TESTQUAL
PROFICIENCY TESTING SCHEMES

# TestQual, S.L.

## (Proficiency Testing Schemes)

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# TestQual 148 PROTOCOL

# *Pesticides Residues in Parsley*

## *CANCELED*

## 0. GLOSARY AND ABREVIATIONS

| Text | Abbreviation |
|---|---|
| TestQual | TQ |
| Proficiency test | PT / P.T. |
| Limit Of Quantification | LOQ |
| NA | Not Analysed |

## 1. INTRODUCTION

This document describes the **protocol** of the **TestQual 148** Proficiency Test (P.T.), belonging to the analysis of **pesticides** in **Parsley**.
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.

## 2. OBJECTIVE

The objective of the **TestQual 148** Proficiency Test is to evaluate the quality and accuracy of the results sent by the participating laboratories. Because of this, proficiency testing is an essential element of laboratory quality assurance. It will help to control and detect errors in their results or methods of analysis.

## 3. CALENDAR

The following table shows the program for this proficiency test:

| Date | Activity | Carried out by |
|---|---|---|
| ***CANCELED*** | Final date to submit applications | Participants |
| ***CANCELED*** | Sample delivery | TestQual |
| ***CANCELED*** | Final date to submit results | Participants |
| ***CANCELED*** | Final report (Email and/or client area) | TestQual |

The dates of this calendar might be slightly changed according to the development of the proficiency test during the year. However, any change would be notified to all participants announcing it on our website *www.TestQual.com*.

The **coordinator** of this proficiency test will be Jose Pedro Navarro. Any question regarding the development of the proficiency test 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 on 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 through the phone or email you used during your registration.
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 be updated via email of any changes regarding this proficiency test 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 least 24h before the shipping of the samples.

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 shopping cart you will enter the page with 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.

If you did not log in before you will be requested to do so and then the website will require you to submit your Limit Of Quantification (LOQ) for the parameters you will study. The compounds left as NA (NOT ANALYSED) will NOT appear in the Results form and therefore will not be able to send results for that parameters through the website.

Once the application has been sent, 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 11-15, being 11 the minimum participants for the proficiency test to take place.

## 5. PREPARATION AND QUALITY CONTROLS

**TestQual 148** scheme is a proficiency test based in the analysis of **pesticides** in **Parsley** that has been spiked with pesticide **standards**. The material will be bought in an ecological shop in Murcia and analysed by a subcontracted laboratory that holds the standard UNE-EN ISO/IEC 17025 into force.
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 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.

Before the samples are distributed, for the assessment of the homogeneity of the lot of samples prepared, ten samples from the lot will be selected randomly and analysed in duplicate by TestQual´s collaborator laboratory under repeatability conditions. 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, three samples are analysed, in duplicate, before, during and at the end (once all laboratories have sent the results) of the proficiency test.

## 6. TEST MATERIAL AND SAMPLE SHIPMENT

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. Specific delivery dates can change from the scheduled dates of the calendar, but all changes will be announced both in the website and by mail to the registered laboratories.
This PT will consist in a single round in which will be sent a sample of approximately **100-150 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 in insulated box that ensure the temperature conditions of the package during the whole shipment. The transit will be 1, 2 or 3 days to the destination country, depending on the location of the receiving laboratory. These boxes will be provided with either dry ice or cold packs 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.

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 it carefully and follow its instructions, as it can help to conserve correctly the sample and increase the reproducibility of the analysis.
You can request a digital copy of this document by letting us know through any communication channel.

## 7. CONCENTRATION RANGES, SIGMA OBJECTIVE AND ANALYTES

The range of concentration for the target analytes of this proficiency test might by between **10** and **200 µg/kg** approximately.
The **sigma objective ($\hat{\sigma}$)** which works in this scheme will be the **25 % of the assigned value**. This value has been chosen according to the experience of similar proficiency tests organized by TestQual.
The **possible pesticides** in the Parsley 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
Norflurazon
Nuarimol
Ofurace
Omethoate
op-TDE (DDD)
Oxadiazon
Oxadixyl
Oxamyl
Oxamyl-oxime
Oxydemeton-methyl
Oxyfluorfen
Paclobutrazol
Parathion
Parathion-methyl
Pebulate
Penconazole
Pendimethalin
Pentachloroanisole
Permethrin
1,1-(2,2-dichloroethylidene)
bis(4-methoxybenzene)
(methoxychlor metabolite)
Phenmedipham
Picoxystrobin
Piperonyl butoxide
Pyraclostrobin
Pyrazphos
Pyridaben
Pyrifenox
Pirimicarb
Pirimicarb-desmethyl
Pirimiphos-ethyl
Pirimiphos-methyl
Pyriproxyfen
pp-DDE
pp-TDE(DDD)
Prochloraz
Procymidone
Propham
Profenofos
Profluralin
Promecarb
Prometryn
Propachlor
Propamocarb
Propanil
Propargite
Propetamphos
Propiconazole
Propyzamide
Propoxur
Prosulfocarb
Prothiofos
Pyridafenthion
Pyrimethanil
Quinalpho
Quinoxyfen
Quintozene
Rotenone
Simazine
Simetryn
Spinosad A+D
Spirodiclofen
Spiromesifen
Spiroxamine
Sulfotep
Sulprofos
Tebuconazole
Tebufenozide
Tebufenpyrad
Tebupirimfos
Tecnazene
Teflubenzuron
Tefluthrin
Terbacil
Terbufos
Terbumeton
Terbuthylazine
Terbutryn
Tetraconazole
Tetradifon
Tetramethrin
Tetrasul
Thiabendazole
Thiacloprid
Thiamethoxam
Thiodicarb
Thiobencarb
Thiometon
Tolclofos-methyl
Triadimefon
Triadimenol
Triazophos
Trichloronate
Tridemorph

| | | |
|---|---|---|
| Trifloxystrobin | Trifluralin | Yodofenfos |
| Triflumuron | Vinclozolin | Zoxamide |

## 8. 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 through the website.
The method used for the analysis of each compound informed should be sent when filling up the results form.
The organizer should get the results before the fixed data of the scheme.
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.

## 9. 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 values by Kernel test, being explained in the final report which is the followed procedure in case there is more than one distribution.

The **assigned value (*X*)** is 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.

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.

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

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

In case this condition is not fulfilled, the participants of the scheme will be informed in the report, and the uncertainty will have to be taking into account for the assigned value assessment.

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

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

Being $b_i = \%_{DSRA} / 100$, and $\%_{DSRA}$ is the assigned 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 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:

| | | | |
|---|---|---|---|
| | $\lvert z \rvert$ | $\leq 2$ | Satisfactory |
| $2 <$ | $\lvert z \rvert$ | $\leq 3$ | Questionable |
| | $\lvert z \rvert$ | $> 3$ | Unsatisfactory |

False negatives: Any analyte not reported in the results that is in the sample above the limit of quantification previously established to the proficiency test established by the organization **(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:**

Once the samples are prepared ten of them will be chosen at random and sent to be analysed by TestQual's collaborator laboratory. Once received the results, a statistical evaluation will be performed, according to the IUPAC Harmonic Protocol.

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:

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

In the first place to check the criterion, $S_{sam}^2$ which is the estimated sampling standard deviation, was calculated from:

$$S_{sam} = (\frac{Vs}{2} - S_{an})$$

Firstly *Vs* is the variance of the sums $S_i$:

$$Vs = \sum \frac{(S_i - \bar{S})^2}{m-1}$$

Where $S_i$ was obtained from the addition of each duplicate result from the homogeneity; $\bar{S}$ is the mean of all $S_i$ and *m* is the number of samples (10 samples).

And secondly $S_{an}^2$ , which is the experimental estimate of analytical standard deviation, is obtained following the next formula:

$$S_{an}^2 = \frac{\sum D_i}{2m}$$

where $D_i$ is the result of the subtraction of each pair of replicates from the homogeneity and *m* is the number of samples.

In second place to check the criterion for sufficient homogeneity the critical value *c* was obtained from:

$$c = F_1 \cdot \sigma_{all}^2 + F_2 \cdot S_{an}^2$$

Being $F_1$ and $F_2$ constants with values equal to 1.88 and 1.01 respectively for 10 samples. $S_{an}^2$ has already been calculated and $\sigma_{all}^2$ is obtained from:

$$\sigma_{all}^2 = (0.3 \cdot \hat{\sigma})^2$$

where $\hat{\sigma}$ is the target standard deviation, which is calculated with the formula:

$$\hat{\sigma} = 0.25 \cdot \bar{X}$$

Being $\bar{X}$, the mean of the 20 values from the homogeneity.

**<u>Testing for sufficient stability:</u>**

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.

## 10. EVALUATION REPORT

Once received and statistically evaluated all of the participating laboratories results, TestQual will send a final report that summarizes the participation of each laboratory.
This final report will be received by the laboratories via e-mail in PDF format, but also can 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.

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.

## 11. 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, first edition 2010-02-01. Conformity assessment- General requirements for proficiency testing.

ISO13528:2015, second edition 2015-08-01. Statistical methods for use in proficiency testing by interlaboratory comparison.

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

SANTE/12682/2019, 1st January 2020, Guidance document on analytical quality control and method validation procedures for pesticides residues analysis in food and feed.