.71	-0.68	a
061	0.114	0.004	2	GC-MS (QqQ)	0.002	-0.13	-0.18	b
063	0.079	0	0	GC-MS (QqQ)	0	-1.32	-1.85	b
064	0.2	0.03	2	GC-MS (IT)	0.015	2.79	3.19	b
065	0.101	0.016	2	GC-MS (Q)	0.008	-0.57	-0.75	b
066	0.109	50	2	GC-MS (QqQ)	25	-0.30	0.00	c
067	0.121	0.024	2	GC-MS (QqQ)	0.012	0.11	0.13	b
068	0.104	0.06	2	GC-MS (Q)	0.03	-0.47	-0.38	c
069	0.14	0.07	2	GC-MS (Q)	0.035	0.75	0.54	c
072	0.11	0.015	2	GC-MS (QqQ)	0.0075	-0.26	-0.35	b
073	0.1	0.02	2		0.01	-0.60	-0.77	b
075	0.11	0.055	2	GC-MS (Q)	0.0275	-0.26	-0.23	a
077	0.0914	0.5	2	GC-MS (QqQ)	0.25	-0.90	-0.11	c
079	0.208	0.017	2	GC-MS (Q)	0.0085	3.06	3.98	b
082	0.113	0.0565	2	GC-MS (QqQ)	0.02825	-0.16	-0.14	a
083	0.11	0.027	2	GC-MS (QqQ)	0.0135	-0.26	-0.31	b
085	0.131	0.062	2	LC-MS (QqQ)	0.031	0.45	0.35	c
086	0.05	0.02	2	GC-MS (Q)	0.01	-2.30	-2.92	b
087	0.205	0.013	2	LC-MS(Q ; QqQ)	0.0065	2.96	3.97	b

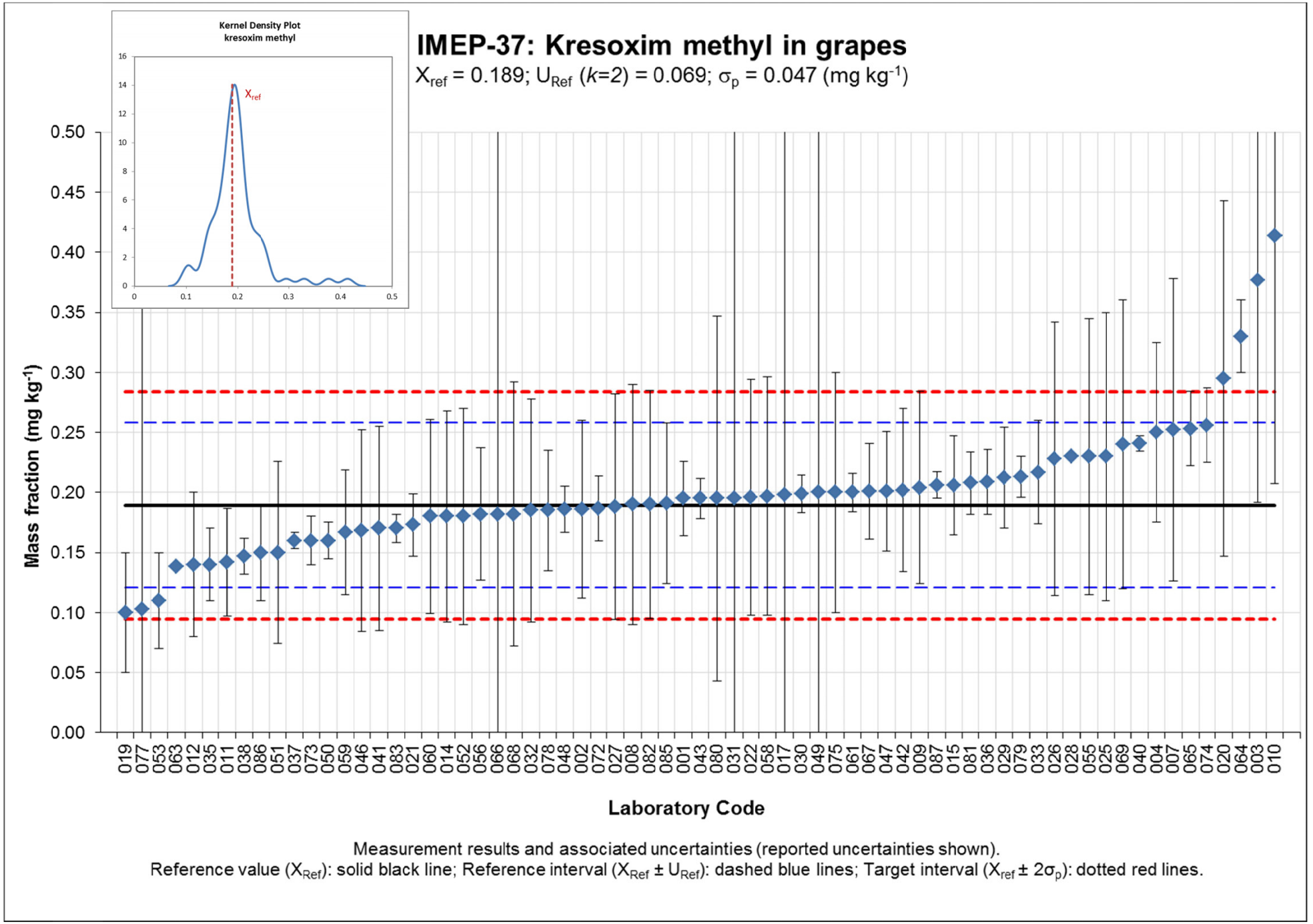


Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 21: Results for Kresoxim Methyl

X_{ref} = 0.189; U_{Ref} (*k=2*) = 0.069; $\hat{\sigma}$ = 0.047 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	0.195	0.031	2	GC-MS (QqQ)	0.0155	0.12	0.15	b
002	0.186	0.074	0.008	GC-MS (QqQ)	9.25	-0.07	0.00	c
003	0.377	0.185	82	LC-MS (QqQ)	0.002256	3.97	5.46	b
004	0.25	0.075	2	GC-MS (QqQ)	0.0375	1.28	1.20	a
007	0.252	0.126	1	LC-MS (QqQ)	0.126	1.33	0.48	c
008	0.19	0.1	2	GC-MS (QqQ)	0.05	0.02	0.01	c
009	0.204	0.08	2	GC-MS (Q)	0.04	0.31	0.28	a
010	0.414	0.207	2	LC-MS (QqQ)	0.1035	4.75	2.06	c
011	0.142	0.045	73	GC-MS (QqQ)	0.000616	-1.00	-1.38	b
012	0.14	0.06	2	LC-MS (QqQ)	0.03	-1.04	-1.08	b
014	0.18	0.088	2	LC-MS (QqQ)	0.044	-0.20	-0.17	a
015	0.206	0.041	2	GC-MS (Q)	0.0205	0.35	0.42	b
017	0.198	30	2	GC-MS (Q)	15	0.19	0.00	c
019	0.1	0.05	2	LC-MS (QqQ)	0.025	-1.89	-2.10	b
020	0.295	0.148	2	LC-MS (QqQ)	0.074	2.24	1.30	c
021	0.173	0.026	2	LC-MS (QqQ)	0.013	-0.34	-0.44	b
022	0.196	0.098	2	LC-MS (QqQ)	0.049	0.14	0.11	c
025	0.23	0.12	2	LC-MS (QqQ)	0.06	0.86	0.59	c
026	0.228	0.114	2	GC-MS (IT)	0.057	0.82	0.58	c
027	0.188	0.094	2	LC-MS (QqQ)	0.047	-0.03	-0.02	a
028	0.23	0	0	GC-MS (Triple AXIS)	0	0.86	1.19	b
029	0.212	0.042	2	GC-MS (QqQ)	0.021	0.48	0.57	b
030	0.1991	0.0157	2	LC-MS (QqQ)	0.00785	0.21	0.28	b
031	0.195	25	2	GC-MS (QqQ)	12.5	0.12	0.00	c
032	0.185	0.093	2	LC-MS (QqQ)	0.0465	-0.09	-0.07	a
033	0.2168	0.043	1	GC-MS (QqQ)	0.043	0.58	0.50	a
035	0.14	0.03	2	GC-MS (QqQ)	0.015	-1.04	-1.31	b
036	0.209	0.027	2	LC-MS (QqQ)	0.0135	0.42	0.54	b
037	0.16	0.007	2	GC/ECD	0.0035	-0.62	-0.85	b
038	0.147	0.015	2	GC-MS (Q)	0.0075	-0.89	-1.20	b
040	0.241	0.0063	2	GC-MS (Q)	0.00315	1.09	1.50	b
041	0.17	0.085	2	GC-MS (QqQ)	0.0425	-0.41	-0.35	a
042	0.202	0.068	2	GC-MS (QqQ)	0.034	0.27	0.26	b
043	0.195	0.0169	2	GC-MS (TOF)	0.00845	0.12	0.16	b
046	0.168	0.084	2	LC-MS (QqQ)	0.042	-0.45	-0.39	a
047	0.201	0.05	0.97	GC-MS (Q)	0.051546	0.25	0.19	c
048	0.186	0.019	94	LC-MS (QqQ)	0.000202	-0.07	-0.09	b
049	0.20	20	1.18	GC-MS (Q)	16.94915	0.23	0.00	c
050	0.16	0.015	2	GC-MS (Q)	0.0075	-0.62	-0.83	b
051	0.15	0.076	2.2	GC-ECD	0.034545	-0.82942	-0.8058	a
052	0.18	0.09	2	GC-MS (QqQ)	0.045	-0.20	-0.16	a
053	0.11	0.04	2	GC-MS (TOF)	0.02	-1.67	-1.99	b
055	0.23	0.115	2	GC-MS (QqQ)	0.0575	0.86	0.61	c
056	0.182	0.055	2	LC-MS (QqQ)	0.0275	-0.15	-0.16	b
058	0.197	0.099	2	LC-MS (QqQ)	0.0495	0.16	0.13	c
059	0.167	0.052	2	GC-ECD/NPD	0.026	-0.47	-0.52	b
060	0.18	0.081	2	LC-MS (QqQ)	0.0405	-0.20	-0.17	a
061	0.2	0.01611	2	LC-MS (QqQ)	0.008055	0.23	0.31	b
063	0.138	0	0	LC-MS (QqQ)	0	-1.08	-1.49	b
064	0.33	0.03	2	GC-MS (IT)	0.015	2.98	3.76	b
065	0.253	0.031	2	GC-MS (Q)	0.0155	1.35	1.69	b
066	0.182	50	2	GC-MS (QqQ)	25	-0.15	0.00	c
067	0.201	0.04	2	GC-MS (QqQ)	0.02	0.25	0.30	b
068	0.182	0.11	2	GC-MS (Q)	0.055	-0.15	-0.11	c
069	0.24	0.12	2	GC-MS (Q)	0.06	1.07	0.73	c
072	0.187	0.027	2	GC-MS (QqQ)	0.0135	-0.05	-0.06	b
073	0.16	0.02	2		0.01	-0.62	-0.82	b
074	0.256	0.031	2	UPLC-MS/MS	0.0155	1.41	1.77	b
075	0.2	0.1	2	GC-MS (Q)	0.05	0.23	0.18	c
077	0.103	0.5	2	LC-MS (QqQ)	0.25	-1.82	-0.34	c
078	0.185	0.05	2	GC-MS (Q)	0.025	-0.09	-0.10	b
079	0.213	0.017	2	GC-MS (Q)	0.0085	0.50	0.67	b
080	0.195	0.152	2	GC-MS	0.076	0.12	0.07	c
081	0.208	0.026	2	GC-MS (Q)	0.013	0.40	0.51	b
082	0.19	0.095	2	GC-MS (QqQ)	0.0475	0.02	0.01	c
083	0.17	0.012	2	GC-MS (QqQ)	0.006	-0.41	-0.55	b
085	0.191	0.067	2	GC-MS (QqQ)	0.0335	0.04	0.04	b
086	0.15	0.04	2	GC-MS (Q)	0.02	-0.83	-0.99	b
087	0.206	0.011	2	LC-MS(Q ; QqQ)	0.0055	0.35	0.48	b

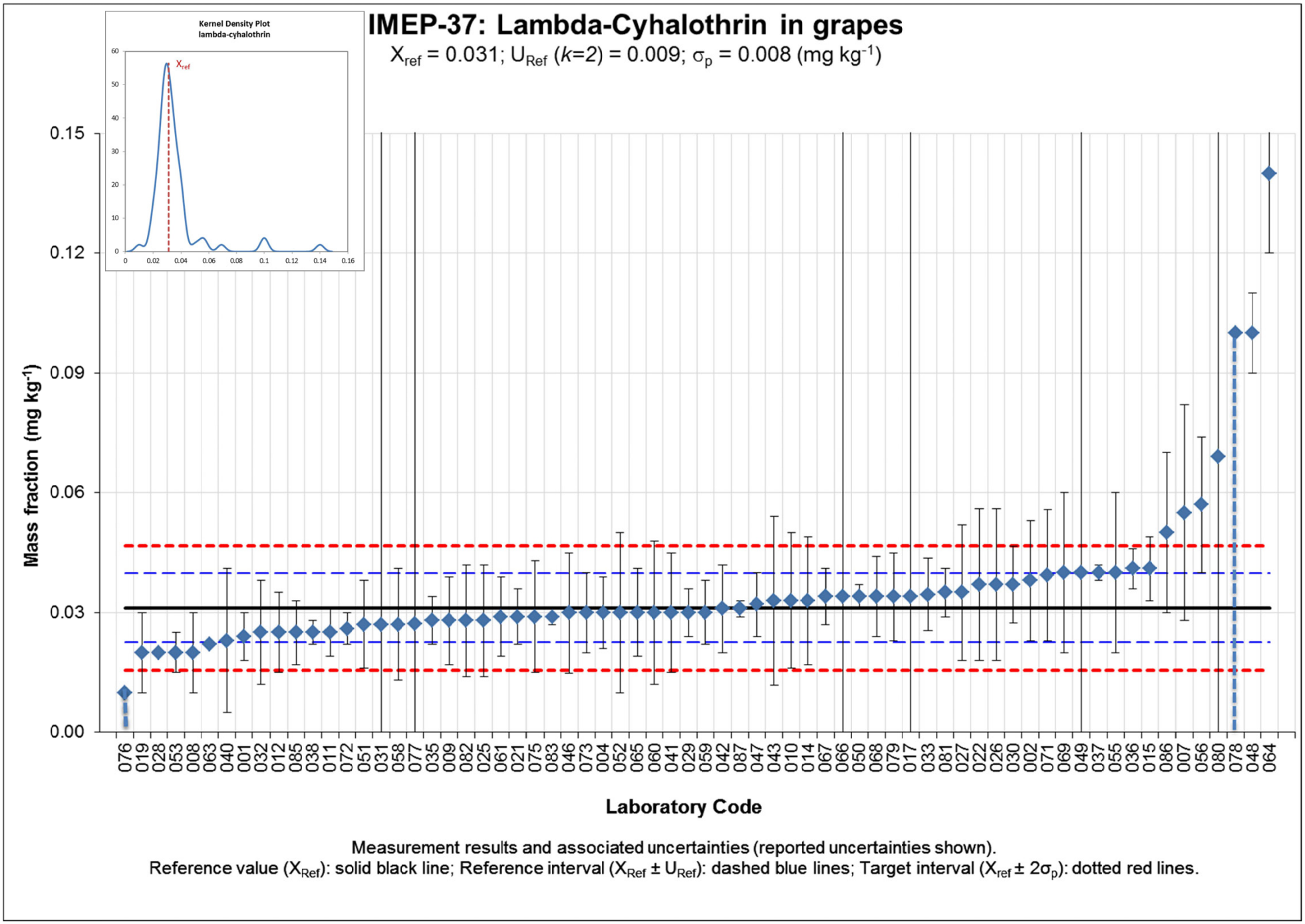


Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 22: Results for Lambda-Cyhalothrin

X_{ref} = 0.031; U_{Ref} (k=2) = 0.009; $\hat{\sigma}$ = 0.008 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	0.024	0.006	2	GC-MS (QqQ)	0.003	-0.92	-1.36	b
002	0.038	0.015	0.057	GC-MS (QqQ)	0.263158	0.88	0.03	c
004	0.03	0.009	2	GC-MS (QqQ)	0.0045	-0.15	-0.19	a
007	0.055	0.027	1	GC-MS (QqQ)	0.027	3.06	0.87	c
008	0.02	0.01	2	GC-MS (QqQ)	0.005	-1.43	-1.69	a
009	0.028	0.011	2	GC-MS (Q)	0.0055	-0.41	-0.45	a
010	0.033	0.017	2	GC-MS (QqQ)	0.0085	0.24	0.19	c
011	0.025	0.006	75	GC-MS (QqQ)	0.00008	-0.79	-1.42	b
012	0.025	0.01	2	GC-MS (QqQ)	0.005	-0.79	-0.93	a
014	0.033	0.016	2	GC-MS (QqQ)	0.008	0.24	0.20	c
015	0.041	0.008	2	GC-MS (Q)	0.004	1.26	1.67	b
017	0.034	30	2	GC-MS (Q)	15	0.36	0.00	c
019	0.02	0.01	2	LC-MS (QqQ)	0.005	-1.43	-1.69	a
021	0.029	0.007	2	GC-MS (Q)	0.0035	-0.28	-0.39	b
022	0.037	0.019	2	LC-MS (QqQ)	0.0095	0.75	0.56	c
025	0.028	0.014	2	GC-MS (Q)	0.007	-0.41	-0.38	a
026	0.037	0.019	2	GC-MS (IT)	0.0095	0.75	0.56	c
027	0.035	0.017	2	GC-MS (QqQ)	0.0085	0.49	0.40	c
028	0.02	0	0	GC-MS (Triple AXIS)	0	-1.43	-2.58	b
029	0.03	0.006	2	GC-MS (QqQ)	0.003	-0.15	-0.22	b
030	0.037	0.0096	2	GC-MS (QqQ)	0.0048	0.75	0.90	a
031	0.027	25	2	GC-MS (QqQ)	12.5	-0.53	0.00	c
032	0.025	0.013	2	GC-MS (QqQ)	0.0065	-0.79	-0.79	a
033	0.0345	0.0091	1	GC-MS (QqQ)	0.0091	0.43	0.33	c
035	0.028	0.006	2	GC-MS (QqQ)	0.003	-0.41	-0.60	b
036	0.041	0.005	2	GC-MS (QqQ)	0.0025	1.26	1.97	b
037	0.04	0.002	2	GC-MS (Q)	0.001	1.13	1.99	b
038	0.025	0.003	2	GC-MS (Q)	0.0015	-0.79	-1.35	b
040	0.023	0.018	2	GC-MS (Q)	0.009	-1.05	-0.82	c
041	0.03	0.015	2	GC-MS (QqQ)	0.0075	-0.15	-0.13	a
042	0.031	0.011	2	GC-MS (QqQ)	0.0055	-0.02	-0.02	a
043	0.033	0.02108	2	GC-MS (TOF)	0.01054	0.24	0.16	c
046	0.0299	0.015	2	GC-MS (Q)	0.0075	-0.16	-0.15	a
047	0.032	0.008	0.92	GC-MS (Q)	0.008696	0.11	0.09	c
048	0.100	0.010	92	GC-MS (Q)	0.000109	8.84	15.92	b
049	0.04	12	1.11	GC-MS (Q)	10.81081	1.13	0.00	c
050	0.034	0.003	2	GC-MS (Q)	0.0015	0.36	0.62	b
051	0.027	0.011	2.1	GC-ECD	0.005238	-0.53	-0.61	a
052	0.03	0.02	2	GC-MS (QqQ)	0.01	-0.15	-0.11	c
053	0.02	0.005	2	GC-MS (TOF)	0.0025	-1.43	-2.23	b
055	0.04	0.02	2	GC-MS (QqQ)	0.01	1.13	0.81	c
056	0.057	0.017	2	GC-MS (Q)	0.0085	3.317073	2.709621	c
058	0.027	0.014	2	GC-MS (QqQ)	0.007	-0.53	-0.51	a
059	0.03	0.008	2	GC-ECD	0.004	-0.15	-0.20	b
060	0.03	0.018	2	GC-MS (QqQ)	0.009	-0.15	-0.12	c
061	0.029	0.01	2	GC-MS (QqQ)	0.005	-0.28	-0.33	a
063	0.022	0	0	GC-MS (QqQ)	0	-1.18	-2.12	b
064	0.14	0.02	2	GC-MS (IT)	0.01	13.97	9.99	c
065	0.03	0.011	2	GC-MS (Q)	0.0055	-0.15	-0.17	a
066	0.034	50	2	GC-MS (QqQ)	25	0.36	0.00	c
067	0.034	0.007	2	GC-MS (QqQ)	0.0035	0.36	0.51	b
068	0.034	0.01	2	GC-MS (Q)	0.005	0.36	0.43	a
069	0.04	0.02	2	GC-MS (Q)	0.01	1.13	0.81	c
071	0.0394	0.0164	2	GC/ECD and comfirmed by	0.0082	1.06	0.89	c
072	0.026	0.004	2	GC-MS (QqQ)	0.002	-0.66	-1.08	b
073	0.03	0.01	2		0.005	-0.15	-0.18	a
075	0.029	0.014	2	GC-MS (Q)	0.007	-0.28	-0.26	a
076	< 0.01			GC-MS (Q)				
077	0.0272	0.5	2	GC-MS (QqQ)	0.25	-0.51	-0.02	c
078	< 0.1			GC-MS (Q)				
079	0.034	0.011	2	GC-MS (Q)	0.0055	0.36457	0.405952	a
080	0.069	0.11	2	GC-MS	0.055	4.86	0.69	c
081	0.035	0.006	2	GC-MS (Q)	0.003	0.49	0.73	b
082	0.028	0.014	2	GC-MS (QqQ)	0.007	-0.41	-0.38	a
083	0.029	0.002	2	GC-MS (QqQ)	0.001	-0.28	-0.49	b
085	0.025	0.008	2	GC-MS (QqQ)	0.004	-0.79	-1.05	b
086	0.05	0.02	2	GC-MS (Q)	0.01	2.42	1.73	c
087	0.031	0.002	2	GC-MS (QqQ)	0.001	-0.02	-0.04	b

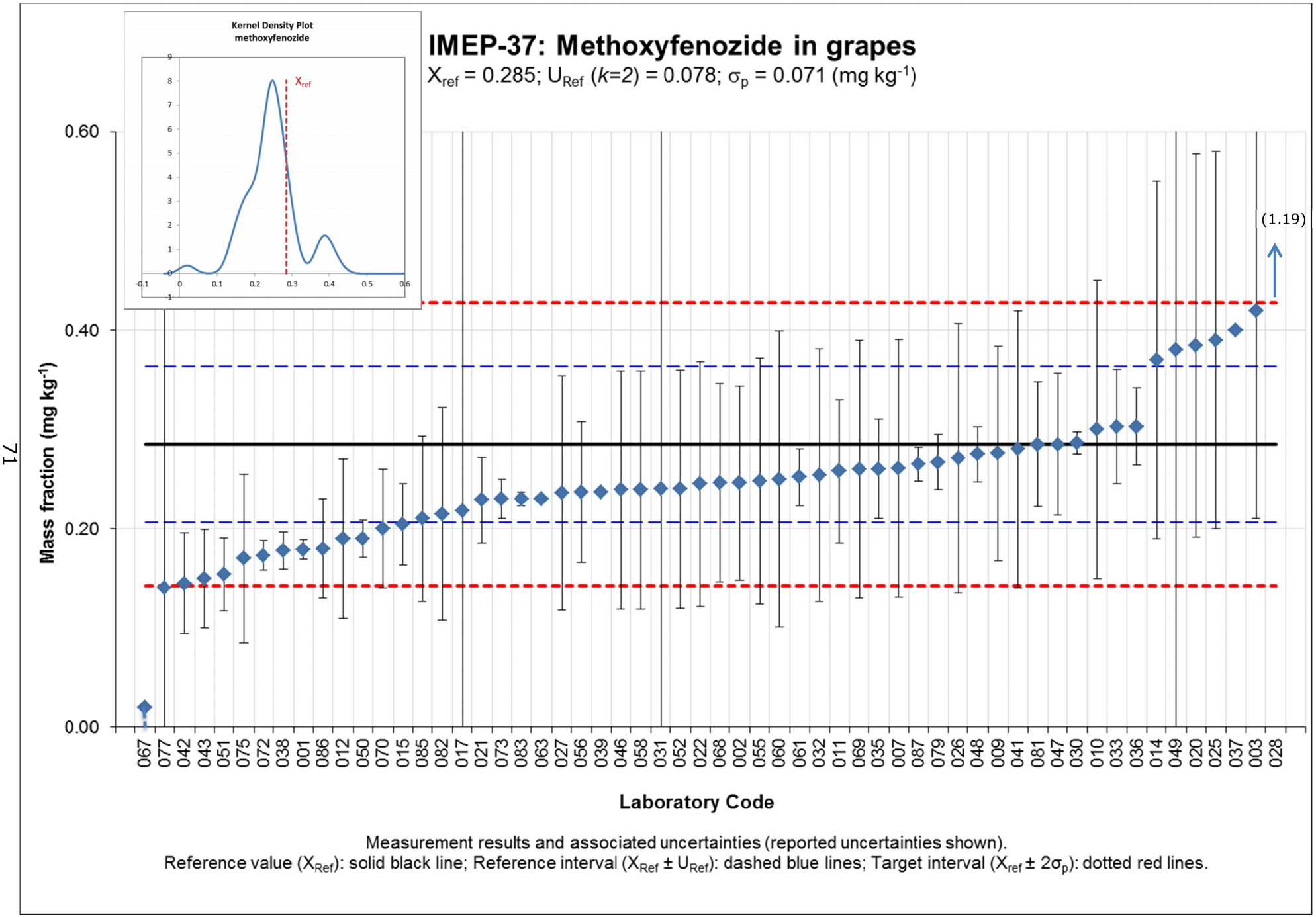


Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 23: Results for Methoxyfenozide

X_{ref} = 0.285; U_{Ref} (*k=2*) = 0.078; $\hat{\sigma}$ = 0.071 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	0.179	0.01	2	LC-MS (QqQ)	0.005	-1.49	-2.68	b
002	0.246	0.098	0.006	LC-MS (QqQ)	16.33333	-0.55	0.00	c
003	0.42	0.21	79.5	LC-MS (QqQ)	0.002642	1.90	3.44	b
007	0.261	0.13	1	LC-MS (QqQ)	0.13	-0.34	-0.18	c
009	0.276	0.108	2	LC-MS (QqQ)	0.054	-0.13	-0.13	a
010	0.3	0.15	2	LC-MS (QqQ)	0.075	0.211413	0.177991	c
011	0.258	0.072	89	LC-MS (QqQ)	0.000809	-0.38	-0.69	b
012	0.19	0.08	2	LC-MS (QqQ)	0.04	-1.33	-1.70	a
014	0.37	0.18	2	LC-MS (QqQ)	0.09	1.19	0.87	c
015	0.204	0.041	2	LC-MS (IT)	0.0205	-1.14	-1.83	b
017	0.218	30	2	LC-MS (Q)	15	-0.94	0.00	c
020	0.385	0.193	2	LC-MS (QqQ)	0.0965	1.40	0.96	c
021	0.229	0.043	2	LC-MS (QqQ)	0.0215	-0.79	-1.25	b
022	0.245	0.123	2	LC-MS (QqQ)	0.0615	-0.56	-0.55	a
025	0.39	0.19	2	LC-MS (QqQ)	0.095	1.47	1.02	c
026	0.271	0.136	2	LC-MS (QqQ)	0.068	-0.20	-0.18	a
027	0.236	0.118	2	LC-MS (QqQ)	0.059	-0.69	-0.69	a
028	1.19	0	0	LC-MS (QqQ)	0	12.71	23.11	b
030	0.2865	0.0113	2	LC-MS (QqQ)	0.00565	0.02	0.04	b
031	0.24	25	2	LC-MS (QqQ)	12.5	-0.63	0.00	c
032	0.254	0.127	2	LC-MS (QqQ)	0.0635	-0.43	-0.41	a
033	0.303	0.058	1	LC-MS (QqQ)	0.058	0.25	0.26	a
035	0.26	0.05	2	LC-MS (QqQ)	0.025	-0.35	-0.54	b
036	0.303	0.039	2	LC-MS (QqQ)	0.0195	0.25	0.41	b
037	0.4	0.002	2	HPLC/UV	0.001	1.62	2.94	b
038	0.178	0.019	2	LC-MS (QqQ)	0.0095	-1.50	-2.65	b
039	0.237	0	0	LC-MS (QqQ)	0	-0.67	-1.22	b
041	0.28	0.14	2	LC-MS (QqQ)	0.07	-0.07	-0.06	a
042	0.145	0.051	2	LC-MS (QqQ)	0.0255	-1.96	-2.99	b
043	0.15	0.04956	2	LC-MS (QqQ)	0.02478	-1.89	-2.91	b
046	0.239	0.12	2	LC-MS (QqQ)	0.06	-0.64	-0.64	a
047	0.285	0.071	1.02	LC-MS (QqQ)	0.069608	0.00	0.00	a
048	0.275	0.028	99	LC-MS (QqQ)	0.000283	-0.14	-0.25	b
049	0.38	12	0.94	LC-MS (QqQ)	12.76596	1.33	0.01	c
050	0.19	0.019	2	LC-MS (QqQ)	0.0095	-1.33	-2.36	b
051	0.154	0.037	2.3	LC-MS (QqQ)	0.016087	-1.84	-3.09	b
052	0.24	0.12	2	LC-MS (QqQ)	0.06	-0.63	-0.63	a
055	0.248	0.124	2	LC-MS (QqQ)	0.062	-0.52	-0.50	a
056	0.237	0.071	2	LC-MS (QqQ)	0.0355	-0.67	-0.91	b
058	0.239	0.12	2	LC-MS (QqQ)	0.06	-0.64	-0.64	a
060	0.25	0.149	2	LC-MS (QqQ)	0.0745	-0.49	-0.42	c
061	0.252	0.02838	2	LC-MS (QqQ)	0.01419	-0.46	-0.79	b
063	0.23	0	0	LC-MS (QqQ)	0	-0.77	-1.40	b
067	< 0.02			GC-MS (QqQ)				
068	0.246	0.1	2	LC-MS (QqQ)	0.05	-0.55	-0.61	a
069	0.26	0.13	2	LC-MS (QqQ)	0.065	-0.35	-0.33	a
070	0.2	0.06	2	LC-MS (QqQ)	0.03	-1.19	-1.72	b
072	0.173	0.015	2	LC-MS (QqQ)	0.0075	-1.57	-2.81	b
073	0.23	0.02	2		0.01	-0.77	-1.36	b
075	0.17	0.085	2	LC-MS (QqQ)	0.0425	-1.61	-1.99	a
077	0.14	0.5	2	LC-MS (QqQ)	0.25	-2.03	-0.57	c
079	0.267	0.028	2	LC-MS (QqQ)	0.014	-0.25	-0.43	b
081	0.285	0.063	2	LC-MS (QqQ)	0.0315	0.00	0.00	b
082	0.215	0.1075	2	LC-MS (QqQ)	0.05375	-0.98	-1.05	a
083	0.23	0.007	2	LC-MS (QqQ)	0.0035	-0.77	-1.40	b
085	0.21	0.083	2	LC-MS (QqQ)	0.0415	-1.05	-1.31	a
086	0.18	0.05	2	LC-MS (Q)	0.025	-1.47	-2.26	b
087	0.265	0.017	2	LC-MS(Q ; QqQ)	0.0085	-0.28	-0.50	b

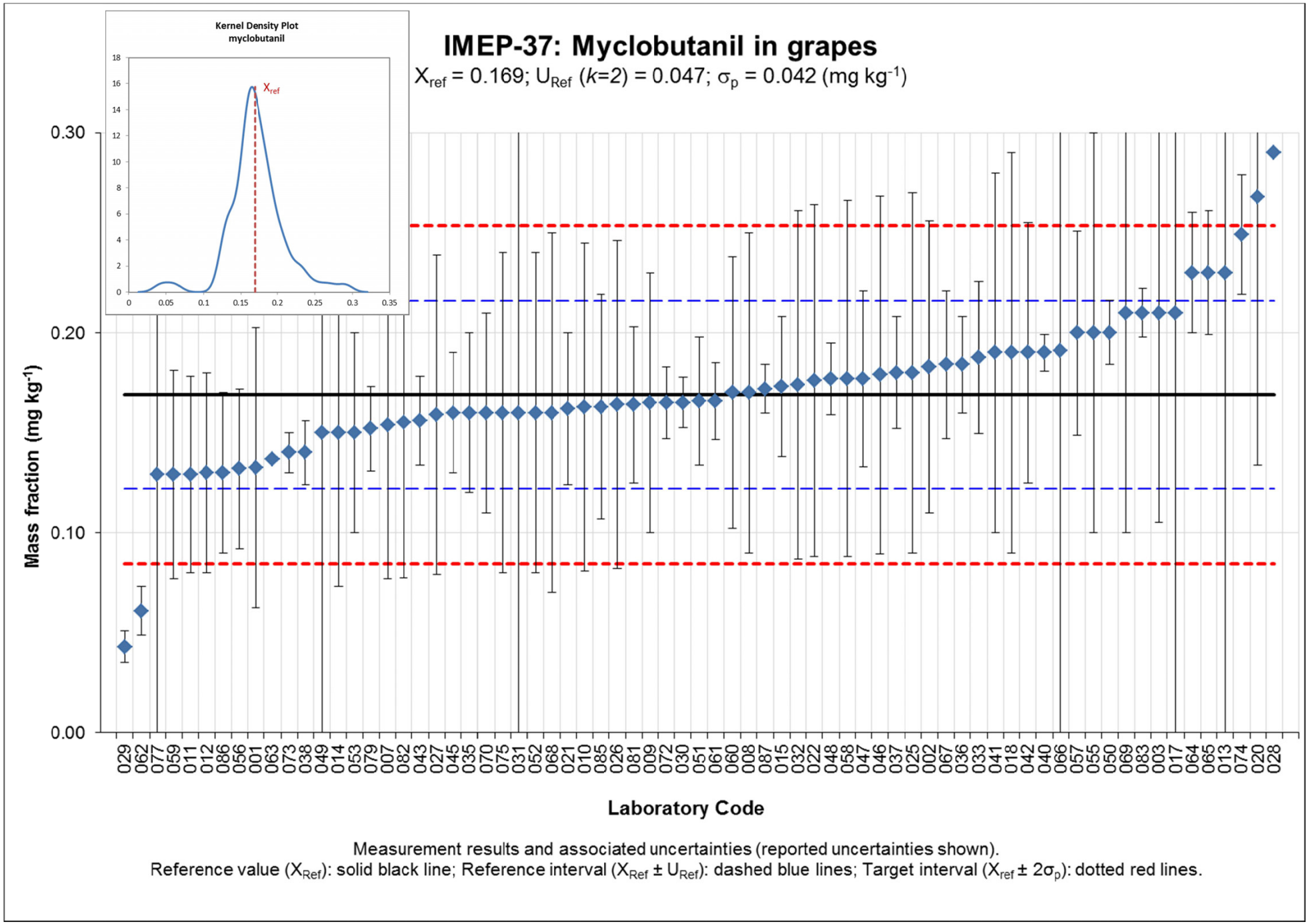


Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 24: Results for Myclobutanil

X_{ref} = 0.169; U_{Ref} (*k=2*) = 0.047; $\hat{\sigma}$ = 0.042 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	0.1326	0.07	2	GC-MS (QqQ)	0.035	-0.86	-0.86	a
002	0.183	0.073	0.015	GC-MS (QqQ)	4.866667	0.329824	0.002864	c
003	0.21	0.105	77.5	LC-MS (QqQ)	0.001355	0.97	1.73	b
007	0.154	0.077	1	GC-MS (QqQ)	0.077	-0.36	-0.19	c
008	0.17	0.08	2	GC-MS (QqQ)	0.04	0.02	0.02	a
009	0.165	0.065	2	GC-MS (Q)	0.0325	-0.10	-0.10	a
010	0.163	0.082	2	GC-MS (QqQ)	0.041	-0.14	-0.13	a
011	0.129	0.049	74	GC-MS (QqQ)	0.000662	-0.95	-1.70	b
012	0.13	0.05	2	GC-MS (QqQ)	0.025	-0.92	-1.14	a
013	0.23	20	2	GC-MS (Q)	10	1.44	0.01	c
014	0.15	0.077	2	LC-MS (QqQ)	0.0385	-0.45	-0.42	a
015	0.173	0.035	2	GC-MS (Q)	0.0175	0.09	0.13	b
017	0.21	30	2	GC-MS (Q)	15	0.97	0.00	c
018	0.19	0.1	2	LC-MS (IT)	0.05	0.50	0.38	c
020	0.268	0.134	2	LC-MS (QqQ)	0.067	2.34	1.39	c
021	0.162	0.038	2	LC-MS (QqQ)	0.019	-0.17	-0.23	b
022	0.176	0.088	2	LC-MS (QqQ)	0.044	0.16	0.14	c
025	0.18	0.09	2	LC-MS (QqQ)	0.045	0.26	0.22	c
026	0.164	0.082	2	GC-MS (IT)	0.041	-0.12	-0.11	a
027	0.159	0.08	2	LC-MS (QqQ)	0.04	-0.24	-0.22	a
028	0.29	0	0	LC-MS (QqQ)	0	2.86	5.13	b
029	0.043	0.008	2	LC-MS (QqQ)	0.004	-2.98	-5.27	b
030	0.1651	0.0125	2	LC-MS (QqQ)	0.00625	-0.09	-0.16	b
031	0.16	25	2	GC-MS (QqQ)	12.5	-0.21	0.00	c
032	0.174	0.087	2	LC-MS (QqQ)	0.0435	0.12	0.10	c
033	0.1876	0.038	1	GC-MS (QqQ)	0.038	0.44	0.41	a
035	0.16	0.04	2	GC-MS (QqQ)	0.02	-0.21	-0.29	b
036	0.184	0.024	2	LC-MS (QqQ)	0.012	0.35	0.56	b
037	0.18	0.028	2	GC-MS (Q)	0.014	0.26	0.40	b
038	0.14	0.016	2	GC-MS (Q)	0.008	-0.69	-1.17	b
040	0.19	0.0093	2	GC-MS (Q)	0.00465	0.50	0.87	b
041	0.19	0.09	2	LC-MS (QqQ)	0.045	0.50	0.41	c
042	0.19	0.065	2	GC-MS (QqQ)	0.0325	0.50	0.52	a
043	0.156	0.02211	2	GC-MS (TOF)	0.011055	-0.31	-0.50	b
045	0.16	0.03	2	GC-MS (EI Quadrapole)	0.015	-0.21	-0.32	b
046	0.179	0.0895	2	GC-MS (Q)	0.04475	0.24	0.20	c
047	0.177	0.044	1.01	GC-MS (Q)	0.043564	0.19	0.16	c
048	0.177	0.018	95	LC-MS (QqQ)	0.000189	0.19	0.34	b
049	0.15	11	1.16	GC-MS (Q)	9.482759	-0.45	0.00	c
050	0.2	0.016	2	GC-MS (Q)	0.008	0.73	1.24	b
051	0.166	0.032	2.3	LC-MS (QqQ)	0.013913	-0.07	-0.11	b
052	0.16	0.08	2	GC-MS (QqQ)	0.04	-0.21	-0.20	a
053	0.15	0.05	2	GC-MS (TOF)	0.025	-0.45	-0.55	a
055	0.2	0.1	2	GC-MS (QqQ)	0.05	0.73	0.56	c
056	0.132	0.04	2	LC-MS (QqQ)	0.02	-0.88	-1.20	b
057	0.1998	0.051	2	GC-MS	0.0255	0.73	0.89	a
058	0.177	0.089	2	LC-MS (QqQ)	0.0445	0.19	0.16	c
059	0.129	0.052	2	GC-ECD/NPD	0.026	-0.95	-1.14	a
060	0.17	0.068	2	GC-MS (QqQ)	0.034	0.02	0.02	a
061	0.166	0.01921	2	LC-MS (QqQ)	0.009605	-0.07	-0.12	b
062	0.061	0.012	2	GC	0.006	-2.56	-4.44	b
063	0.137	0	0	LC-MS (QqQ)	0	-0.76	-1.36	b
064	0.23	0.03	2	GC-MS (IT)	0.015	1.44	2.18	b
065	0.23	0.031	2	GC-MS (Q)	0.0155	1.44	2.16	b
066	0.191	50	2	GC-MS (QqQ)	25	0.52	0.00	c
067	0.184	0.037	2	GC-MS (QqQ)	0.0185	0.35	0.50	b
068	0.16	0.09	2	GC-MS (Q)	0.045	-0.21	-0.18	c
069	0.21	0.11	2	GC-MS (Q)	0.055	0.97	0.68	c
070	0.16	0.05	2	LC-MS (QqQ)	0.025	-0.21	-0.26	a
072	0.165	0.018	2	GC-MS (QqQ)	0.009	-0.10	-0.16	b
073	0.14	0.01	2		0.005	-0.69	-1.21	b
074	0.249	0.03	2	UPLC-MS/MS	0.015	1.89	2.86	b
075	0.16	0.08	2	GC-MS (Q)	0.04	-0.21	-0.20	a
077	0.129	0.5	2	GC-MS (QqQ)	0.25	-0.95	-0.16	c
079	0.152	0.021	2	GC-MS (Q)	0.0105	-0.40	-0.66	b
081	0.164	0.039	2	LC-MS (QqQ)	0.0195	-0.12	-0.17	b
082	0.155	0.0775	2	GC-MS (QqQ)	0.03875	-0.33	-0.31	a
083	0.21	0.012	2	LC-MS (QqQ)	0.006	0.97	1.68	b
085	0.163	0.056	2	GC-MS (QqQ)	0.028	-0.14	-0.17	a
086	0.13	0.04	2	GC-MS (Q)	0.02	-0.92	-1.26	b
087	0.172	0.012	2	LC-MS(Q ; QqQ)	0.006	0.07	0.12	b

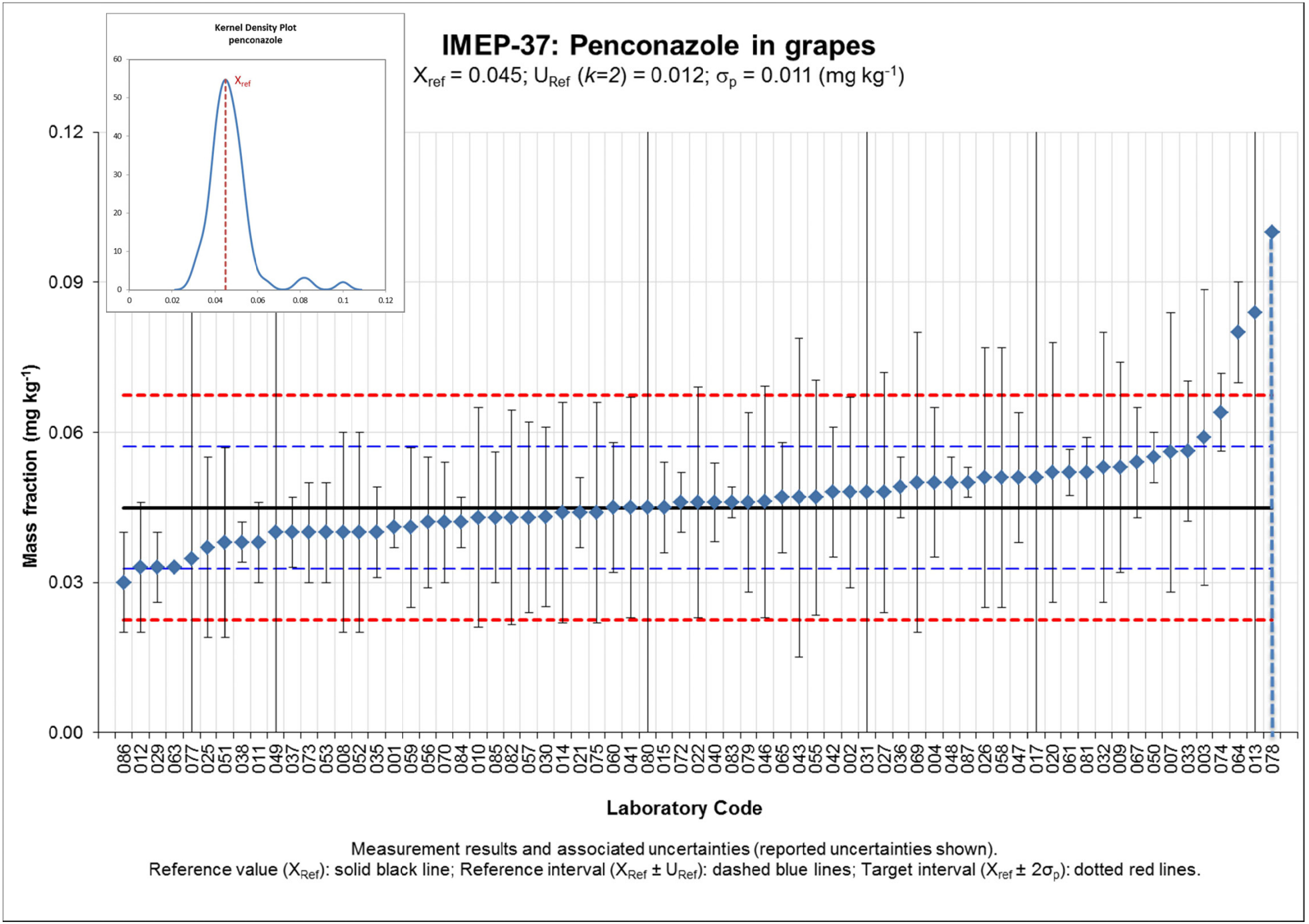


Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 25: Results for Penconazole

X_{ref} = 0.045; U_{Ref} (*k=2*) = 0.012; $\hat{\sigma}$ = 0.011 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	0.041	0.004	2	GC-MS (QqQ)	0.002	-0.35	-0.62	b
002	0.048	0.019	0.059	GC-MS (QqQ)	0.322034	0.27	0.01	c
003	0.059	0.0295	81.5	LC-MS (QqQ)	0.000362	1.25	2.29	b
004	0.05	0.015	2	GC-MS (QqQ)	0.0075	0.45	0.52	a
007	0.056	0.028	1	LC-MS (QqQ)	0.028	0.98	0.39	c
008	0.04	0.02	2	GC-MS (QqQ)	0.01	-0.44	-0.42	a
009	0.053	0.021	2	GC-MS (Q)	0.0105	0.72	0.66	a
010	0.043	0.022	2	GC-MS (QqQ)	0.011	-0.17	-0.16	a
011	0.038	0.008	81	GC-MS (QqQ)	9.88E-05	-0.62	-1.14	b
012	0.033	0.013	2	LC-MS (QqQ)	0.0065	-1.06	-1.34	a
013	0.084	20	2	GC-MS (Q)	10	3.47	0.00	c
014	0.044	0.022	2	LC-MS (QqQ)	0.011	-0.09	-0.08	a
015	0.045	0.009	2	GC-MS (Q)	0.0045	0.00	0.01	b
017	0.051	30	2	GC-MS (Q)	15	0.54	0.00	c
020	0.052	0.026	2	LC-MS (QqQ)	0.013	0.63	0.49	c
021	0.044	0.007	2	LC-MS (QqQ)	0.0035	-0.09	-0.14	b
022	0.046	0.023	2	LC-MS (QqQ)	0.0115	0.09	0.08	c
025	0.037	0.018	2	LC-MS (QqQ)	0.009	-0.71	-0.73	a
026	0.051	0.026	2	GC-MS (IT)	0.013	0.54	0.42	c
027	0.048	0.024	2	LC-MS (QqQ)	0.012	0.27	0.23	c
029	0.033	0.007	2	GC-MS (QqQ)	0.0035	-1.06	-1.70	b
030	0.0431	0.0179	2	LC-MS (QqQ)	0.00895	-0.17	-0.17	a
031	0.048	25	2	GC-MS (QqQ)	12.5	0.27	0.00	c
032	0.053	0.027	2	LC-MS (QqQ)	0.0135	0.72	0.54	c
033	0.0563	0.014	1	GC-MS (QqQ)	0.014	1.01	0.74	c
035	0.04	0.009	2	GC-MS (QqQ)	0.0045	-0.44128	-0.65301	b
036	0.049	0.006	2	LC-MS (QqQ)	0.003	0.36	0.59	b
037	0.04	0.007	2	GC-MS (Q)	0.0035	-0.44	-0.70	b
038	0.038	0.004	2	GC-MS (Q)	0.002	-0.62	-1.08	b
040	0.046	0.0079	2	GC-MS (Q)	0.00395	0.09	0.14	b
041	0.045	0.022	2	GC-MS (QqQ)	0.011	0.00	0.00	a
042	0.048	0.013	2	GC-MS (QqQ)	0.0065	0.27	0.34	a
043	0.047	0.03185	2	GC-MS (TOF)	0.015925	0.18	0.12	c
046	0.0461	0.0231	2	GC-MS (Q)	0.01155	0.10	0.09	c
047	0.051	0.013	0.9	GC-MS (Q)	0.014444	0.54	0.39	c
048	0.05	0.005	89	LC-MS (QqQ)	5.62E-05	0.45	0.82	b
049	0.04	22	1.13	GC-MS (Q)	19.46903	-0.44	0.00	c
050	0.055	0.005	2	GC-MS (Q)	0.0025	0.89	1.52	b
051	0.038	0.019	2.2	GC-ECD	0.008636	-0.62	-0.66	a
052	0.04	0.02	2	GC-MS (QqQ)	0.01	-0.44	-0.42	a
053	0.04	0.01	2	GC-MS (TOF)	0.005	-0.44	-0.63	b
055	0.047	0.0235	2	GC-MS (QqQ)	0.01175	0.18	0.15	c
056	0.042	0.013	2	LC-MS (QqQ)	0.0065	-0.26	-0.33	a
057	0.043	0.019	2	GC-MS	0.0095	-0.17	-0.17	a
058	0.051	0.026	2	LC-MS (QqQ)	0.013	0.54	0.42	c
059	0.041	0.016	2	GC-ECD/NPD	0.008	-0.35	-0.39	a
060	0.045	0.013	2	LC-MS (QqQ)	0.0065	0.00	0.00	a
061	0.052	0.00464	2	LC-MS (QqQ)	0.00232	0.63	1.08	b
063	0.033	0	0	LC-MS (QqQ)	0	-1.06	-1.95	b
064	0.08	0.01	2	GC-MS (IT)	0.005	3.12	4.43	b
065	0.047	0.011	2	GC-MS (Q)	0.0055	0.18	0.25	b
067	0.054	0.011	2	GC-MS (QqQ)	0.0055	0.80	1.10	b
069	0.05	0.03	2	GC-MS (Q)	0.015	0.45	0.31	c
070	0.042	0.012	2	LC-MS (QqQ)	0.006	-0.26	-0.35	b
072	0.046	0.006	2	GC-MS (QqQ)	0.003	0.09	0.15	b
073	0.04	0.01	2		0.005	-0.44	-0.63	b
074	0.064	0.0078	2	UPLC-MS/MS	0.0039	1.69	2.62	b
075	0.044	0.022	2	GC-MS (Q)	0.011	-0.09	-0.08	a
077	0.0348	0.5	2	GC-MS (QqQ)	0.25	-0.90	-0.04	c
078	< 0.1			GC-MS (Q)				
079	0.046	0.018	2	GC-MS (Q)	0.009	0.09	0.10	a
080	0.045	0.098	2	GC-MS	0.049	0.00	0.00	c
081	0.052	0.007	2	GC-MS (Q)	0.0035	0.63	1.00	b
082	0.043	0.0215	2	GC-MS (QqQ)	0.01075	-0.17	-0.16	a
083	0.046	0.003	2	GC-MS (QqQ)	0.0015	0.09	0.17	b
084	0.042	0.005	2	GC-ECD	0.0025	-0.26	-0.45	b
085	0.043	0.013	2	LC-MS (QqQ)	0.0065	-0.17	-0.22	a
086	0.03	0.01	2	LC-MS (Q)	0.005	-1.33096	-1.89317	b
087	0.05	0.003	2	LC-MS(Q ; QqQ)	0.0015	0.45	0.80	b

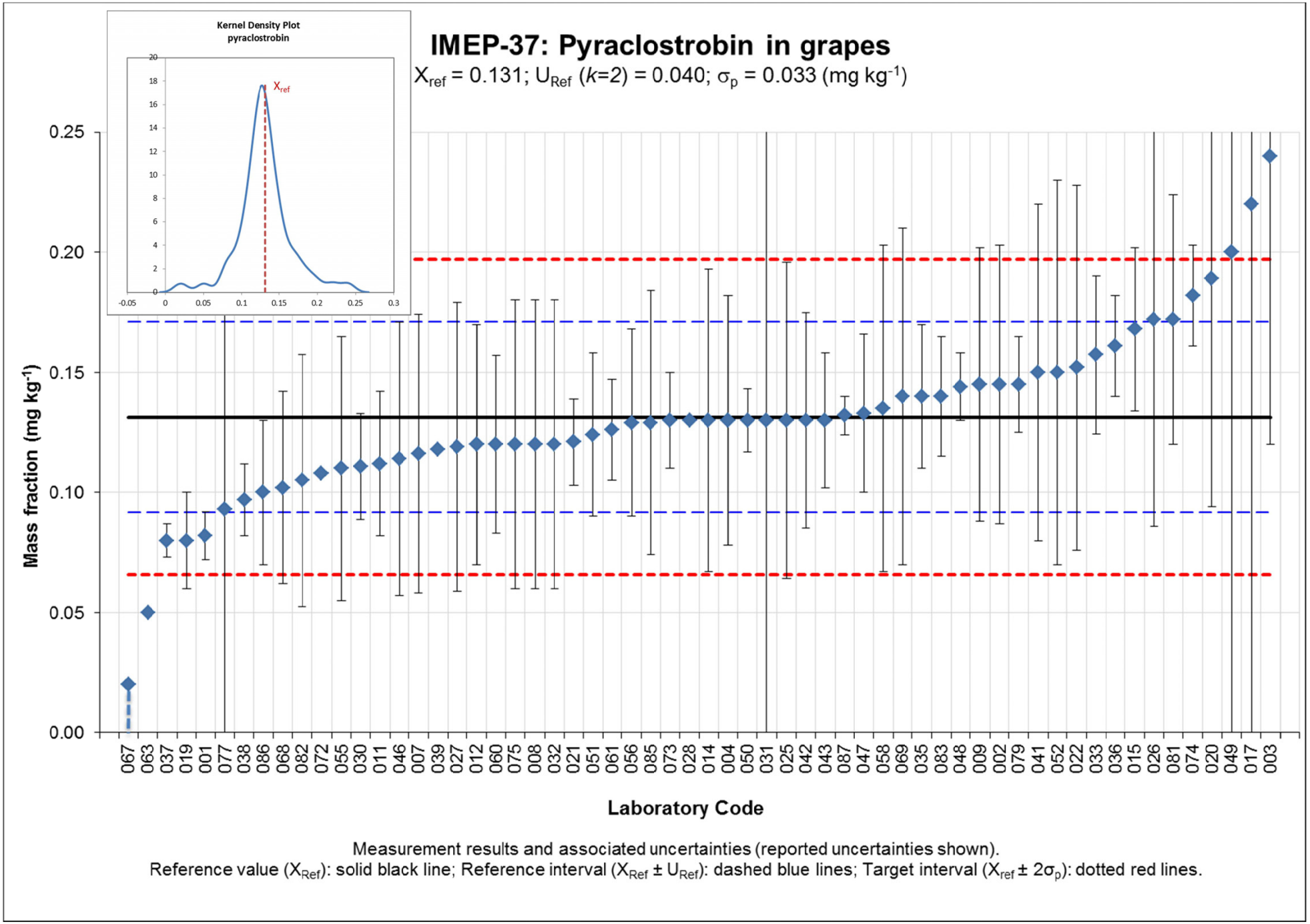


Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 26: Results for Pyraclostrobin

X_{ref} = 0.131; U_{Ref} (*k=2*) = 0.040; $\hat{\sigma}$ = 0.033 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	0.082	0.01	2	LC-MS (QqQ)	0.005	-1.50	-2.42	b
002	0.145	0.058	0.02	LC-MS (QqQ)	2.9	0.41	0.00	c
003	0.24	0.12	84	LC-MS (QqQ)	0.001429	3.31	5.48	b
004	0.13	0.052	2	GC-MS (QqQ)	0.026	-0.04	-0.04	a
007	0.116	0.058	1	LC-MS (QqQ)	0.058	-0.47	-0.25	c
008	0.12	0.06	2	LC-MS (QqQ)	0.03	-0.35	-0.32	a
009	0.145	0.057	2	LC-MS (QqQ)	0.0285	0.41	0.39	a
011	0.112	0.03	97	LC-MS (QqQ)	0.000309	-0.59	-0.98	b
012	0.12	0.05	2	LC-MS (QqQ)	0.025	-0.35	-0.36	a
014	0.13	0.063	2	LC-MS (QqQ)	0.0315	-0.04	-0.04	a
015	0.168	0.034	2	GC-MS (Q)	0.017	1.11	1.40	b
017	0.22	30	2	LC-MS (Q)	15	2.70	0.01	c
019	0.08	0.02	2	LC-MS (QqQ)	0.01	-1.56	-2.32	b
020	0.189	0.095	2	LC-MS (QqQ)	0.0475	1.75	1.12	c
021	0.121	0.018	2	LC-MS (QqQ)	0.009	-0.32	-0.48	b
022	0.152	0.076	2	LC-MS (QqQ)	0.038	0.63	0.48	c
025	0.13	0.066	2	LC-MS (QqQ)	0.033	-0.04	-0.04	c
026	0.172	0.086	2	GC-MS (IT)	0.043	1.24	0.86	c
027	0.119	0.06	2	LC-MS (QqQ)	0.03	-0.38	-0.35	a
028	0.13	0	0	LC-MS (QqQ)	0	-0.04262	-0.07077	b
030	0.1109	0.022	2	LC-MS (QqQ)	0.011	-0.62	-0.91	b
031	0.13	25	2	LC-MS (QqQ)	12.5	-0.04	0.00	c
032	0.12	0.06	2	LC-MS (QqQ)	0.03	-0.35	-0.32	a
033	0.1573	0.033	1	LC-MS (QqQ)	0.033	0.79	0.67	c
035	0.14	0.03	2	LC-MS (QqQ)	0.015	0.26	0.35	b
036	0.161	0.021	2	LC-MS (QqQ)	0.0105	0.90	1.32	b
037	0.08	0.007	2	GC/ECD	0.0035	-1.56	-2.56	b
038	0.097	0.015	2	GC-MS (Q)	0.0075	-1.05	-1.63	b
039	0.118	0	0	LC-MS (QqQ)	0	-0.41	-0.68	b
041	0.15	0.07	2	LC-MS (QqQ)	0.035	0.57	0.46	c
042	0.13	0.045	2	LC-MS (QqQ)	0.0225	-0.04	-0.05	a
043	0.13	0.02811	2	LC-MS (QqQ)	0.014055	-0.04	-0.06	b
046	0.114	0.057	2	LC-MS (QqQ)	0.0285	-0.53	-0.50	a
047	0.133	0.033	0.99	LC-MS (QqQ)	0.033333	0.05	0.04	c
048	0.144	0.014	98	LC-MS (QqQ)	0.000143	0.38	0.64	b
049	0.20	7	0.91	LC-MS (QqQ)	7.692308	2.09	0.01	c
050	0.13	0.013	2	LC-MS (QqQ)	0.0065	-0.04	-0.07	b
051	0.124	0.034	2.3	LC-MS (QqQ)	0.014783	-0.23	-0.30	b
052	0.15	0.08	2	LC-MS (QqQ)	0.04	0.57	0.42	c
055	0.11	0.055	2	LC-MS (QqQ)	0.0275	-0.65	-0.63	a
056	0.129	0.039	2	LC-MS (QqQ)	0.0195	-0.07	-0.09	b
058	0.135	0.068	2	LC-MS (QqQ)	0.034	0.11	0.09	c
060	0.12	0.037	2	LC-MS (QqQ)	0.0185	-0.35	-0.42	b
061	0.126	0.02092	2	LC-MS (QqQ)	0.01046	-0.16	-0.24	b
063	0.05	0	0	LC-MS (QqQ)	0	-2.48	-4.11	b
067	< 0.02			GC-MS (QqQ)				
068	0.102	0.04	2	LC-MS (QqQ)	0.02	-0.89	-1.05	a
069	0.14	0.07	2	LC-MS (QqQ)	0.035	0.26	0.21	c
072	0.108	0.001	2	LC-MS (QqQ)	0.0005	-0.71	-1.18	b
073	0.13	0.02	2		0.01	-0.04	-0.06	b
074	0.182	0.021	2	UPLC-MS/MS	0.0105	1.54	2.26	b
075	0.12	0.06	2	GC-MS (Q)	0.03	-0.35	-0.32	a
077	0.093	0.5	2	LC-MS (QqQ)	0.25	-1.17	-0.15	c
079	0.145	0.02	2	GC-MS (Q)	0.01	0.41	0.61	b
081	0.172	0.052	2	LC-MS (QqQ)	0.026	1.24	1.24	a
082	0.105	0.0525	2	LC-MS (QqQ)	0.02625	-0.80	-0.80	a
083	0.14	0.025	2	LC-MS (QqQ)	0.0125	0.26	0.37	b
085	0.129	0.055	2	LC-MS (QqQ)	0.0275	-0.07	-0.07	a
086	0.1	0.03	2	LC-MS (Q)	0.015	-0.96	-1.26	b
087	0.132	0.008	2	LC-MS(Q ; QqQ))	0.004	0.02	0.03	b

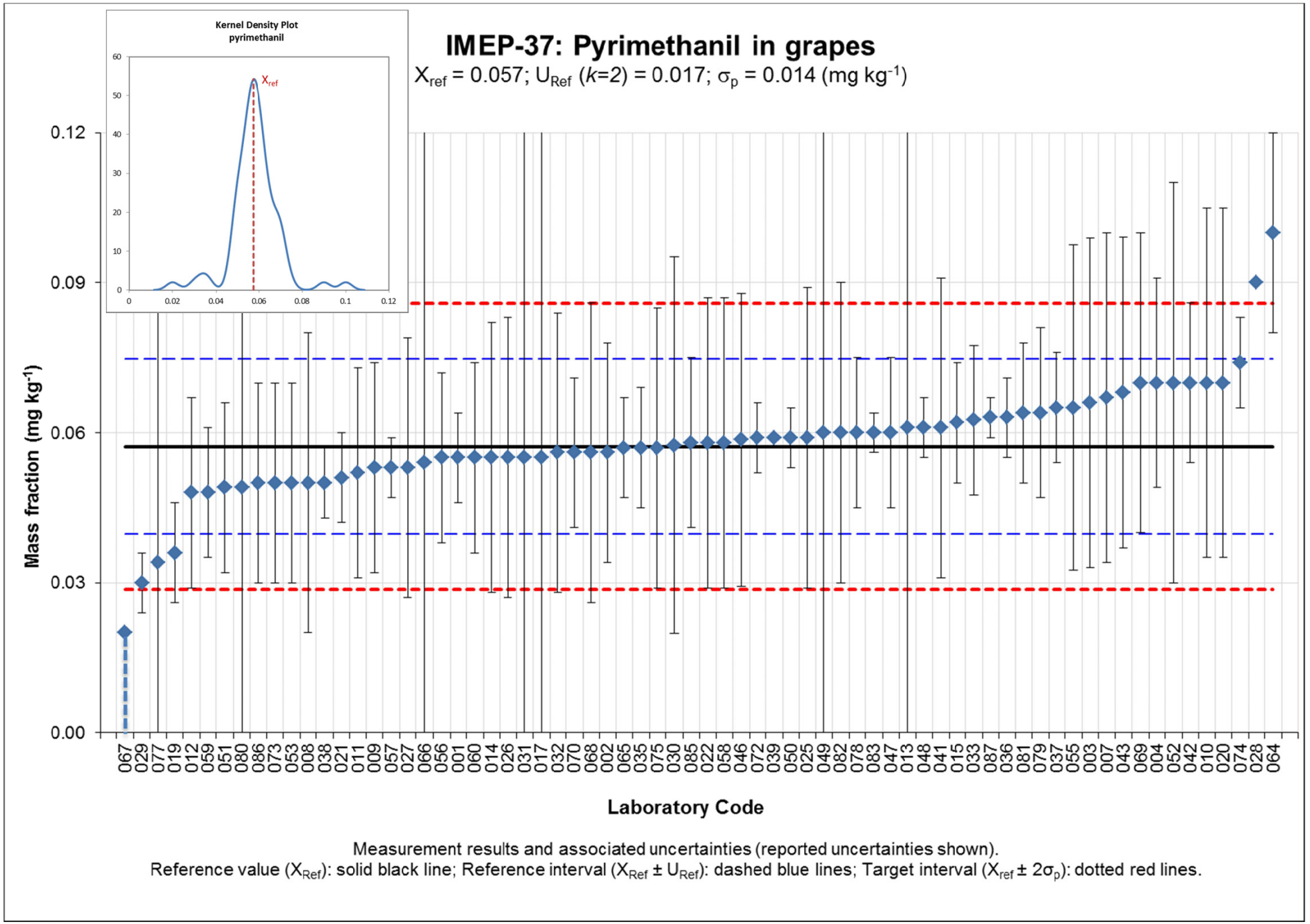


Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 27: Results for Pyrimethanil

X_{ref} = 0.057; U_{Ref} (*k=2*) = 0.017; $\hat{\sigma}$ = 0.014 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	0.055	0.009	2	GC-MS (QqQ)	0.0045	-0.16	-0.23	b
002	0.056	0.022	0.038	GC-MS (QqQ)	0.578947	-0.09	0.00	c
003	0.066	0.033	80.5	LC-MS (QqQ)	0.00041	0.61	1.00	b
004	0.07	0.021	2	GC-MS (QqQ)	0.0105	0.89	0.93	a
007	0.067	0.033	1	GC-MS (QqQ)	0.033	0.68	0.29	c
008	0.05	0.03	2	GC-MS (QqQ)	0.015	-0.51	-0.42	c
009	0.053	0.021	2	GC-MS (Q)	0.0105	-0.30	-0.31	a
010	0.07	0.035	2	GC-MS (QqQ)	0.0175	0.89	0.65	c
011	0.052	0.021	74	GC-MS (QqQ)	0.000284	-0.37	-0.60	b
012	0.048	0.019	2	LC-MS (QqQ)	0.0095	-0.65	-0.72	a
013	0.061	21	2	GC-MS (Q)	10.5	0.26	0.00	c
014	0.055	0.027	2	GC-MS (QqQ)	0.0135	-0.15788	-0.14053	a
015	0.062	0.012	2	GC-MS (Q)	0.006	0.33	0.45	b
017	0.055	30	2	GC-MS (Q)	15	-0.16	0.00	c
019	0.036	0.01	2	LC-MS (QqQ)	0.005	-1.49	-2.11	b
020	0.07	0.035	2	LC-MS (QqQ)	0.0175	0.89	0.65	c
021	0.051	0.009	2	LC-MS (QqQ)	0.0045	-0.44	-0.64	b
022	0.058	0.029	2	LC-MS (QqQ)	0.0145	0.05	0.04	c
025	0.059	0.03	2	GC-MS (Q)	0.015	0.12	0.10	c
026	0.055	0.028	2	GC-MS (IT)	0.014	-0.16	-0.14	a
027	0.053	0.026	2	LC-MS (QqQ)	0.013	-0.30	-0.27	a
028	0.09	0	0	LC-MS (QqQ)	0	2.29	3.75	b
029	0.03	0.006	2	LC-MS (QqQ)	0.003	-1.90	-2.95	b
030	0.0575	0.0377	2	GC-MS (QqQ)	0.01885	0.02	0.01	c
031	0.055	25	2	GC-MS (QqQ)	12.5	-0.16	0.00	c
032	0.056	0.028	2	LC-MS (QqQ)	0.014	-0.09	-0.08	a
033	0.0625	0.015	1	GC-MS (QqQ)	0.015	0.37	0.30	c
035	0.057	0.012	2	GC-MS (QqQ)	0.006	-0.02	-0.02	b
036	0.063	0.008	2	GC-MS (QqQ)	0.004	0.40	0.60	b
037	0.065	0.011	2	GC-MS (Q)	0.0055	0.54	0.75	b
038	0.05	0.007	2	GC-MS (Q)	0.0035	-0.51	-0.77	b
039	0.059	0	0	LC-MS (QqQ)	0	0.12	0.20	b
041	0.061	0.03	2	GC-MS (QqQ)	0.015	0.261264	0.215435	c
042	0.07	0.016	2	GC-MS (QqQ)	0.008	0.89	1.08	b
043	0.068	0.03107	2	GC-MS (TOF)	0.015535	0.75	0.60	c
046	0.0586	0.0293	2	LC-MS (QqQ)	0.01465	0.09	0.08	c
047	0.06	0.015	0.96	GC-MS (Q)	0.015625	0.19	0.15	c
048	0.061	0.006	93	LC-MS (QqQ)	6.45E-05	0.26	0.43	b
049	0.06	3	1.14	LC-MS (QqQ)	2.631579	0.19	0.00	c
050	0.059	0.006	2	GC-MS (Q)	0.003	0.12	0.19	b
051	0.049	0.017	2.3	LC-MS (QqQ)	0.007391	-0.58	-0.72	b
052	0.07	0.04	2	GC-MS (QqQ)	0.02	0.89	0.58	c
053	0.05	0.02	2	GC-MS (TOF)	0.01	-0.51	-0.55	a
055	0.065	0.0325	2	GC-MS (QqQ)	0.01625	0.54	0.42	c
056	0.055	0.017	2	LC-MS (QqQ)	0.0085	-0.16	-0.19	b
057	0.053	0.006	2	GC-MS	0.003	-0.30	-0.46	b
058	0.058	0.029	2	LC-MS (QqQ)	0.0145	0.05	0.04	c
059	0.048	0.013	2	GC-NPD	0.0065	-0.65	-0.85	b
060	0.055	0.019	2	GC-MS (QqQ)	0.0095	-0.16	-0.18	a
064	0.1	0.02	2	GC-MS (IT)	0.01	2.99	3.22	a
065	0.057	0.01	2	GC-MS (Q)	0.005	-0.02	-0.03	b
066	0.054	50	2	GC-MS (QqQ)	25	-0.23	0.00	c
067	< 0.02			GC-MS (QqQ)				
068	0.056	0.03	2	GC-MS (Q)	0.015	-0.09	-0.07	c
069	0.07	0.03	2	GC-MS (Q)	0.015	0.89	0.73	c
070	0.056	0.015	2	LC-MS (QqQ)	0.0075	-0.09	-0.11	b
072	0.059	0.007	2	GC-MS (QqQ)	0.0035	0.12	0.18	b
073	0.05	0.02	2		0.01	-0.51	-0.55	a
074	0.074	0.0091	2	UPLC-MS/MS	0.00455	1.17	1.70	b
075	0.057	0.028	2	GC-MS (Q)	0.014	-0.02	-0.02	a
077	0.034	0.5	2	GC-MS (QqQ)	0.25	-1.62	-0.09	c
078	0.06	0.015	2	GC-MS (Q)	0.0075	0.19	0.24	b
079	0.064	0.017	2	GC-MS (Q)	0.0085	0.47	0.55	b
080	0.049	0.218	2	GC-MS	0.109	-0.58	-0.08	c
081	0.064	0.014	2	GC-MS (Q)	0.007	0.47	0.60	b
082	0.06	0.03	2	LC-MS (QqQ)	0.015	0.19	0.16	c
083	0.06	0.004	2	LC-MS (QqQ)	0.002	0.19	0.31	b
085	0.058	0.017	2	GC-MS (QqQ)	0.0085	0.05	0.06	b
086	0.05	0.02	2	GC-MS (Q)	0.01	-0.51	-0.55	a
087	0.063	0.004	2	LC-MS(Q ; QqQ)	0.002	0.40	0.64	b

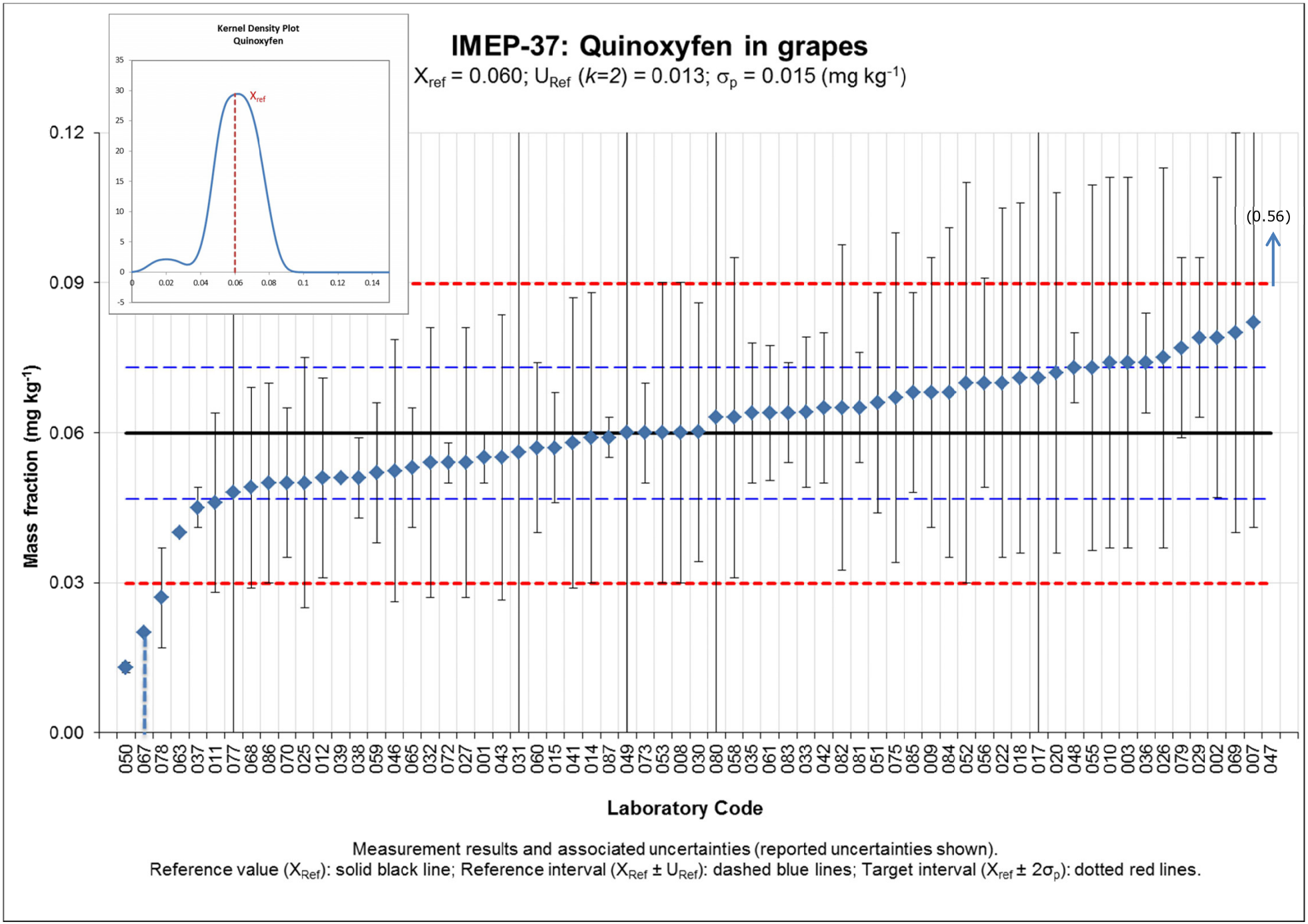


Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 28: Results for Quinoxyfen

X_{ref} = 0.060; U_{Ref} (*k=2*) = 0.013; $\hat{\sigma}$ = 0.015 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	0.055	0.005	2	GC-MS (QqQ)	0.0025	-0.33	-0.70	b
002	0.079	0.032	0.018	LC-MS (QqQ)	1.777778	1.28	0.01	c
003	0.074	0.037	80.5	LC-MS (QqQ)	0.00046	0.94	2.14	b
007	0.082	0.041	1	LC-MS (QqQ)	0.041	1.48	0.53	c
008	0.06	0.03	2	GC-MS (QqQ)	0.015	0.01	0.01	c
009	0.068	0.027	2	GC-MS (Q)	0.0135	0.54	0.54	a
010	0.074	0.037	2	GC-MS (QqQ)	0.0185	0.94	0.72	c
011	0.046	0.018	72	GC-MS (QqQ)	0.00025	-0.93	-2.11	b
012	0.051	0.02	2	GC-MS (QqQ)	0.01	-0.59432	-0.74391	a
014	0.059	0.029	2	LC-MS (QqQ)	0.0145	-0.06	-0.06	a
015	0.057	0.011	2	GC-MS (Q)	0.0055	-0.19	-0.34	b
017	0.071	30	2	GC-MS (Q)	15	0.74	0.00	c
018	0.071	0.035	2	LC-MS (IT)	0.0175	0.74	0.59	c
020	0.072	0.036	2	LC-MS (QqQ)	0.018	0.81	0.63	c
022	0.07	0.035	2	LC-MS (QqQ)	0.0175	0.67	0.54	c
025	0.05	0.025	2	LC-MS (QqQ)	0.0125	-0.66	-0.70	a
026	0.075	0.038	2	GC-MS (IT)	0.019	1.01	0.75	c
027	0.054	0.027	2	LC-MS (QqQ)	0.0135	-0.39	-0.39	a
029	0.079	0.016	2	LC-MS (QqQ)	0.008	1.28	1.85	a
030	0.0601	0.0259	2	GC-MS (QqQ)	0.01295	0.01	0.01	a
031	0.056	25	2	GC-MS (QqQ)	12.5	-0.26	0.00	c
032	0.054	0.027	2	LC-MS (QqQ)	0.0135	-0.39	-0.39	a
033	0.0641	0.015	1	GC-MS (QqQ)	0.015	0.28	0.26	c
035	0.064	0.014	2	LC-MS (QqQ)	0.007	0.27379	0.427149	a
036	0.074	0.01	2	LC-MS (QqQ)	0.005	0.94	1.71	b
037	0.045	0.004	2	GC/ECD	0.002	-0.99	-2.17	b
038	0.051	0.008	2	GC-MS (Q)	0.004	-0.59	-1.16	b
039	0.051	0	0	LC-MS (QqQ)	0	-0.59	-1.36	b
041	0.058	0.029	2	GC-MS (QqQ)	0.0145	-0.13	-0.12	a
042	0.065	0.015	2	GC-MS (QqQ)	0.0075	0.34	0.51	a
043	0.055	0.0285	2	GC-MS (TOF)	0.01425	-0.33	-0.31	a
046	0.0524	0.0262	2	GC-MS (Q)	0.0131	-0.50	-0.51	a
047	0.56	0.014	0.87	GC-MS (Q)	0.016092	33.40	28.77	c
048	0.073	0.007	97	LC-MS (QqQ)	7.22E-05	0.87	1.99	b
049	0.06	20	0.97	GC-MS (Q)	20.61856	0.01	0.00	c
050	0.013	0.001	2	GC-MS (Q)	0.0005	-3.13	-7.12	b
051	0.066	0.022	2.3	LC-MS (QqQ)	0.009565	0.41	0.53	a
052	0.07	0.04	2	LC-MS (QqQ)	0.02	0.67	0.48	c
053	0.06	0.03	2	GC-MS (TOF)	0.015	0.01	0.01	c
055	0.073	0.0365	2	GC-MS (QqQ)	0.01825	0.87	0.68	c
056	0.07	0.021	2	LC-MS (QqQ)	0.0105	0.67	0.82	a
058	0.063	0.032	2	LC-MS (QqQ)	0.016	0.21	0.18	c
059	0.052	0.014	2	GC-ECD/NPD	0.007	-0.53	-0.82	a
060	0.057	0.017	2	GC-MS (QqQ)	0.0085	-0.19	-0.27	a
061	0.064	0.0135	2	LC-MS (QqQ)	0.00675	0.27	0.44	a
063	0.04	0	0	LC-MS (QqQ)	0	-1.33	-3.03	b
065	0.053	0.012	2	GC-MS (Q)	0.006	-0.46	-0.78	b
067	< 0.02			GC-MS (QqQ)				
068	0.049	0.02	2	GC-MS (Q)	0.01	-0.73	-0.91	a
069	0.08	0.04	2	GC-MS (Q)	0.02	1.34	0.95	c
070	0.05	0.015	2	LC-MS (QqQ)	0.0075	-0.66	-0.99	a
072	0.054	0.004	2	LC-MS (QqQ)	0.002	-0.39	-0.86	b
073	0.06	0.01	2		0.005	0.01	0.01	b
075	0.067	0.033	2	GC-MS (Q)	0.0165	0.47	0.40	c
077	0.048	0.5	2	LC-MS (QqQ)	0.25	-0.79	-0.05	c
078	0.027	0.01	2	GC-MS (Q)	0.005	-2.20	-3.99	b
079	0.077	0.018	2	GC-MS (Q)	0.009	1.14	1.53	a
080	0.063	0.136	2	GC-MS	0.068	0.21	0.05	c
081	0.065	0.011	2	GC-MS (Q)	0.0055	0.34	0.60	b
082	0.065	0.0325	2	GC-MS (QqQ)	0.01625	0.34	0.29	c
083	0.064	0.01	2	LC-MS (QqQ)	0.005	0.27	0.50	b
084	0.068	0.033	2	GC-ECD	0.0165	0.54	0.46	c
085	0.068	0.02	2	GC-MS (QqQ)	0.01	0.54	0.68	a
086	0.05	0.02	2	GC-MS (Q)	0.01	-0.66	-0.83	a
087	0.059	0.004	2	LC-MS(Q ; QqQ)	0.002	-0.06	-0.13	b

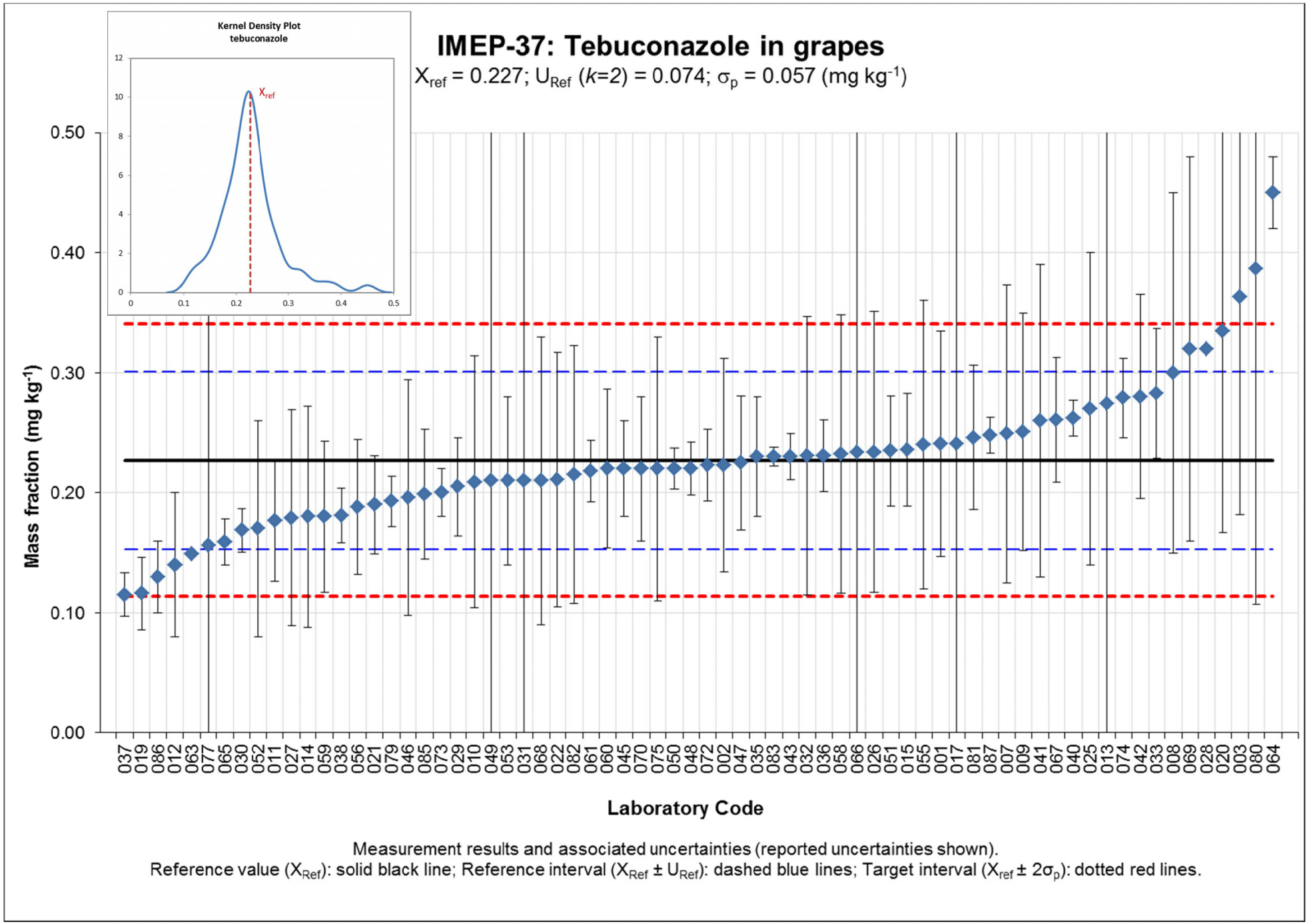


Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 29: Results for Tebuconazole

X_{ref} = 0.227; U_{Ref} (k=2) = 0.074; $\hat{\sigma}$ = 0.057 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}	z-score	ζ-score	uncert.
001	0.241	0.094	2	GC-MS (QqQ)	0.047	0.25	0.23	a
002	0.223	0.089	0.016	GC-MS (QqQ)	5.5625	-0.07	0.00	c
003	0.363	0.181	80	LC-MS (QqQ)	0.002263	2.40	3.66	b
007	0.249	0.124	1	LC-MS (QqQ)	0.124	0.39	0.17	c
008	0.3	0.15	2	LC-MS (QqQ)	0.075	1.29	0.87	c
009	0.251	0.099	2	GC-MS (Q)	0.0495	0.42	0.39	a
010	0.209	0.105	2	GC-MS (QqQ)	0.0525	-0.32	-0.28	a
011	0.177	0.051	78	GC-MS (QqQ)	0.000654	-0.88	-1.35	b
012	0.14	0.06	2	LC-MS (QqQ)	0.03	-1.53	-1.82	b
013	0.274	20	2	GC-MS (Q)	10	0.83	0.00	c
014	0.18	0.092	2	LC-MS (QqQ)	0.046	-0.83	-0.79	a
015	0.236	0.047	2	GC-MS (Q)	0.0235	0.16	0.21	b
017	0.241	30	2	GC-MS (Q)	15	0.25	0.00	c
019	0.116	0.03	2	LC-MS (QqQ)	0.015	-1.96	-2.77	b
020	0.335	0.168	2	LC-MS (QqQ)	0.084	1.90	1.18	c
021	0.19	0.041	2	LC-MS (QqQ)	0.0205	-0.65	-0.87	b
022	0.211	0.106	2	LC-MS (QqQ)	0.053	-0.28	-0.25	a
025	0.27	0.13	2	LC-MS (QqQ)	0.065	0.76	0.57	c
026	0.234	0.117	2	GC-MS (IT)	0.0585	0.12	0.10	c
027	0.179	0.09	2	LC-MS (QqQ)	0.045	-0.84554	-0.82245	a
028	0.32	0	0	LC-MS (QqQ)	0	1.64	2.51	b
029	0.205	0.041	2	LC-MS (QqQ)	0.0205	-0.39	-0.52	b
030	0.1686	0.018	2	LC-MS (QqQ)	0.009	-1.03	-1.53	b
031	0.21	25	2	GC-MS (QqQ)	12.5	-0.30	0.00	c
032	0.231	0.116	2	LC-MS (QqQ)	0.058	0.07	0.06	c
033	0.283	0.054	1	LC-MS (QqQ)	0.054	0.99	0.85	a
035	0.23	0.05	2	GC-MS (QqQ)	0.025	0.05	0.07	b
036	0.231	0.03	2	LC-MS (QqQ)	0.015	0.07	0.10	b
037	0.115	0.018	2	GC-MS (Q)	0.009	-1.97	-2.93	b
038	0.181	0.023	2	GC-MS (Q)	0.0115	-0.81	-1.18	b
040	0.262	0.0148	2	GC-MS (Q)	0.0074	0.62	0.93	b
041	0.26	0.13	2	LC-MS (QqQ)	0.065	0.58	0.44	c
042	0.28	0.085	2	GC-MS (QqQ)	0.0425	0.93	0.94	a
043	0.23	0.01922	2	GC-MS (TOF)	0.00961	0.05	0.08	b
045	0.22	0.04	2	GC-MS (EI Quadrapole)	0.02	-0.12301	-0.16552	b
046	0.196	0.098	2	LC-MS (QqQ)	0.049	-0.55	-0.50	a
047	0.225	0.056	0.98	GC-MS (Q)	0.057143	-0.03	-0.03	c
048	0.22	0.022	98	LC-MS (QqQ)	0.000224	-0.12	-0.19	b
049	0.21	20	1.17	GC-MS (Q)	17.09402	-0.30	0.00	c
050	0.22	0.017	2	GC-MS (Q)	0.0085	-0.12	-0.18	b
051	0.235	0.046	2.3	LC-MS (QqQ)	0.02	0.14	0.19	b
052	0.17	0.09	2	GC-MS (QqQ)	0.045	-1.00	-0.98	a
053	0.21	0.07	2	GC-MS (TOF)	0.035	-0.30	-0.33	b
055	0.24	0.12	2	GC-MS (QqQ)	0.06	0.23	0.18	c
056	0.188	0.056	2	LC-MS (QqQ)	0.028	-0.69	-0.84	b
058	0.232	0.116	2	LC-MS (QqQ)	0.058	0.09	0.07	c
059	0.18	0.063	2	GC-NPD	0.0315	-0.83	-0.96	b
060	0.22	0.066	2	LC-MS (QqQ)	0.033	-0.12	-0.14	b
061	0.218	0.02575	2	LC-MS (QqQ)	0.012875	-0.16	-0.23	b
063	0.149	0	0	LC-MS (QqQ)	0	-1.37	-2.10	b
064	0.45	0.03	2	GC-MS (IT)	0.015	3.93	5.57	b
065	0.159	0.019	2	GC-MS (Q)	0.0095	-1.20	-1.77	b
066	0.234	50	2	GC-MS (QqQ)	25	0.12	0.00	c
067	0.261	0.052	2	GC-MS (QqQ)	0.026	0.60	0.75	b
068	0.21	0.12	2	GC-MS (Q)	0.06	-0.30	-0.24	c
069	0.32	0.16	2	GC-MS (Q)	0.08	1.64	1.05	c
070	0.22	0.06	2	LC-MS (QqQ)	0.03	-0.12	-0.15	b
072	0.223	0.03	2	GC-MS (QqQ)	0.015	-0.07	-0.10	b
073	0.2	0.02	2		0.01	-0.48	-0.70	b
074	0.279	0.033	2	UPLC-MS/MS	0.0165	0.92	1.28	b
075	0.22	0.11	2	GC-MS (Q)	0.055	-0.12	-0.11	a
077	0.156	0.5	2	LC-MS (QqQ)	0.25	-1.25	-0.28	c
079	0.193	0.021	2	GC-MS (Q)	0.0105	-0.60	-0.88	b
080	0.387	0.28	2	GC-MS	0.14	2.82	1.10	c
081	0.246	0.06	2	GC-MS (Q)	0.03	0.34	0.40	b
082	0.215	0.1075	2	LC-MS (QqQ)	0.05375	-0.21	-0.18	a
083	0.23	0.008	2	LC-MS (QqQ)	0.004	0.05	0.08	b
084								
085	0.199	0.054	2	LC-MS (QqQ)	0.027	-0.49	-0.61	b
086	0.13	0.03	2	LC-MS (Q)	0.015	-1.71	-2.42	b
087	0.248	0.015	2	LC-MS(Q ; QqQ)	0.0075	0.37	0.55	b

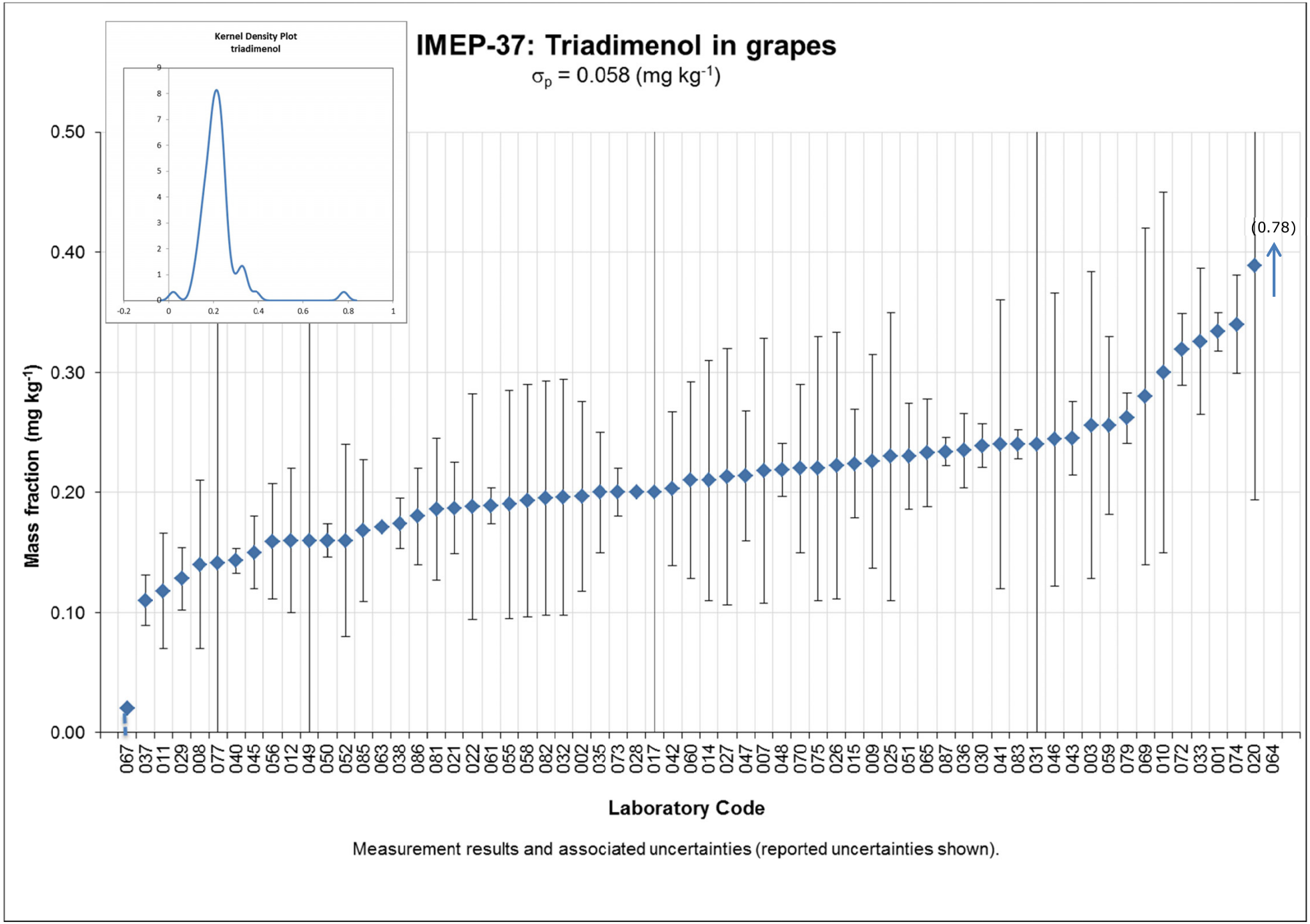


Measurement results and associated uncertainties (reported uncertainties shown).
Reference value (X_{Ref}): solid black line; Reference interval ($X_{Ref} \pm U_{Ref}$): dashed blue lines; Target interval ($X_{ref} \pm 2\sigma_p$): dotted red lines.

Annex 30: Results for Triadimenol

$\hat{\sigma}$ = 0.058 (mg kg^{-1})

Lab Code	X_{lab}	U_{lab}	k	Technique	u_{lab}
001	0.334	0.016	2	GC-MS (QqQ)	0.008
002	0.197	0.079	0.014	GC-MS (QqQ)	5.642857
003	0.256	0.128	73.5	LC-MS (QqQ)	0.001741
007	0.218	0.11	1	LC-MS (QqQ)	0.11
008	0.14	0.07	2	GC-MS (QqQ)	0.035
009	0.226	0.089	2	GC-MS (Q)	0.0445
010	0.3	0.15	2	LC-MS (QqQ)	0.075
011	0.118	0.048	97	LC-MS (QqQ)	0.000495
012	0.16	0.06	2	LC-MS (QqQ)	0.03
014	0.21	0.1	2	LC-MS (QqQ)	0.05
015	0.224	0.045	2	GC-MS (Q)	0.0225
017	0.2	30	2	GC-MS (Q)	15
020	0.389	0.195	2	LC-MS (QqQ)	0.0975
021	0.187	0.038	2	LC-MS (QqQ)	0.019
022	0.188	0.094	2	LC-MS (QqQ)	0.047
025	0.23	0.12	2	LC-MS (QqQ)	0.06
026	0.222	0.111	2	GC-MS (IT)	0.0555
027	0.213	0.107	2	LC-MS (QqQ)	0.0535
028	0.2	0	0	LC-MS (QqQ)	0
029	0.128	0.026	2	LC-MS (QqQ)	0.013
030	0.239	0.0181	2	LC-MS (QqQ)	0.00905
031	0.24	25	2	GC-MS (QqQ)	12.5
032	0.196	0.098	2	LC-MS (QqQ)	0.049
033	0.3257	0.061	1	GC-MS (QqQ)	0.061
035	0.2	0.05	2	GC-MS (QqQ)	0.025
036	0.235	0.031	2	LC-MS (QqQ)	0.0155
037	0.11	0.021	2	GC-MS (Q)	0.0105
038	0.174	0.021	2	GC-MS (Q)	0.0105
040	0.143	0.0102	2	GC-MS (Q)	0.0051
041	0.24	0.12	2	LC-MS (QqQ)	0.06
042	0.203	0.064	2	GC-MS (QqQ)	0.032
043	0.245	0.03084	2	GC-MS (TOF)	0.01542
045	0.15	0.03	2	GC-MS (Q)	0.015
046	0.244	0.122	2	LC-MS (QqQ)	0.061
047	0.214	0.054	1.02	GC-MS (Q)	0.052941
048	0.219	0.022	99	LC-MS (QqQ)	0.000222
049	0.16	20	1.14	GC-MS (Q)	17.54386
050	0.16	0.014	2	GC-MS (Q)	0.007
051	0.23	0.044	2.3	LC-MS (QqQ)	0.01913
052	0.16	0.08	2	GC-MS (QqQ)	0.04
055	0.19	0.095	2	LC-MS (QqQ)	0.0475
056	0.159	0.048	2	LC-MS (QqQ)	0.024
058	0.193	0.097	2	LC-MS (QqQ)	0.0485
059	0.256	0.074	2	GC-NPD	0.037
060	0.21	0.082	2	LC-MS (QqQ)	0.041
061	0.189	0.01513	2	LC-MS (QqQ)	0.007565
063	0.171	0	0	LC-MS (QqQ)	0
064	0.78	0.03	2	GC-MS (IT)	0.015
065	0.233	0.045	2	GC-MS (Q)	0.0225
067	< 0.02			GC-MS (QqQ)	
069	0.28	0.14	2	GC-MS (Q)	0.07
070	0.22	0.07	2	LC-MS (QqQ)	0.035
072	0.319	0.03	2	GC-MS (QqQ)	0.015
073	0.2	0.02	2		0.01
074	0.34	0.041	2	UPLC-MS/MS	0.0205
075	0.22	0.11	2	GC-MS (Q)	0.055
077	0.141	0.5	2	GC-MS (QqQ)	0.25
079	0.262	0.021	2	GC-MS (Q)	0.0105
081	0.186	0.059	2	LC-MS (QqQ)	0.0295
082	0.195	0.0975	2	GC-MS (QqQ)	0.04875
083	0.24	0.012	2	LC-MS (QqQ)	0.006
085	0.168	0.059	2	GC-MS (QqQ)	0.0295
086	0.18	0.04	2	GC-MS (Q)	0.02
087	0.234	0.012	2	LC-MS(Q ; QqQ)	0.006



Measurement results and associated uncertainties (reported uncertainties shown).

European Commission
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Title: **IMEP-37: Determination of pesticides in grapes. Interlaboratory Comparison Report**

Author(s): Pieter Dehouck, Fernando Cordeiro, Ioannis Fiamegkos, Piotr Robouch, Aneta Cizek-Stroh, Beatriz de la Calle

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Abstract

This report presents the results of a proficiency test exercise (PT) which focussed on the determination of pesticides in grapes in support of Regulation 396/2005/EC of the European Parliament and of the Council on maximum residue levels of pesticides in or on food and feed of plant and animal origin.
Eighty-seven participants from thirty-three different countries registered to the exercise, of which eighty-one reported results. From these eighty-one participants, forty were from EU countries while forty-one were from outside the EU.
The test item was a grapes sample spiked with 20 selected pesticides. The assigned values were obtained as the average of results reported by five expert laboratories having demonstrated experience in the analysis of pesticides in vegetable and fruit matrices. The standard uncertainties related to the assigned values (Uref) were calculated by combining the uncertainty of the characterisation (Uchar) with a contribution for homogeneity (Ubb) and for stability (Ust). Uchar was calculated following the ISO guide 35.
Laboratory results were rated with z- and zeta (ζ-) scores in accordance with ISO 13528 and ISO 17043. The z-score compares the participant's deviation from the reference value with the standard deviation for proficiency assessment (σp) used as common quality criterion, the ζ-score states if the laboratory result agrees with the assigned value within the respective uncertainty. The standard deviation for the proficiency assessment, σp, was set by the advisory board of this PT at 25% for the 20 measured pesticides based on previous experience with similar measurands. Participants were not scored for triadimenol due to the large Uref associated to the assigned value.
According to the results obtained in the frame of the IMEP-37 study, the participants performed satisfactorily for the 19 scored pesticides ranging from 81 % (carbendazim) to 97 % (azoxystrobin, penconazole, pyrimethanil) of satisfactory z-scores. When analysing the results of the group of non-EU countries separately, similar results were obtained. It can be concluded that the performance in this PT is satisfactory for the laboratories world-wide.

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