Ring Test Certified Standard Solutions

(2020)

1. INTRODUCTION

The use of certified standard solutions prepared by external companies leads to important savings in terms of time and laboratory work. However, there is not enough evidence of the quality of these solutions and a poor performance in their preparation can lead to grave mistakes in the quantitation of the analytes and subsequent consequences derived from it.

In 2018, the European Union Reference Laboratory for Pesticide Residues in Fruits and Vegetables (EURL-FV) performed a preliminary Ring Test to assess a range of solutions prepared by four specialized companies, each one containing 30 LC-amenable pesticide standards. The study involved seven European laboratories with a wide experience in the analysis of these contaminants, which analysed aliquots of these solutions. The conclusions reached in the study suggested that, in some cases, the companies might produce flawed solutions in which certain compounds are not at the certified concentration. In addition, a lack of knowledge regarding the properties and incompatibilities of the compounds could be observed in some cases, as demonstrated by the fact that, in most cases, the companies did not oppose to mix together two incompatible compounds (benomyl and its metabolite carbendazim). However, due to the implications of such results, no definitive conclusions were drew from this study and a large-scale monitoring, including more firms and standards, was designed for the future.

The present Ring Test is aimed at extending the preliminary study performed in 2018, including five companies that were requested to prepare a mix -or group of mixes- containing 150 GC and LC-amenable pesticide residues included in the European Union Multi-Annual Control Programme (EU-MACP). The complete list of standards requested to the companies is shown in **Appendix A**. Eight laboratories took part in the analysis of the aliquots. This study was performed in the framework of the EURL-FV working programme for 2019-2020.

2. EXPERIMENTAL

2.1. Test items and laboratories

The present Ring Test was based on the analysis of five certified standard solutions, each one containing up to 150 GC and LC-amenable pesticides included in the scope of the EU-MACP. The solutions were prepared by five external specialised firms, that will be kept confidential, with a certified concentration of 50 or 100 mg/L. After reception in the EURL-FV, the solutions were diluted to 1 mg/L in acetonitrile and stored at -20°C prior to shipment.

A 1-mL aliquot of each solution was sent in amber glass vials sealed with Parafilm to every laboratory participating in the study. These participants were warned that some standard solutions may not contain all the pesticides object of this study and might also contain additional pesticides that were not intended for analysis. They were requested to store the solutions at -20 °C until their pre-treatment and analysis. The participant laboratories are listed below.

European Union Reference Laboratory for Pesticide Residues in Fruits and Vegetables (EURL-FV), Almería, Spain.

Dr. Andrija Štampar. Department of Environmental Protection and Health Ecology-Zagreb, Croatia.

National Center for Technology and Food Safety (CNTA), San Adrián-Navarra, Spain.

APPA Bolzano. Laboratory for analysis and chromatography, Bolzano, Italy.

SGS Cambridge ltd., Cambridge, United Kingdom.

Analytica Alimentaria GmbH, Almería, Spain.

General Chemical State Laboratory (GCSL), Athens, Greece.

Czech Agriculture and Food Inspection Authority (CAFIA), Praha, Czech Republic.

LOVAP NV, Geel, Belgium.

Lower Saxony State Office for Consumer Protection and Food Safety (LAVES), Oldenburg, Germany.

Laboratorio Arbitral Agroalimentario, Madrid, Spain.

Groen Agro Control, Delft, the Netherlands.

Chemical and Veterinary Investigation Office Rhein-Ruhr-Wupper (CVUA RRW), Krefeld, Germany.

Wageningen Food Safety Research (WFSR), Wageningen, the Netherlands.

2.2. Analytical procedure

The procedure followed by each participant was as follows:

1. The test items were delivered by courier on November 23rd 2020 in polystyrene boxes containing dry ice. A confirmation email was sent out the day of the shipment.
2. A 20-fold dilution should be performed to the standard solutions, so that the expected concentration values were 50 µg/L. This dilution was performed following the laboratory´s own procedures and using the appropriate solvents for each analytical technique.
3. Each solution was analysed five times in pure solvent by LC, and following the laboratory´s own procedures by GC (recommended injection in tomato matrix). The sequence included the laboratory's own standard solution following the order: Lab std. mix, A, B, C, D, E, Lab std. mix, A, B, C, D, E… A fresh standard solution was recommended for the quantification, and the participants were requested to indicate the preparation date.
4. The areas of the compound signals for each injection were reported in a template (Excel document) sent out by the EURL-FV in the confirmation email. This template was designed to calculate automatically the concentration of each standard in the test items using the laboratory's own standard solution.
5. Laboratories were requested to submit their results between December 2020 and January 2021.

2.3. Data treatment

The data treatment was performed in the EURL-FV using the reporting templates provided by the participants. The statistical analysis of the results was performed at two levels: intra-laboratory and inter-laboratory results.

Intra-laboratory data treatment

As described above, the participant laboratories analyzed five replicates of each solution, in addition to five replicates of their own standards. The first step in the data pre-treatment was to calculate the average response and the relative standard deviation (RSD) of each individual compound in every commercial solution and the laboratory's standard.

- RSD value higher than 25 %: the compound's response in the solution was not considered consistent enough to be included in the analysis. The result of the laboratory was removed.

- RSD value in the range of 15-25 %: the individual responses were revised manually. In the cases where there was only one differing result (at least 20 % different from the rest), it was removed and the RSD was re-calculated. If the RSD was still in the range of 15-25 %, or if any value could be removed, the average response was included in the subsequent steps, but considered as a suspicious result (*see section Inter-laboratory data treatment*).
- RSD value lower than 15 %: the average response was included in the subsequent analytical steps without further consideration.

The average responses obtained this way were employed to calculate the concentration of each compound in the commercial solutions, using the laboratory's own standard as a reference.

Inter-laboratory data treatment

For each standard and each solution, up to 14 results were obtained (one result per laboratory). The average concentration was obtained from the mean of the results reported by each laboratory. Previously, the mean and the median had been compared, and the difference between them was lower than 5 %. Therefore, the results proved to fit into a Gaussian distribution, and the mean could be considered as an estimator of the population. The individual results were not rounded for the calculation of the mean. The inter-laboratory RSD was calculated for each set of up to 14 results, and the following criteria were applied:

- Inter-laboratory RSD higher than 20 %: the concentrations reported by each laboratory were revised manually. If a maximum of two differing results (at least 20 % different from the rest) were found, they were considered to arise from mistakes in the laboratories' quantification and they were removed. However:
  - If there was a suspicious concentration in the set outside the range of the remaining concentrations, it was removed in order to reduce the inter-laboratory RSD.
  - If removing an individual concentration resulted in a change in the status (acceptable/not acceptable) of the pesticide in the solution, it was not removed. However, if the difference with the rest of results was higher than 50 % (i.e. only one remarkably high or remarkably low concentration), it was removed.
- Inter-laboratory RSD lower than 20 %: the average concentration reported by all laboratories was calculated.

3. RESULTS AND DISCUSSION: MANUFACTURING OF SOLUTIONS

3.1. General characteristics

The companies that took part in the present study were Agilent, Scharlab, LabService Analytica, LGC and LabStandard®, which were requested to prepare a mix containing 150 GC and LC-amenable pesticide residues (see **Appendix A**) at 50 mg/L and in acetonitrile solvent, when possible. In all cases, the companies split the original 150-standard list into a number of sub-mixes. Some of the mixes provided were commercial solutions with a predefined composition –i.e. in some cases, more pesticide residues than the original list were included– and, in other cases, only custom mixes were prepared.

Each company was assigned a random letter A-E to ensure they remain anonymous. **Table 1** summarizes the distribution and main characteristics of the mixes initially offered by the companies. The number of sub-mixes ranged between 8 and 15, combining custom-made and commercial predefined solutions. Most companies used only acetonitrile as the solvent, but company D employed acetone in four of the provided solutions. Companies A, B and E included all of the requested pesticide standards in their mixes, whereas company C offered only 137 of the standards, and company D, 145. As mentioned above, in some cases, the total number of pesticide standards was higher than 150 due to the inclusion –in the commercial mixes– of additional standards. These were not considered nor included in the present study, and the analytical laboratories were requested to ignore them.

Table 1. Main properties of the mixes offered by the companies

Company	A	B	C	D	E
No. of solutions (total)	**8**	**9**	**10**	**15**	**9**
Commercial solutions	*0*	*0*	*7*	*14*	*0*
Custom solutions	*8*	*9*	*3*	*1*	*9*
Solvent/s	**AcN**	**AcN**	**AcN**	**AcN, Acetone**	**AcN**
Concentration (mg/kg)	**50**	**50**	**100**	**50**	**50**
No. of pesticides*	**150***	**150**	**137**	**145**	**150**

*Pesticides included in the original composition

The final composition of the mixes was in some cases slightly different from the one shown in **Table 1** due to different causes that will be discussed in the next section.

The preparation and shipment of solutions by the companies took between one and three months. In some cases, measures were taken by the companies to ensure the integrity of the mixes –tracking numbers provided and cold packs included. However, in some cases, the shipment took place without notice to the laboratory and in boxes at room temperature, even though the certificates of analysis provided by the own company specified the need of storage at low temperature.

3.2. Deviations from the original compositions

The communication with the companies was performed by email. During the course of these communications, several basic stages took place:

1. Laboratory. Initial request of quotation, submission of the list of 150 standards to be included (with the corresponding CAS number), specification of the solvent and concentration.
2. Company. Response and general specifications of their offer, specifying (when applicable) the list of pesticides not included in their mixes due to availability or technical concerns. In some cases, the distribution of standards in the different mixes was also provided.
3. Laboratory. Acceptance of the quotation and formal request for the mixes.
4. Company. Submission of the final composition and/or distribution of the mixes.

Some companies provided the final distribution list prior to the acceptance of the quotation, whereas others did not provide this information until the official order or even after the shipment of the solutions. A detailed exam of these lists revealed the presence of some issues that were subsequently discussed with each company.

- Company A initially included the compound tefluthrin in the composition of two custom mixes. After notification by the laboratory, the duplicate was removed from one of the solutions.
- Company D also duplicated the compounds imidacloprid and spinetoram. This company did not provide a list with the composition of the custom mix prior to its shipment, and this solution contained both compounds even though they were already present in the commercial mixes. After notification, the duplicate imidacloprid was removed from the custom solution and a new custom solution was sent to the EURL-FV. Nevertheless, spinetoram was still included in the new custom solution and, although the company was notified of this second mistake, a new custom mix was not prepared due to a lack of time and spinetoram was not included in the present study.
- A different company confirmed the pesticide standards that would be included in the mixes but, in the final compositions, any pyrethroid was present. After notification, a new mix including all pyrethroid standards was included. Due to external causes, this company was finally not selected for the study.

There is a different source of deviations from the original composition, unnoticeable until the reception in the laboratory: the shipment of a non-requested solution instead of the requested one. This happened with Company A, which sent a solution whose code differed in one number with regard to the specified in the quotation –e.g. if the code of the solution was 204, the solution received in the laboratory was the 214 (*not real* *numbers*). The received solution did not contain any of the standards requested and included in the quotation and, therefore, 27 pesticide standards were missing and not evaluated from this company.

3.3. Financial evaluation

A total of ten companies were contacted and sent a quotation for the requested list of pesticides. The average price of the standard solutions for the ten companies was 6721 €; however, without the strong contribution of company 9 (quotation of 17474 €), the average price drops to 5527 €. The selection of companies for the present study was performed in such a way that allowed maximizing the number of participants within the budget of the activity (**Figure 1**).

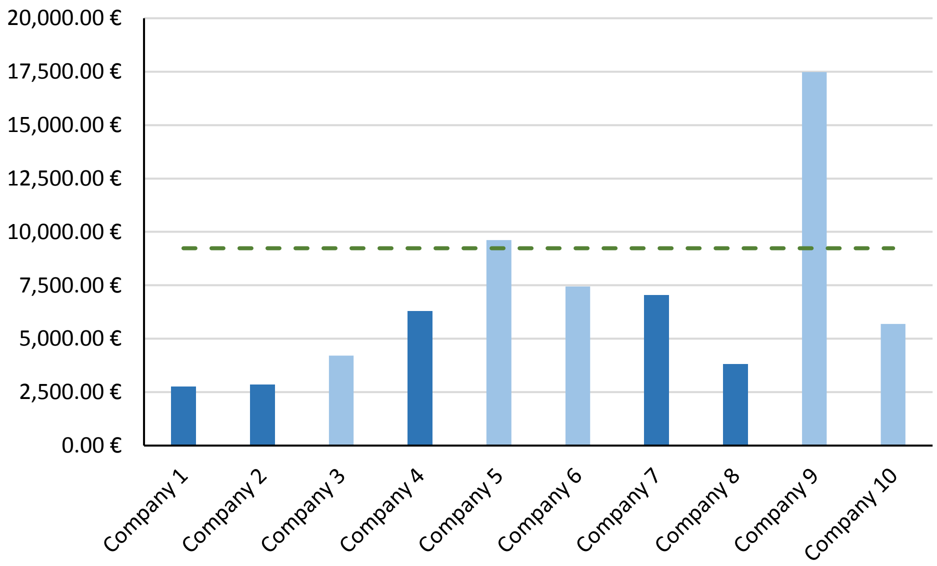

Figure 1. Quotation provided by the ten companies contacted by the EURL-FV. The deep blue bars represent the companies that were finally selected for the study. The dashed horizontal line represents the total price of the 150 if they were purchased individually as pure standards.

During the financial evaluation, the price of purchasing the individual standards was also calculated through a search on two of the main chemical suppliers: Sigma-Aldrich (Merck) and LGC Standards. The estimated price of the individual standards was 9235 € (dashed line in **figure 1**). As can be seen, the purchase of individual standards involves in most cases a higher cost than the acquisition of custom standard solutions (the exceptions being companies 5 and 9). The purchase of these individual standards also entails the need of preparing stock solutions and mixes in the own laboratory, resulting in additional time and expenses. However, the individual pure standards can usually be employed for the preparation of several solutions due to the higher amount of substance, and their expiry date is in most cases higher than the same standards in solution. This could also result in long-time savings.

4. RESULTS AND DISCUSSION: ASSESSMENT OF THE SOLUTIONS

4.1. General performance

Only those pesticides that showed consistent results in all cases were used for the general assessment of the solutions. With that purpose, a maximum inter-laboratory RSD of 20 % was stablished to ensure that most participants reported very similar concentrations. Only two pesticides did not fulfill this requirement: dichlorvos in solution E (inter-laboratory RSD 23 %) and formetanate (30-31 % inter-laboratory RSD). Dichlorvos was, however, included in the general assessment of the solutions, as will be discussed in the following section. The calculated concentrations and inter-laboratory RSDs for all compounds can be found in **Appendix B**.

To identify the acceptable results, a maximum deviation of 10 % with regard to the certified concentration was set. Therefore, all concentrations between 45 and 55 mg/L were considered as "correct". However, an extended range covering concentrations higher than 40 mg/L or lower than 60 mg/L was set as "questionable" concentrations. All concentrations outside the 40-60 mg/L range were considered as "unacceptable".

As can be seen in **figure 2**, there are significant differences among the solutions provided by the companies: except for solution B, all solutions contained at least one pesticide at a level that was extremely different to the certified concentration (i. e. lower than 40 mg/L or higher than 60 mg/L). In solution B, there were only two pesticides outside the acceptable range and with "questionable" values (oxydemeton-methyl and tebuconazole, 56 and 57 mg/L respectively). There are also differences in terms of the dispersion of the results, with solutions A and E showing a remarkably high dispersion in the average concentration of the standards.

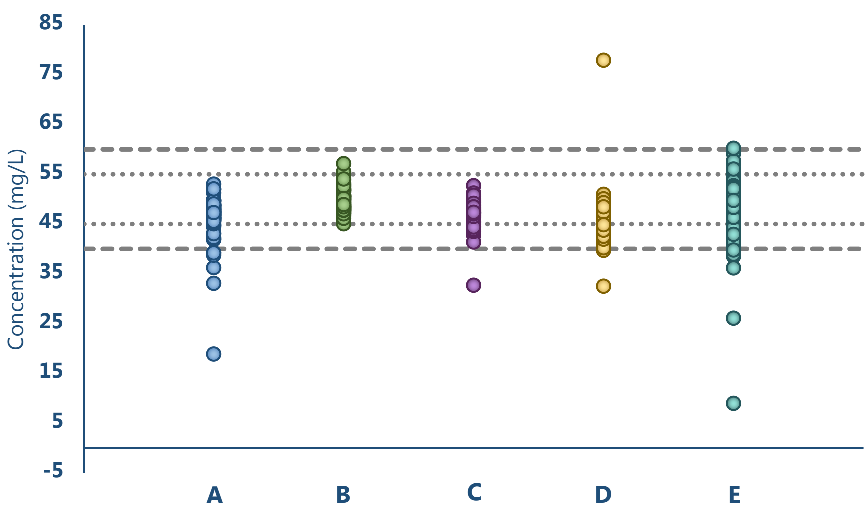

Figure 2. Average concentrations of the pesticides in the five certified solutions. The dotted lines represent the acceptable concentration range (45-55 mg/L, i.e. ± 10 % deviation), and the dotted lines represent the questionable range (40-60 mg/L, i.e. ± 20 % deviation).

The percentage of compounds at a correct concentration ranges from 78 % (solution D) to 99 % (solution B). However, if the questionable results are not considered, the percentage of unacceptable results ranges from 0 % (solution B) to 5 % (solution A).

In terms of the individual standards, any of them was found to be at questionable/unacceptable concentrations in all five solutions, nor in four of them. However, a total of six pesticides were found at questionable and/or unacceptable concentrations in three solutions. These were ametoctradin, chlorothalonil, fludioxonil, methamidophos, parathion-methyl and pyridalyl. In most of these cases, the average concentration was lower than 45 mg/L. On the contrary, 88 standards (59 %) were found at a correct concentration in the five solutions, and 47 standards (32 %) had a questionable or unacceptable concentration in only one solution.

As regards endosulfan, the residue definition of this compound involves the sum of its alpha and beta isomers and endosulfan-sulphate. During the communication with the companies, endosulfan was included in the request list as the technical mix of alpha and beta isomers (CAS number 115-29-7). However, company C provided 50 mg/L of each individual isomer, so the concentration of each one was assessed individually instead of as a sum (**table 2**). No unacceptable results were obtained in any case for this compound.

Table 2. Concentration and inter-laboratory RSD for endosulfan in the different solutions

Compound	A		B		C		D		E	
	Conc. (mg/L)	RSD (%)	Conc. (mg/L)	RSD (%)	Conc. (mg/L)	RSD (%)	Conc. (mg/L)	RSD (%)	Conc. (mg/L)	RSD (%)
Endosulfan-alpha	29	15	25	14	**44**	14	35	14	25	14
Endosulfan-beta	12	19	17	17	**46**	18	9	23	25	19
Endosulfan (sum)	**41**	-	**43**	-	-	-	**43**	-	**50**	-

4.2. Unacceptable results attributed to the preparation of certified standard solutions

Table 3 shows the name and concentrations of the pesticides which were found to be at unacceptable levels by all laboratories (i.e. results with a low inter-laboratory RSD). As can be seen, in most cases the actual concentration was notably lower than the certified level, the only exception being deltamethrin in solution D (78 mg/L). By contrast, the lowest concentrations were 9 mg/L (dichlorvos in solution E), 19 mg/L (spirodiclofen in solution A), 26 mg/L (fenpropidin in solution E) and 33 mg/L (parathion-methyl in solution A, ametoctradin in solution C and tetraconazole in solution D).

Table 3. Standards with an unacceptable concentration		
Company	**Standard name**	**Average conc. (lowest-highest conc. reported by a lab) (mg/L)**
A	Ametoctradin	36 (29-43)
	Methamidophos	39 (31-42)
	Oxamyl	39 (32-43)
	Parathion-methyl	33 (27-38)
	Propamocarb	39 (34-46)
	Spirodiclofen	19 (15-23)
C	Ametoctradin	33 (26-42)
D	Deltamethrin	78 (57-90)
	Tetraconazole	33 (24-38)
E	Dichlorvos	9 (7-13)
	Dieldrin	39 (32-49)
	Fenpropidin	26 (21-30)
	Fenpropimorph	39 (31-44)
	Triadimefon	36 (24-44)

Even if the companies certified a concentration of 50 mg/L for all compounds in their solutions, at least 10 different and independent laboratories reported the concentrations shown in **table 3**, which indicates that the mistakes were made in the companies during the preparation of the solutions. As an example, **figure 3** shows the individual results of fenpropidin reported by the 13 laboratories that analyzed this compound. It can be seen that, although there are small variations in the results reported by each laboratory, the concentration of this compound in solution E was consistently lower than in the rest of solutions (average concentration 26 mg/L), and in any case higher than 30 mg/L.

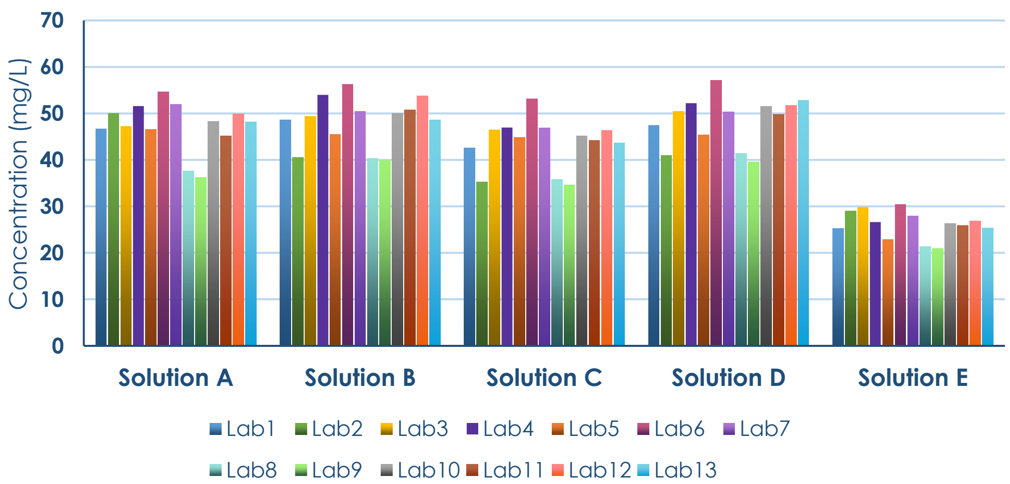

Figure 3. Individual concentrations of fenpropidin in each solution, reported by 13 independent laboratories

Dichlorvos as a special case

Dichlorvos is a very volatile organophosphate pesticide (vapour pressure 2100 mPa, 20 °C), which makes it difficult to analyze. This could explain the fact that the inter-laboratory RSDs encountered in all solutions where it was included were in the range of 17-23 %, slightly higher than the rest of compounds (see **Appendix B**). Nevertheless, the most remarkable result regarding dichlorvos is its extremely low concentration in solution E: an average of 9 mg/L. In this case, the results provided by the participant laboratories ranged between 7 and 13 mg/L –i.e. any of the participant laboratories reported a higher concentration for this compound in solution E. This low concentration level explains the deviations in the individual results reported by the laboratories (and the higher inter-laboratory RSD value). It was, therefore, included in the general assessment of the solutions.

4.3. Results of formetanate, attributed to the analyses performed in the laboratories

Formetanate was provided by only three of the five companies (A, B and E) and was analyzed by nine laboratories. In this case, the inter-laboratory RSDs were close to 30 % and the individual results reported by the laboratories showed significant differences (**table 5** and **figure 4**).

Table 5. Concentration and inter-laboratory RSD for formetanate in the different solutions

A		B		C		D		E	
Conc. (mg/L)	RSD (%)	Conc. (mg/L)	RSD (%)	Conc. (mg/L)	RSD (%)	Conc. (mg/L)	RSD (%)	Conc. (mg/L)	RSD (%)
63	30	22	31	-	-	-	-	57	30

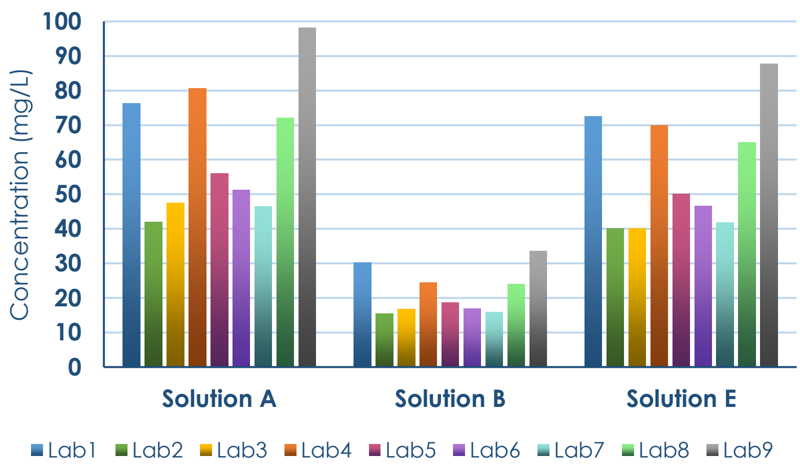

Figure 4. Individual concentrations of formetanate reported by the laboratories in solutions A, B and E

Formetanate is a typically troublesome compound because of several factors including:

a) Low solubility in organic solvents including acetonitrile.

b) Degradation due to oxidation processes in aqueous solution (for instance, when adding water to the injection vials for LC-MS/MS prior to analysis). This effect is illustrated in **figure 4**, which shows an increase of its stability in the presence of ascorbic acid (antioxidant).

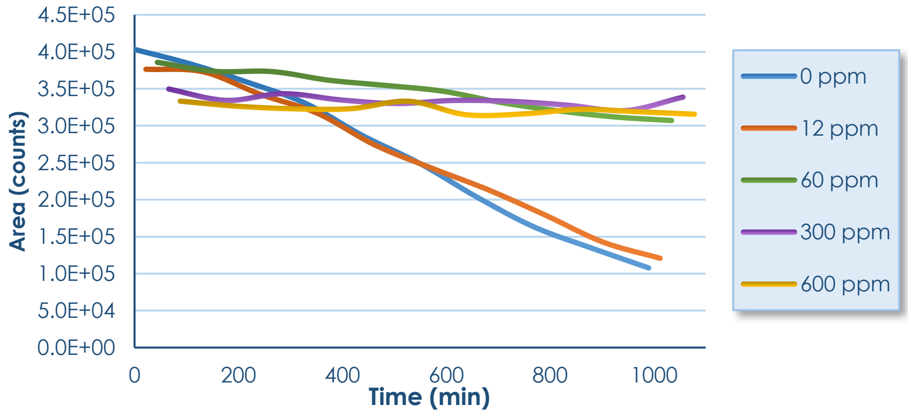

Figure 5. Stability over time of formetanate in a mixture of acetonitrile-water (20:80) with the presence of an ascorbic acid solution at different concentrations (0 ppm to 600 mg/L of ascorbic acid)

c) Presence of the chloride anion, which should be carefully considered by the laboratories during the preparation of their stock solutions and the quantitation of samples. This could explain the different concentrations reported by labs 1, 4, 8 and 9 (higher) when compared to labs 2, 3, 5, 6 and 7 (lower).

However, despite the high variations in the results reported by the laboratories, it can be seen in **figure 4** that any of the participant laboratories reported a concentration higher than 34 mg/L for formetanate in solution B so, in all chance, the compound was not prepared correctly by the company in this case.

5. CONCLUSIONS

A considerable improvement in the solutions provided by the companies has been observed. As happened in the previous study, deviations with some specific compounds were detected. However, when comparing the 150 compounds included in each solution in the present study with the 30 compounds per solution in the previous one, the percentage of unacceptable results decreases, which implies a better performance of the companies. Consequently, a clear improvement process in the manufacturers motivated by the control established by the EURL-FV has been observed. However, further evaluations to cover acceptable results in 100 % of the cases are needed.

Out of the five companies that took part in the present study, only one provided acceptable or questionable concentrations for all of the compounds included in their solution. The remaining companies produced solutions that contained up to 6 compounds (out of 150) with unacceptable results, with a deviation higher than 20 % from the certified value.

Therefore, the results shown in this Technical Report demonstrate that, even if the companies provide the laboratories with certified standard solutions, it seems necessary to have a more exhaustive internal evaluation of certified standard solutions. It is important that laboratories implement effective internal controls of certified standard solutions before their use.

Moreover, during the communication with the companies, the laboratories must always check carefully the quotations and distribution lists provided prior to the preparation of the solutions and, also, after their reception.

Authors

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APPENDIX I. Pesticides provided the companies

	Comp. A	Comp. B	Comp. C	Comp. D	Comp. E
2,4-D	X		X	X	X
Acephate		X		X	X
Acetamiprid	X	X	X	X	X
Acrinathrin	X	X			X
Aldicarb	X	X	X	X	X
Ametoctradin	X	X	X	X	X
Azinphos-methyl		X	X		X
Azoxystrobin	X	X	X	X	X
Bifenthrin		X	X	X	X
Bitertanol	X	X	X	X	X
Boscalid	X	X	X	X	X
Bromopropylate	X	X	X	X	X
Bupirimate		X	X	X	X
Buprofezin	X	X	X	X	X
Carbaryl	X	X	X	X	X
Carbofuran	X	X		X	X
Chlorantraniliprole	X	X	X	X	X
Chlorfenapyr	X	X	X	X	X
Chlorothalonil	X	X	X	X	X
Chlorpropham	X	X	X	X	X
Chlorpyrifos		X	X	X	X
Chlorpyrifos-methyl		X	X	X	X
Clofentezine		X	X	X	X
Cyazofamid	X	X		X	X
Cyflufenamid	X	X	X	X	X
Cyfluthrin		X	X	X	X
Cymoxanil	X	X	X	X	X
Cypermethrin		X	X	X	X
Cyproconazole		X	X	X	X
Cyprodinil	X	X	X	X	X
Deltamethrin	X	X		X	X
Diazinon		X	X	X	X
Dichlorvos		X	X	X	X
Dicloran	X	X	X	X	X
Dieldrin	X	X	X	X	X
Diethofencarb	X	X	X	X	X
Difenoconazole		X	X	X	X
Diflubenzuron	X	X	X	X	X
Dimethoate		X	X	X	X
Dimethomorph	X	X	X	X	X
Diniconazole		X	X	X	X
Diphenylamine	X	X	X	X	X
Endosulfan	X	X	X	X	X
Epoxiconazole		X	X	X	X
Ethion		X	X	X	X
Ethirimol	X	X	X	X	X
Etofenprox	X	X	X	X	X
Etoxazole	X	X	X	X	X
Famoxadone	X	X	X	X	X
Fenamidone	X	X	X	X	X
Fenamiphos		X	X	X	X
Fenarimol		X	X	X	X

Fenazaquin		X	X	X	X
Fenbuconazole		X	X	X	X
Fenhexamid		X	X	X	X
Fenitrothion	X	X	X	X	X
Fenoxycarb	X	X	X	X	X
Fenpropathrin	X	X	X	X	X
Fenpropidin	X	X	X	X	X
Fenpropimorph		X	X	X	X
Fenpyrazamine	X	X	X		X
Fenpyroximate (E-Z)	X	X	X	X	X
Fenvalerate	X	X	X	X	X
Fipronil		X	X	X	X
Flonicamid	X	X	X	X	X
Flubendiamide	X	X	X	X	X
Fludioxonil	X	X	X	X	X
Flufenoxuron	X	X	X	X	X
Fluopicolide	X	X	X	X	X
Fluopyram	X	X	X	X	X
Fluquinconazole		X	X	X	X
Flusilazole	X	X	X	X	X
Flutriafol		X	X	X	X
Fluxapyroxad	X	X	X	X	X
Formetanate	X	X			X
Fosthiazate		X	X	X	X
Hexaconazole	X	X	X	X	X
Hexythiazox	X	X	X	X	X
Imidacloprid	X	X	X	X	X
Indoxacarb	X	X	X	X	X
Iprovalicarb	X	X	X	X	X
Isocarbophos	X	X	X	X	X
Isoprothiolane	X	X	X	X	X
Kresoxim-methyl	X	X	X	X	X
Lambda-cyhalothrin	X	X	X	X	X
Linuron	X	X	X	X	X
Lufenuron	X	X		X	X
Malathion	X	X	X	X	X
Mandipropamid	X	X	X	X	X
Mepanipyrim	X	X	X	X	X
Metalaxyl	X	X	X	X	X
Methamidophos	X	X	X	X	X
Methidathion	X	X	X	X	X
Methiocarb	X	X	X	X	X
Methomyl	X	X	X	X	X
Methoxyfenozide	X	X		X	X
Metrafenone	X	X	X	X	X
Monocrotophos	X	X	X	X	X
Myclobutanil	X	X	X	X	X
Oxamyl	X	X	X	X	X
Oxydemeton-methyl	X	X		X	X
Paclobutrazole	X	X	X	X	X
Parathion methyl	X	X	X	X	X
Penconazole	X	X	X	X	X
Pencycuron	X	X	X	X	X
Pendimethalin	X	X	X	X	X
Permethrin	X	X	X	X	X
Phosmet	X	X	X	X	X
Pirimicarb	X	X	X	X	X

Pirimiphos-methyl	X	X	X	X	X
Procymidone	X	X		X	X
Profenofos	X	X	X	X	X
Propamocarb	X	X	X	X	X
Propargite	X	X	X	X	X
Propiconazole	X	X	X	X	X
Propyzamide	X	X	X	X	X
Proquinazid	X	X	X	X	X
Prosulfocarb	X	X	X	X	X
Pymetrozine	X	X	X	X	X
Pyraclostrobin	X	X	X	X	X
Pyridaben	X	X	X	X	X
Pyridalyl	X	X	X	X	X
Pyrimethanil	X	X	X	X	X
Pyriproxyfen	X	X	X	X	X
Quinoxyfen	X	X	X	X	X
Spinetoram (J-L)	X	X	X	X	X
Spirodiclofen	X	X		X	X
Spiromesifen	X	X	X	X	X
Spiroxamine	X	X	X	X	X
Tau-Fluvalinate	X	X	X		X
Tebuconazole	X	X	X	X	X
Tebufenozide	X	X	X	X	X
Tebufenpyrad	X	X	X	X	X
Teflubenzuron	X	X		X	X
Tefluthrin	X	X	X	X	X
Terbuthylazine	X	X	X	X	X
Tetraconazole	X	X	X	X	X
Tetradifon	X	X	X	X	X
Thiabendazole	X	X	X	X	X
Thiacloprid	X	X	X	X	X
Thiamethoxam	X	X	X	X	X
Thiodicarb	X	X		X	X
Tolclofos-methyl	X	X	X	X	X
Triadimefon	X	X	X	X	X
Triadimenol	X	X	X	X	X
Triazophos	X	X	X	X	X
Tricyclazole	X	X	X	X	X
Trifloxystrobin	X	X	X	X	X
Triflumuron	X	X	X	X	X
Vinclozolin	X	X	X	X	X
TOTAL	**123**	**149**	**137**	**145**	**150**

APPENDIX II. Average concentration and inter-laboratory RSD of the standards employed for the assessment of the solutions

Company	A		B		C		D		E	
Value	Avg. conc. (mg/L)	RSD (%)	Avg. conc. (mg/L)	RSD (%)	Avg. conc. (mg/L)	RSD (%)	Avg. conc. (mg/L)	RSD (%)	Avg. conc. (mg/L)	RSD (%)
2,4-D	49	6	51	4	47	10	46	8	44	11
Acephate			49	8			43	8	53	8
Acetamiprid	47	10	51	10	48	9	48	10	47	9
Acrinathrin	49	11	50	12					53	14
Aldicarb	47	14	48	13	49	12	47	11	48	13
Ametoctradin	36	14	48	13	33	14	41	15	50	12
Azinphos-methyl			50	8	48	6	47	8	46	11
Azoxystrobin	49	11	49	11	47	13	49	11	48	12
Bifenthrin			48	8	47	8	44	8	52	10
Bitertanol	49	6	50	10	46	10	47	11	53	10
Boscalid	47	8	48	9	47	10	46	10	48	10
Bromopropylate	48	12	48	13	44	12	47	13	45	14
Bupirimate			50	12	49	13	50	12	55	14
Buprofezin	46	14	47	15	47	13	45	14	48	13
Carbaryl	49	12	52	10	47	10	50	11	52	11
Carbofuran	48	14	47	17			51	13	49	13
Chlorantraniliprole	47	11	50	11	53	9	48	9	48	10
Chlorfenapyr	48	8	48	11	46	9	45	11	49	13
Chlorothalonil	42	9	45	11	43	8	41	15	49	10
Chlorpropham	47	8	50	12	48	12	45	11	42	14
Chlorpyrifos			49	14	47	12	47	11	52	14
Chlorpyrifos-methyl			48	10	45	13	41	12	53	11
Clofentezine			50	11	48	9	44	8	42	10
Cyazofamid	52	7	54	9			48	6	52	7
Cyflufenamid	48	12	51	12	47	13	46	13	44	14
Cyfluthrin			50	10	46	11	44	10	57	14
Cymoxanil	47	10	49	10	47	10	44	12	47	10
Cypermethrin			47	12	48	10	45	13	55	14
Cyproconazole			49	12	47	11	44	13	52	14
Cyprodinil	48	6	51	7	48	8	47	7	55	8
Deltamethrin	47	12	52	10			78	15	51	14
Diazinon			49	11	48	12	45	12	45	11
Dichlorvos			49	17	51	17	45	17	9	23
Dicloran	46	10	47	13	46	13	43	12	53	10
Dieldrin	47	14	51	14	41	14	46	14	39	13
Diethofencarb	47	10	48	15	50	13	46	13	41	14
Difenoconazole			51	9	49	9	46	10	53	10
Diflubenzuron	50	9	50	10	48	9	46	10	49	10
Dimethoate			50	13	46	12	44	11	46	13
Dimethomorph	48	8	48	10	51	10	48	10	58	11
Diniconazole			48	14	48	13	47	15	52	14
Diphenylamine	47	7	48	7	47	8	46	8	52	9
Endosulfan-alpha	29	15	25	14	44	14	35	14	25	14
Endosulfan-beta	12	19	17	17	46	18	9	23	25	19
Epoxiconazole			50	10	47	12	47	9	59	12
Ethion			48	14	47	12	45	13	52	15
Ethirimol	48	10	53	9	49	10	50	8	51	10
Etofenprox	48	8	50	7	47	9	45	9	53	10
Etoxazole	49	11	49	8	47	9	48	5	52	8
Famoxadone	47	14	49	12	47	13	45	12	58	11

Fenamidone	50	9	53	10	48	11	48	11	52	10
Fenamiphos			48	8	50	8	43	14	53	7
Fenarimol			52	9	49	9	47	11	51	9
Fenazaquin			50	9	47	10	48	8	48	9
Fenbuconazole			50	8	47	8	46	7	53	9
Fenhexamid			52	14	44	10	48	15	47	10
Fenitrothion	46	9	49	8	45	14	42	12	47	15
Fenoxycarb	48	8	52	9	47	8	46	9	48	8
Fenpropathrin	46	8	50	10	47	10	45	10	53	12
Fenpropidin	47	11	48	11	44	12	49	11	26	11
Fenpropimorph			52	11	49	11	50	11	39	12
Fenpyrazamine	42	11	48	8	48	9			53	7
Fenpyroximate (E-Z)	50	12	50	9	49	9	49	9	55	8
Fenvalerate	47	8	50	12	48	11	44	14	43	14
Fipronil			49	14	50	14	46	11	51	9
Flonicamid	47	8	48	8	45	7	45	8	48	8
Flubendiamide	50	14	50	13	46	13	46	14	52	14
Fludioxonil	42	14	52	11	47	11	40	7	56	7
Flufenoxuron	47	11	48	10	47	9	46	10	54	9
Fluopicolide	48	11	48	12	49	11	46	10	54	11
Fluopyram	47	9	50	9	48	10	47	9	51	10
Fluquinconazole			48	12	47	12	45	14	50	13
Flusilazole	48	13	48	13	47	12	45	12	46	14
Flutriafol			47	13	46	14	46	13	49	14
Fluxapyroxad	48	9	49	10	48	11	47	13	47	11
Formetanate	63	30	22	31					57	30
Fosthiazate			50	6	49	6	48	7	47	8
Hexaconazole	47	9	50	11	50	10	47	10	55	10
Hexythiazox	48	11	53	10	46	10	47	11	52	11
Imidacloprid	48	9	52	9	49	8	47	8	45	9
Indoxacarb	48	12	48	11	47	11	43	9	47	12
Iprovalicarb	48	8	47	8	48	8	47	8	45	7
Isocarbophos	44	13	48	12	46	14	48	13	50	10
Isoprothiolane	47	8	50	10	47	11	47	10	46	11
Kresoxim-methyl	46	12	48	13	47	13	47	11	52	14
Lambda-cyhalothrin	46	10	48	14	47	14	42	10	48	12
Linuron	49	10	49	10	47	9	46	8	49	10
Lufenuron	50	7	51	6			44	6	56	5
Malathion	46	13	51	9	48	9	45	12	46	13
Mandipropamid	49	8	48	7	48	9	44	8	53	8
Mepanipyrim	45	13	49	13	44	14	47	12	45	15
Metalaxyl	48	8	48	10	50	9	47	9	51	11
Methamidophos	39	9	55	9	47	10	41	9	40	8
Methidathion	45	10	47	13	44	14	43	14	46	14
Methiocarb	47	14	53	12	48	11	49	11	53	8
Methomyl	53	9	53	9	45	9	47	8	49	8
Methoxyfenozide	48	9	51	11			47	10	45	8
Metrafenone	46	7	52	8	46	6	47	9	50	8
Monocrotophos	46	12	47	14	45	13	45	9	48	14
Myclobutanil	45	12	49	13	45	13	45	13	53	14
Oxamyl	39	8	48	8	49	11	47	8	48	14
Oxydemeton-methyl	49	8	56	10			51	10	49	9
Paclobutrazole	46	13	51	10	51	10	50	11	54	11
Parathion methyl	33	12	47	13	45	15	40	12	43	13
Penconazole	46	9	48	11	47	12	48	10	50	13
Pencycuron	43	11	49	11	50	9	46	12	51	10
Pendimethalin	47	12	50	10	46	15	46	15	48	10
Permethrin	46	11	48	10	51	13	42	14	48	13
Phosmet	42	14	47	14	45	12	44	14	54	13

Pirimicarb	48	7	49	9	48	9	49	9	51	9
Pirimiphos-methyl	49	14	53	12	46	14	50	10	54	12
Procymidone	46	8	49	10			45	8	43	11
Profenofos	50	15	51	15	49	14	47	14	53	10
Propamocarb	39	10	48	15	49	13	46	16	42	12
Propargite	47	11	47	15	47	15	48	13	42	15
Propiconazole	48	15	52	13	48	12	48	12	55	14
Propyzamide	49	14	48	14	45	15	44	15	48	13
Proquinazid	47	11	49	12	48	11	49	12	49	12
Prosulfocarb	49	8	52	9	48	8	49	7	50	10
Pymetrozine	51	13	45	12	51	13	44	14	45	11
Pyraclostrobin	49	9	51	13	46	9	46	12	56	12
Pyridaben	48	8	49	10	49	10	47	11	60	12
Pyridalyl	52	10	51	9	44	8	42	9	44	8
Pyrimethanil	46	10	50	13	48	12	47	11	46	14
Pyriproxyfen	47	7	50	8	48	9	49	8	52	9
Quinoxyfen	48	7	50	7	47	7	49	7	50	9
Spirodiclofen	19	12	53	14			49	14	56	14
Spiromesifen	43	11	51	11	49	11	48	10	44	12
Spiroxamine	49	15	49	9	45	9	50	10	44	7
Tau-Fluvalinate	48	11	46	14	47	14			43	14
Tebuconazole	46	14	57	12	48	12	47	11	55	11
Tebufenozide	46	10	48	11	47	10	43	9	50	8
Tebufenpyrad	46	13	50	14	48	14	46	13	51	14
Teflubenzuron	50	9	52	14			48	10	54	9
Tefluthrin	46	7	49	12	49	14	47	11	54	6
Terbuthylazine	47	10	52	11	46	11	46	10	48	11
Tetraconazole	49	10	52	13	47	12	33	11	47	13
Tetradifon	46	7	49	8	44	10	45	7	46	12
Thiabendazole	45	10	47	10	48	9	46	9	52	9
Thiacloprid	47	8	51	9	48	9	44	9	54	7
Thiamethoxam	47	8	52	9	47	9	44	9	52	10
Thiodicarb	52	14	52	15			49	13	56	10
Tolclofos-methyl	46	9	48	13	47	13	46	10	48	14
Triadimefon	46	11	53	13	47	13	47	12	36	15
Triadimenol	46	11	50	9	47	12	47	13	51	10
Triazophos	45	13	48	15	47	14	46	14	40	15
Tricyclazole	46	8	49	9	47	8	46	7	53	8
Trifloxystrobin	47	10	54	9	48	9	47	9	52	9
Triflumuron	49	12	48	10	48	11	48	13	52	12
Vinclozolin	47	8	49	11	47	12	45	10	50	13