TESTQUAL
PROFICIENCY TESTING SCHEMES

TestQual, S.L.

(Proficiency Testing Schemes)

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ENAC
ISO 17043
Nº9 / PPI014

Parameters marked (*) are not accredited

TestQual 177 PROTOCOL

Multi-analysis *in Lettuce:*

- ***Multi-residues pesticides***
- ***Chlorate, Perchlorate***
- ***QAC***
- ***Glyphosate, Glufosinate (*) and related analytes (*)***

SUMMARY OF CHANGES

Changes are marked with electric blue or blue highlighted white.
Rev00 → rev01:
·Dates of the PT updated
·No blank will be available for this PT, text is removed.
·Temperature changed from -25ºC to "approximately -20ºC".
·Homogenization statistic synthetized
·Bibliography updated
Rev01 → rev02:
· Title of group of analytes 4 updated (analytes are not changed).
· Added an option to submit Glufosinate SUM as EURL definition (it can be obtained from results already in the list of possible positives; therefore, the list of possible analytes is not modified).
·Better comments for results submitting are included.
·Analytes from group 4 are included in the glossary/abbreviations.

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0. GLOSARY AND ABREVIATIONS

Text	Abbreviation
TestQual	TQ
Proficiency test	PT / P.T.
Limit Of Quantification	LOQ
Not Analysed	NA
Quaternary Ammonium Compounds	QAC
DidecylDimethylAmmonium Chlorides	DDAC
AlkylBenzyldimethyAmmonium Chlorides	BAC
3-(Hydroxymethylphosphinyl)propionic acid	***MPP or MPPA***
N-acetyl-glufosinate	***NAG***
Aminomethylphosphonic acid	***AMPA***

1. INTRODUCTION

This document describes the **protocol** of the **TestQual 177 multi-analysis** Proficiency Test (P.T.), belonging to the analysis in lettuce of the analytes of interest of each participant:

Group of analytes	Name
1	Multi-residues pesticides
2	Chlorate, Perchlorate
3	Quaternary Ammonium Compounds (QAC)
4	Glyphosate, Glufosinate (*) ***and related analytes (*)***
5	Ethephon

In the present document is detailed how to start working with TestQual, send your application to participate, the statistic that will be applied and information about the evaluation report.

TestQual, S.L. is committed to maintaining confidentiality with the information of each laboratory from the beginning of the proficiency test and after it is finished.

2. OBJECTIVE

The objective of the **TestQual 177** Proficiency Test is to evaluate the quality and accuracy of the results sent by the participating laboratories of the analytes of their interest. Proficiency testing is an essential element of laboratory quality assurance. It can help to control and detect errors in their results or methods of analysis, qualify employees, compare or evaluate equipment, compare methods are much more benefits.

3. CALENDAR

The following table shows the program for this proficiency test:

Date (YYYY/mm/dd)	Activity	Carried out by
-	Deadline to reserve PT sample.	Participants
2023/05/18	Deadline to request participation *	Participants
2023/05/ 22-24	Sample delivery	TestQual
2023/06/09	Final date to submit results	Participants
2023/06/23	Final report (Email and/or client area)	TestQual

*Acceptance of the participation between the deadline to reserve the PT sample and the deadline to request the participation will depend on availability of the proficiency test.

Participants are requested in the application to submit their LOQ/LOQs. For PTs with multiple groups of analytes, for each group that the participant has submitted LOQ/LOQs, if a certain percentage (described in our internal procedure) of the present/planned analytes is analysed, then the participation is accepted, and a laboratory code is generated and sent by email to confirm the participation acceptance to the user of the TestQual's account.

The dates of this calendar and the definitive shipping distribution might be changed depending on the development of the proficiency test. The definitive distribution date is confirmed when the sample instructions are sent, which, besides the instructions for the sample, contains the deadline to submit the results (which might update and override the here displayed deadline).
The sample instructions are exclusively sent to inscribed participants. These possible changes would be notified to all participants through our website *www.TestQual.com* and/or by email.

The **coordinator** of this proficiency test will be Jose Pedro Navarro. Vicente. Any question regarding the development of the proficiency test, the application status or any other query can can be consulted by email to jpnavarro@testqual.com.

4. REGISTER AND PARTICIPATION REQUEST (APPLICATION FORM)

NEW CLIENT

If your laboratory has not participated before in one of our proficiency tests you will have to register using the REGISTER form.
Once you have completed and sent the form you will have to wait until the activation of the account from the website administrator. If some more information is needed someone from our team will get in contact with you. You can find our contact data at the end of this protocol.

For those laboratories that require more than one contact per account or are in a situation not contemplated in this protocol will have to contact the organizer using the Contact tab to be instructed how to proceed.

APPLICATION FOR THE PROFICIENCY TEST

To participate in this proficiency test or to be updated via email of any changes regarding this this, it is required to have a laboratory code. To get your laboratory code is needed to apply through the website or have it arranged by the coordinator at the latest, on the deadline to request the participation.

In the "Proficiency Tests" tab on our website, you will have to select the proficiency test you want to participate, by clicking its name or the image you will enter the proficiency test page, which contains general information and a summary of that proficiency test, there you can find the present document (the protocol) and the button to start the application.

You will be required to log in to start the application and then the website will require you to submit your Limit Of Quantification (LOQ) for the parameters you will study. **The analytes left as NA (NOT ANALYSED) will NOT appear in the Results form** and therefore will not be able to send results for those parameters through the website.

Once the participation has been requested, as soon as possible, it will be checked by the website administrator, and you will be sent an email with the participation code. This code will be just known only by the organizer and the participant and will be kept confidential **at all times**, even after the proficiency test finishes.

You can check on the dashboard of your client area if an application you sent has been accepted or is still pending.

Just one application per exercise can be sent by each laboratory, being not allowed for a laboratory to participate with two different codes.

The applications of the laboratories will be studied and accepted in base of the quantification limits of the analytes of the proficiency test and if the logistics allow the sample shipping without risk of deterioration.

According to the experience, TestQual can anticipate that the number of participants of this proficiency test will be around ***25-35***, being 11 the minimum participants for the proficiency test to take place.

5. TEST MATERIAL. CONTROL AND DISTRIBUTION.

TestQual **177** scheme is a proficiency test based in the analysis of Multi-residues pesticides, QAC, Glyphosate, AMPA(*), Ethefon, MPPa(*), NAG(*) Glufosinate(*) Chlorate and perchlorate in Lettuce that has been spiked or were present in the matrix.
The material will be bought in a specialized shop in Spain and verified as adequate to prepare the samples by a subcontracted laboratory that holds the standard UNE-EN ISO/IEC 17025 into force. The subcontracted laboratory will analyse randomly selected sample to ensure the homogeneity and during and after the proficiency test more samples to check the stability of the parameters through the duration of the round.

Once the matrix is deemed adequate the material is cut in very small pieces, dropped into liquid N_2, once it is fully frozen, it is grounded into a fine powder, puree or juice, which will be spiked with a solution with the chosen analytes of the PROFICIENCY TEST and poured into a homogenizer with controlled temperature to ensure complete homogeneity.
Once the lot of samples is ready they will be stored in a temperature-controlled freezer below -20ºC until the dispatch of the samples.

As previously mentioned, before the samples are distributed, the homogeneity of the lot will be assessed analysing in repeatability conditions randomly selected samples in duplicate. If the mean concentration obtained from this study is not within the planned range, the participants will be informed and a new distribution day might be scheduled if another spiking is deemed as necessary.

For stability assessment purpose, a total of three samples will be analysed, in duplicate, before, during and at the end (once all laboratories have sent the results) of the proficiency test.

The quality controls subcontracted by TestQual, including verification of adequacy of the matrix, homogeneity/stability quality controls and any other analytical study required by TestQual will be subcontracted to an accredited laboratory in ISO/IEC 17025 into force.
In the evaluation report will be included the conclusions and if applies, any comment regarding homogeneity &/or stability. Additionally, the results of these tests and the spiking evaluation is available to all participants of this proficiency test upon request.

The shipment of the test materials will take place on the date shown in the calendar*, to the address provided by each laboratory in the application. The participant is responsible to communicating TestQual if the address is changed or update the delivery address in their client area at least 2 working days before the shipping.
*Specific delivery dates can be changed from the scheduled dates of the calendar, but all changes will be announced either in the website or by email to the registered laboratories. Before shipping the samples TestQual will email the registered laboratories the sample instructions and will confirm the definitive distribution date, deadline to submit results and date of the report, if necessary, the dates shown in the sample instructions override the calendar here shown and the new dates will be updated in the PT page.

This PT will consist in a single round in which will be sent a sample of approximately **200 g** of test material. The samples will be sent by courier service (MRW, FedEx, DHL or TNT, depending on the destination). The material will be sent with materials and package that ensures the samples arrives correctly. The transit will be 1, 2 or 3 days to the destination country, depending on the location of the receiving laboratory.

The shipping conditions for this PT are:
FROZEN, isothermal boxes will be uses and filled with either dry ice or cold packs (-20ºC approximately) to keep the temperature.
The shipping costs are not included in the price displayed on the website, which can only be seen if you are registered and logged in. To get an approximation of the shipping costs you can get your quotation by using the contact data at the end of this protocol.

The distribution of samples was subcontracted to a courier previously homologated by TestQual. The main criteria being the courier's delivery time to ensure the receival of the sample is correct in the participant's facilities.
In addition to this, TestQual stablished other characteristics important for a courier like shipping management (tracking, notifications, exceptions), and ensuring the delivery conditions are proper (low breakage/lost ratio, keeping of cold chain, required documentation), always checking and evaluating they are complying with TestQual's requirements.

A second test material can be requested date if necessary. If the package and/or the sample arrived damaged, defective, or not valid the participating laboratory will have to notify of this to the coordinator before two working days to get another sample.

Before the shipment, TestQual will send the instructions for storage and analysis via email and confirm the distribution date. You can request a paper copy to be attached to the package and/or TestQual might decide to include it in addition to have it sent by email.
From TestQual we encourage our participants to read the samples instructions carefully and follow them, as it can help to correctly conserve the sample and increase the reproducibility of the analysis. You can request a digital copy of this document (sample instructions) by letting us know through any communication channel.

6. CONCENTRATION RANGES, SIGMA OBJECTIVE AND ANALYTES

For this proficiency tests, the range of concentration for the target analytes might by between **10** and **300 µg/Kg approximately.** This range is not absolute and depending on the various factors some or no analyte might be within this range. This range is given to provide participants a sense of the concentration ranges we usually work and what to expect in these kind of proficiency tests (combination of analyte/matrix). The maximum concentration can vary depending on the MRL of the analytes in the matrix.

The **sigma objective ($\hat{\sigma}$)** which works in this scheme can be checked on section 9 of this protocol.

In this proficiency test for each group of analytes, a percentage of them will be present (ranging from >1% (the % is determined internally in our procedure) to possibly all of the analytes of the list). Therefore, this PT should be useful to check each of the groups, possibly in different degrees, depending on the number of selected/present analytes.

In the following table you can check the groups of analytes for this proficiency test, below you can find the lists of possible positives and how the website and the results are expected to be sent:

Group of analytes	Name
1	Multi-residues pesticides
2	Chlorate, Perchlorate
3	Quaternary Ammonium Compounds (QAC)
4	Glyphosate, Glufosinate (*) ***and related analytes (*)***
5	Ethephon

The list of possible multi- residues pesticides in the matrix are from the list below:

2-Phenylphenol
3,5-Dichloroaniline
3-Hydroxy-carbofuran
4,4-Dichlorobenzophenone
Abamectin
Acephate
Acetamiprid
Acetochlor
Aclonifen
Acrinathrin
Alachlor
Aldicarb
Aldicarb sulfone
Aldicarb sulfoxide
Aldrin
Anthraquinone
Atrazine
Azaconazole
Azinphos-ethyl
Azinphos-methyl
Azoxystrobin
Benalaxyl
Bendiocarb
Benfluralin
Benfuresate
Bentazone
Bifenthrin
Bitertanol
Boscalid
Brodifacoum
Bromacil
Bromocyclen
Bromophos-ethyl
Bromophos
Bromopropylate
Bromuconazole
Bupirimate
Buprofezin
Butafenacil
Butamifos
Butoxycarboxim
Butralin
Buturon
Cadusafos
Captan
Carbaryl
Carbendazim
Carbophenothion
Carbofuran
Chlorantraniliprole
Chlorbromuron
Chlorfenapyr
Chlorfenvinphos
Chlormephos
Chloroneb
Chloropropylate
Chlorpyrifos
Chlorpyrifos Methyl
Chlorthion
Chlorthiophos
Cyanazine
Cyazofamid
Cyfluthrin
Cymoxanil
Cypermethrin
Cyproconazole
Clethodim
Clofentezine
Clomazone
Cloquintocet-mexyl
Chlorfenson
Chlorotoluron
Chloroxuron
Chlorpropham
Chlorsulfuron
Chlorthal-dimethyl
Clothianidin
Coumaphos
Kresoxim-methyl
Crimidine
Cyanofenphos
Cyanophos
Cycloxydim
Cyprodinil
Deltamethrin
Demeton-S-methyl
Demeton-S-methyl sulfone
Desmetryn
Dialifos
Diazinon
Dicapthon
Dichlofenthion
Dichlormid
Dichlobenil
Diclobutrazol
Dichlofluanid
Diclofop-methyl
Dicloran
Dicrotophos
Dieldrin
Diethofencarb
Difenoconazole
Difenoxuron
Diflubenzuron
Diflufenican
Dimethenamid
Dimethoate
Dimethomorph
Dimoxystrobin
Diniconazole
Dioxacarb
Dioxathion
Diphenylamine
Dipropetryn
Disulfoton
Ditalimfos
Diuron
Dodine
Emamectin benzoate B1a
Endosulfan-alpha
Endosulfan-beta
Endosulfan-sulfate
Endrin
EPN
Epoxiconazole
Etaconazole
Ethion
Ethoprophos
Etoxazole
Ethiofencarb
Ethiofencarb - sulfone
Ethiofencarb - sulfoxide
Etofenprox
Ethofumesate
Etrimfos
Famoxadone
Famphur
(Famophos)
Fenarimol
Fenazaquin
Fenbuconazole
Fenbutatin oxide
Fenchlorphos
Fenhexamid
Fenitrothion
Fenoxycarb
Fenpropathrin
Fenpropimorph
Fenpyroximate
Fensulfothion
Fenthion
Phenthoate
Fenuron
Fenvalerate
Fipronil
Flonicamid
Fluazifop-P-butyl
Fluchloralin
Flucythrinate
Fludioxinil
Flufenoxuron
Flumetralin
Fluometuron
Fluotrimazole
Fluquinconazole
Flusilazole
Flutolanil
Flutriafol
Folpet
Fonofos
Formothion
Phosalone
Phosphamidon
Phosmet
Furalaxyl
Furathiocarb
HCH-Alpha
HCH-Beta
HCH-Delta
HCH-Gamma (lindane)
Heptachlor
Heptachlor-epoxide
Heptenophos
Hexachlorobenzene
Hexaconazole
Hexaflumuron
Hexazinone
Hexythiazox
Imazalil
Imazamethabenz-methyl
Imidacloprid
Indoxacarb
Iprobenfos
Iprodione
Iprovalicarb
Isazofos
Isocarbophos
Isofenphos
Isofenphos-methyl
Isoproturon
Lambda-Cyhalothrin
Lenacil
Leptophos
Linuron
Lufenuron
Malaoxon
Malathion
Mecarbam
Mefenpyr-diethyl
Mepanipyrim
Mepronil
Metalaxyl
Metamitron
Metazachlor
Methacrifos
Methamidophos
Methidathion
Methomyl
Methoxychlor
Methoxyfenozide
Metobromuron
Metolachlor
Methoprotryne
Metoxuron
Metribuzin
Mevinphos
Myclobutanil
Molinate
Monocrotophos
Monolinuron
Monuron
Napropamide
Neburon
Nitenpyram
Nitrofen

Nitrothal-isopropyl	Phenmedipham	Propyzamide	Terbuthylazine
Norflurazon	Picoxystrobin	Propoxur	Terbutryn
Nuarimol	Piperonyl butoxide	Prosulfocarb	Tetraconazole
Ofurace	Pyraclostrobin	Prothiofos	Tetradifon
Omethoate	Pyrazphos	Pyridafenthion	Tetramethrin
op-TDE (DDD)	Pyridaben	Pyrimethanil	Tetrasul
Oxadiazon	Pyrifenox	Quinalpho	Thiabendazole
Oxadixyl	Pirimicarb	Quinoxyfen	Thiacloprid
Oxamyl	Pirimicarb-desmethyl	Quintozene	Thiamethoxam
Oxamyl-oxime	Pirimiphos-ethyl	Rotenone	Thiodicarb
Oxydemeton-methyl	Pirimiphos-methyl	Simazine	Thiobencarb
Oxyfluorfen	Pyriproxyfen	Simetryn	Thiometon
Paclobutrazol	pp-DDE	Spinosad A+D	Tolclofos-methyl
Parathion	pp-TDE(DDD)	Spirodiclofen	Triadimefon
Parathion-methyl	Prochloraz	Spiromesifen	Triadimenol
Pebulate	Procymidone	Spiroxamine	Triazophos
Penconazole	Propham	Sulfotep	Trichloronate
Pendimethalin	Profenofos	Sulprofos	Tridemorph
Pentachloroanisole	Profluralin	Tebuconazole	Trifloxystrobin
Permethrin	Promecarb	Tebufenozide	Triflumuron
1,1-(2,2-dichloroethylidene) bis(4-methoxybenzene) (methoxychlor metabolite)	Prometryn	Tebufenpyrad	Trifluralin
	Propachlor	Tebupirimfos	Vinclozolin
	Propamocarb	Tecnazene	Yodofenfos
	Propanil	Teflubenzuron	Zoxamide
	Propargite	Tefluthrin	
	Propetamphos	Terbacil	
	Propiconazole	Terbufos	
		Terbumeton	

The list of possible QAC in the matrix are from the list below:

DDAC C8	DDAC C10	DDAC C12	BAC C10
BAC C12	BAC C14	BAC C16	BAC C18

Benzalkonium chloride (mixture of alkylbenzyldimethylammonium chlorides with alkyl chain lengths of C8, C10, C12, C14, C16 and C18)

Didecyldimethylammonium chloride (mixture of alkyl-quaternary ammonium salts with alkyl chain lengths of C8, C10 and C12)

The results for Glyphosate will have to be reported as EU applicable legislation No 293/2013 of 20 March 2013 amending Annexes II and III to Regulation (EC) No 396/2005 (..), Glyphosate (..)

- "Glyphosate" as "Glyphosate"

The list of possible metabolites and related with Glyphosate are:

- ***N-Acetyl-Glyphosate (*) that will be submitted as N-Acetyl-Glyphosate.***
- ***AMPA (*) that will be submitted as AMPA.***
- ***N-Acetyl-AMPA (*) that will be submitted as N-Acetyl-AMPA.***

The list of possible metabolites and related with Glufosinate ammonium are:

- ***Glufosinate (*) (NOT the sum) submitted/reported as Glufosinate.***

- ***MPP (*) submitted/reported as MPPa.***
- ***NAG (*) submitted/reported as NAG.***

These lists from glyphosate-related and Glufosinate-related analytes, if analyzed and present, will be submitted through our result's form in our website according to the instructions sent to the participants.

The definition for Glufosinate, as EU applicable regulation 2016/1002 (…) regards maximum residue levels for (…), glufosinate (…) in or on certain products is:

- ***Glufosinate (sum of glufosinate isomers, its salts and its metabolites 3-[hydroxy(methyl)phosphinoyl]propionic acid (MPP) and N-acetyl-glufosinate (NAG), expressed as glufosinate)***

This parameter Glufosinate "SUM of…" is NOT requested in the result's form in our website, however it can be submitted following the instructions sent to the participants.

In case of doubt how to submit results, please contact the PT coordinator.

And the results for Chlorate will have to be reported as EU applicable legislation Commission Regulation (EU) 2020/749 of 4 June 2020 amending Annex III to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for chlorate in or on certain products

- "Chlorate" as "Chlorate"

The results for Chlorate will have to be reported as EU applicable legislation Commission Regulation (EU) 2020/685 of 20 May 2020 amending Regulation (EC) No 1881/2006 as regards maximum levels of perchlorate in certain foods (Text with EEA relevance)

- "Perchlorate" as "Perchlorate"

The results for Ethephon will have to be reported in the results form EU applicable legislation 2017/1777 of 29 September 2017 amending Annexes II, III and IV to Regulation (EC) No 396/2005 (..), Ethephon, (..)

- "Ethephon" as "Ethephon"

7. RESULTS EXPRESSION

Each participant laboratory must analyse the sample received according to their routine procedure and fill up the RESULTS form of its client are of the website www.TestQual.com with just one value per analyte/parameter.

The results should be expressed in **µg/Kg**. The number of significant figures and the units are to be chosen by laboratories and will be displayed in the report as received from the participant.
The method used for the analysis of each compound informed should be sent when filling up the results form.
If you have any problem logging in to your client area or submitting your results you can contact the coordinator of the PT for guidance or help.

Once the results are sent you can check if they were correctly recorded by accessing the detailed information of this proficiency test, which can be accessed in your client area. You are allowed to modify results within the stipulated period range, until the deadline to submit results, included. Currently our website, once the results are sent, cannot be changed, therefore, for any modification you will be required to open an issue in your client area for this PT and send the required modifications through that communication channel.

The organizer should get the results before the fixed data of the scheme.

8. STATISTICAL EVALUATION

TestQual will develop the following statistical evaluation:

TestQual considers as an **extreme outlier** any data which differs more than **50 %** of the average of all results reported by the laboratories, according to the Harmonize Protocol of the IUPAC. These extreme values will not be included in the calculation of the assigned value.

Once received all the results, TestQual evaluates the unimodality of all the valid values with a test using the kernel's density representation, being explained in the final report which is the followed procedure in case there is more than one distribution.

If enough valid results (determined in our internal procedure) are provided and the uncertainty is negligible the **assigned value (*X*)** will be determined using the robust average of the results considered valid for statistical computing (after eliminating the extreme outliers), according to the standard ISO 13528 into force.

If the number of participants or valid results do not meet the required minimum accepted by TestQual (11) the evaluation of the analyte will be issued not accredited.

The **standard uncertainty *(u_x)*** when the assigned value is obtained from the consensus it is calculated using robust statistics from the following formula:

The **standard uncertainty *(u_x)*** is calculated using robust statistics from the following formula:

$$u_x = s^*/\sqrt{p}$$

Being s^* the robust standard deviation of the data and p the number of results considered.

When the assigned value is obtained from the spiking done, the uncertainty is calculated accounting all sources of uncertainty according to our internal procedure and according to ISO 13528 into force.

The following condition must be fulfilled in order to discard the contribution of the uncertainty:

$$u_x \leq 0{,}3\ \hat{\sigma}$$

The **standard deviation for proficiency assessment**, also named **target standard deviation, ($\hat{\sigma}$),** comes from this formula:

$$\hat{\sigma} = b_i \cdot X$$

Being $b_i = \%_{tRSD} / 100$, and $\%_{tRSD}$ is the target relative standard deviation.

In this case, the assigned relative standard deviation is **25 %**.
This value is fixed previously by the organizer based in the experience of TestQual organizing this and similar proficiency tests.
Proficiency assessment (z-score): This parameter shows the competence and accuracy of the laboratory. It is calculated using the following formula:

$$z = (x_i - X)/\hat{\sigma}$$

Where x_i is the value reported by the laboratories, X is the assigned value, and $\hat{\sigma}$ is the target standard deviation for each analyte.
The criteria for defining the z-score values are:

	$\lvert z \rvert$	≤ 2	Satisfactory
$2 <$	$\lvert z \rvert$	≤ 3	Questionable
	$\lvert z \rvert$	> 3	Unsatisfactory

In case the inequation $u_x \leq 0{,}3\ \hat{\sigma}$ is not fulfilled, the participants of the scheme will be informed in the report that the uncertainty is not negligible. For the parameters/analytes in which this situation occurs, the following calculation will be made:

$$z'\text{-score} = (x_i - X)/\sqrt{\hat{\sigma}^2 + U_x^2}$$

Where x_i is the value reported by the laboratories, X is the assigned value, $\hat{\sigma}$ is the target standard deviation for each analyte and Ux is the uncertainty of the assigned value.

The criteria for defining the z'-score values are:

$\lvert z' \rvert$	≤ 2	Satisfactory

2 <	|z'|	≤3	Questionable
	|z'|	>3	Unsatisfactory

The z'-score is a underestimation of the z-score, for this reason, for those analytes in which the uncertainty of the assigned value cannot be neglected and a z'-score is issued, it will be accompanied by the percentual difference against z-score, this way participants should be able to complete evaluate their performance.

Both z-score and z'-score will be issued accredited if the criteria of our technical annex are met.

The evaluation scores could be informative if the difference between scores surpasses the limit contemplated in our procedure. If any analyte or evaluation is informative it will be indicated in the report through marking and a legend.

False negatives: Any analyte not reported in the results that is in the sample above the limit of quantification previously established for this proficiency test by the organization and above the LOQ of the participant laboratory (**10 *µg/Kg*)**. TestQual assigns to all false negatives a result equal to half the laboratory limit of quantitation (LOQ/2).

False positives: Those analytes reported in the results, which is not present in the test material, and is reported by the participant at concentrations higher than the limit of quantification of the P.T. **(10 *µg/Kg*).**

Testing for sufficient homogeneity:

Ten samples will be chosen at random and sent to be analysed by TestQual's subcontracted laboratory in duplicate in repeatability conditions.
Once received the results, a statistical evaluation will be performed, with the homogeneity evaluation of the Harmonic Protocol published by IUPAC and based in ISO 13528 into force.

The acceptance criterion to ensure that the randomly chosen samples are homogeneous is that the square of the estimated sampling standard deviation is below the critical value for accepting proper homogeneity:

$$S_{sam}^2 < c$$

Being $S_{sam}^2$the estimated sampling standard deviation, obtained from the variance of the results sums and the experimental estimate of analytical standard deviation (S_{an}), which in turn is obtained from the differences between replicates of the same sample. Lastly, c is the limit value, which is obtained as ISO 13528 states, it takes into account two constants, obtained from two significance groups, which are multiplied with a term related to the target standard deviation and the S_{an}.

If $S_{sam}^2 < c$ is true, then the lot prepared will be considered sufficiently homogeneous and only then it would be distributed. With this test what we achieve is to check if the intra-sample deviation is lower than the inter-sample deviation.

If the results from the homogeneity test does not meet the criteria TestQual would communicate any change required in the proficiency test (new lot will be prepared, new calendar, etc.).

Testing for sufficient stability:

Three samples will be analysed, in duplicate, before, during and at the end (once all laboratories have sent the results) of the proficiency test.

With these values, a study is performed according to the up-to-date SANTE guide (SANTE/12682/2019 Guidance document on analytical quality control), referred to analysis under repeatability conditions.

The acceptance criteria to ensure the samples have been stable during the whole proficiency test are the following:

$$|(X_{t1} - X_{t2})/ X_{t1}| \cdot 100 \leq 10\%$$
$$|(X_{t1} - X_{t3})/ X_{t1}| \cdot 100 \leq 10\%$$

Being $|(X_{t1} - X_{tn})/ X_{t1}|$ the difference between the average of the samples analysed before, during and at the end of the proficiency test.

9. EVALUATION REPORT/S

Once received and statistically evaluated all of the laboratories' results, TestQual will send a global report that summarizes the participation of each laboratory.

This global report will be received by the laboratories via e-mail in PDF format or an email notifying that the report is now available to be downloaded from the private area of each participant in www.TestQual.com.

If desired, the laboratory may request the report in paper, and it will be sent to its laboratory by mail.

Likewise, the participant can request an "individual" report for each of the groups of the analytes of their interest, the "individual" report is only a summary, which will reference the global report to complete the required information. The individual report will not be accredited but will reference if the evaluation is accredited on the global report.

In the event that a participant wishes to appeal against the assessment program performance, a written appellation must be sent by e-mail to jpnavarro@testqual.com explaining the reasons for it, there will be a 60-day period to communicate any appellation.

10. CONTACT

TestQual puts at your disposal any of the following means to contact our team:

Website:	Contact
Email:	jpnavarro@testqual.com
Office phone:	+34 868 94 94 86
Mobile phone:	+34 676 367 555

12. REFERENCES

TestQual Proficiency Testing Schemes are based on the following standards:

UNE-EN ISO/IEC 17043:2010 Conformity assessment- General requirements for proficiency testing.

ISO13528:2022, Statistical methods for use in proficiency testing by interlaboratory comparison.

THE INTERNATIONAL HARMONIZED PROTOCOL FOR THE PROFICIENCY TESTING OF ANALYTICAL CHEMISTRY LABORATORIES

EU Pesticides database (v.2.2) Search Pesticides residues

SANTE/11312/2021 (Implemented by 01/01/2022) Guidance document on analytical quality control and method validation procedures for pesticides residues analysis in food and feed.

COMMISSION REGULATION (EU) 2020/749 of 4 June 2020 amending Annex III to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for **CHLORATE** in or on certain products
OJ L 178, 8.6.2020, p. 7–20

COMMISSION REGULATION (EU) 2020/685 of 20 May 2020 amending Regulation (EC) No 1881/2006 as regards maximum levels of **PERCHLORATE** in certain foods
OJ L 160, 25.5.2020, p. 3–5

Commission Regulation (EU) No 293/2013 of 20 March 2013 amending Annexes II and III to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for emamectin benzoate, etofenprox, etoxazole, flutriafol, **GLYPHOSATE**, phosmet, pyraclostrobin, spinosad and spirotetramat in or on certain products
DO L 96 de 5.4.2013, p. 1/30

Commission Regulation (EU) 2017/1777 of 29 September 2017 amending Annexes II, III and IV to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for Bacillus amyloliquefaciens strain FZB24, Bacillus amyloliquefaciens strain MBI 600, clayed charcoal, dichlorprop-P, **ETHEPHON**, etridiazole, flonicamid, fluazifop-P, hydrogen peroxide, metaldehyde, penconazole, spinetoram, tau-fluvalinate and Urtica spp. in or on certain products. DO L 253 de 30.9.2017, p. 1/31

Commission Regulation (EU) 2016/1002 of 17 June 2016 amending Annexes II, III and V to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for AMTT, diquat, dodine, GLUFOSINATE and tritosulfuron in or on certain products OJ L 167, 24.6.2016, p. 1–45

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