



TestQual, S.L.
(Proficiency Testing Schemes)

Pol. Industrial Oeste
Av. Principal, Parcela 21/1
CP 30169, San Ginés, Murcia
Telephone: 868 949 486 / 676 367 555

TestQual 136 PROTOCOL
Pesticides residues in White wine

1. INTRODUCTION

This document describes the **protocol** of the **TestQual 136** Proficiency Test, belonging to the analysis of **pesticides residues** in **White wine**.

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 136** 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
30/Oct/20 (Week 44)	Final date to receive applications	Participants
17/Nov/20 (Week 47)	Sample delivery	TestQual
04/Dec/20 (Week 49)	Final date to receive results	Participants
18/Dec/20 (Week 51)	Final report	TestQual

The dates of this calendar can slightly change according to the development of the proficiency test during the year. However, any modification in the dates will be announced in advance on our website www.testqual.com.

The **coordinator** of this proficiency test will be Jose Pedro Navarro. Any question regarding the development of the PT 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.

In case of urgency or if you have a doubt you can contact our team through the [Contact](#) tab from our website.

For those laboratories that require more than one contact per account or that works with more than one laboratories at the same time will have to contact us using the Contact tab to be instructed how to proceed.

APPLICATION FOR THE PROFICIENCY TEST

To participate in this proficiency test is needed to apply through the website.

In the Proficiency Tests Tab on our website will have to be selected the proficiency test you want to participate, by clicking it you will enter the page with general information regarding that proficiency test, the present document (the protocol) and at the bottom of the page will be a link to start the APPLICATION FORM, all inscriptions must be done before the scheduled date in the calendar.

During the application you will have to enter your Limit Of Quantification (LOQ) for the pesticides you will study. Those compounds that are left as NA (NOT ANALYSED) will NOT appear in the Results form and therefore will not be able to send results through the form. There are helping tools to help you go through your first application or you can share the LOQs from past participations in these rounds.

Once send the application, 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 by the organizer and the laboratory, and will be kept confidential at all times.

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 its geographical location, so 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 15, being 11 the minimum participants of any proficiency test.

5. TEST MATERIAL

TestQual 136 scheme is a proficiency test based in the analysis of **pesticides residues** in **White wine** that has been treated with pesticide **standards**. The material has been bought in an ecological shop and analysed by a subcontracted that holds the standard UNE-EN ISO/IEC 17025 into force.

The material is spiked with a solution with the analytes of the proficiency test, homogenised and stored in a refrigerator between +1 and +9°C without light until further distribution to participants.

For **homogeneity** assessment purpose, ten of the prepared samples are analysed in duplicate by TestQual collaborator laboratory under repeatability conditions.

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. 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 email to the registered laboratories.

About **100 ml** of test material will be sent by courier service (MRW, DHL or TNT, depending on the destination). The material will be sent in a sealed flask within a padded envelope.

The shipping costs are not included in the price displayed on the website. To get an approximation you can get your quotation by using the contact data at the end of this protocol.

A second test material can be requested if the participating laboratory justify, within two days from the reception of the sample, that the received package or the sample is damaged.

Along with the shipment, TestQual includes a document with extra instructions for the storage and analysis. 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 the extra instructions by letting us know through any communication channel you can find below, in this protocol.

7. CONCENTRATION RANGES, SIGMA OBJECTIVE AND ANALYTES

In this proficiency test, any of the analytes to inform are in a concentration higher than **10 µg/Kg**. 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 residues** in the White wine are from the list below:

2-Fenilfenol	Abamectina	Aclonifen
3,5-Dicloroanilina	Acefato	Acrinatrina
3-Hidroxicarbofurano	Acetamiprid	Alacloro
4,4-Diclorobenzofenona	Acetocloro	Aldicarb

Aldicarb sulfona	Ciprodinilo	Diflufenican
Aldicarba sulfóxido	Cletodim	Dimetenamida
Aldrin	Clofentezina	Dimetoato
Antraquinona	Clomazona	Dimetomorf
Atrazina	Cloquintocet-mexyl	Dimoxistrobina
Azaconazol	Clorantraliniprole	Diniconazol
Azinfos-etilo	Clorbromuron	Dioxacarb
Azinfos-metilo	Clorfenapir	Dioxation
Azoxistrobina	Clorfenvinfos	Dipropetrin
Benalaxilo	Clormefos	Disulfoton
Bendiocarb	Clorofenson	Ditalimfos
Benfluralina	Cloropropilato	Diuron
Benfuresato	Clorotoluron	Dodina
Bentazona	Cloroxuron	Emamectina
Bifentrina	Clorpirifos	Endosulfan-alfa
Bitertanol	Clorpirifos-metilo	Endosulfan-beta
Boscalida	Clorprofam	Endosulfan-sulfato
Brodifacum	Clorsulfuron	Endrin
Bromacilo	Clortal-dimetil	EPN
Bromociclono	Clortiofos	Epoxiconazol
Bromofos-etilo	Clotianidina	Espirodiclofeno
Bromofos-metilo	Coumaphos	Espiromesifeno
Bromopropilato	Cresoxim-metilo	Espiroxamina
Bromuconazol	Crimidina	Etaconazole
Bupirimato	Cyanofenphos	Etiofencarb
Buprofecina	Cyanophos	Etiofencarb-sulfona
Butamifos	Deltametrina	Etiofencarb-sulfóxido
Butafenacil	Demeton-S-metil	Etion
Butoxicarboxin	Demeton-S-metilsulfona	Etofenprox
Butoxido de Piperonilo	Desmetrina	Etofumesato
Butralina	Dialifos	Etoprofos
Buturon	Diazinon	Etoxazol
Cadusafos	Dicapthon	Etrimfos
Captan	Diclobenilo	Famoxadona
Carbaril	Diclobutrazol	Famphur (Famophos)
Carbendazina	Diclofention	Fenarimol
Carbofenotion	Diclofluanida	Fenazaquina
Carbofurano	Diclofop-metilo	Fenbuconazol
Cloroneb	Dicloran	Fenclorfos
Chlortion	Diclormid	Fenhexamida
Cianazina	Dicrotofos	Fenitrotrion
Ciazofamida	Dieldrin	Fenmedifam
Cicloxidim	Dietofencarb	Fenoxicarb
Ciflutrin	Difenilamina	Fenpiroximato
Cimoxanilo	Difenoconazol	Fenpropatrin
Cipermetrina	Difenoxuron	Fenpropimorfo
Ciproconazol	Diflubenzuron	Fensulfotion

TestQual 136 Pesticides in wine. Protocol. Rev. 00
TestQual, S.L. Proficiency Testing Schemes

Fention	Isofenfos	Oxamyl-oxima
Fentoato	Isofenfos-metilo	Oxidemeton-metilo
Fenuron	Isoproturon	Oxido de Fenbutaestan
Fenvalerato	Lambda-Cihalotrina	Oxifluorfen
Fipronil	Lenacilo	Paclobutrazol
Fonicamid	Leptophos	Paration
Fluacifop-P-butil	Linuron	Paration-metilo
Flucloralin	Lufenuron	Pebulato
Flucitrinato	Malaoxon	Penconazol
Fludioxinil	Malation	Pendimetalina
Flufenoxuron	Mecarbam	Pentachloroanisole
Flumetralin	Mefenpyr-diethyl	Permetrin
Fluometuron	Mepanipirima	Pertano (1,1-dicloro-2,2-bis (4-etilfenil)etano
Fluotrimazole	Mepronilo	Picoxistrobina
Fluquinconazol	Metacrifos	Piraclostrobina
Flusilazol	Metalaxilo	Pirazofos
Flutolanil	Metamidofos	Piridaben
Flutriafol	Metamitrona	Piridafention
Folpet	Metazacloro	Pirifenox
Fonofos	Metidation	Pirimetanil
Formotion	Metobromuron	Pirimicarb
Fosalon	Metolacloro	Pirimicarb-desmetil
Fosfamidon	Metomilo	Pirimifos-etilo
Fosmet	Metoprotrina	Pirimifos-metil
Furalaxilo	Metoxicloro	Piriproxifen
Furatiocarb	Metoxifenzida	pp-DDE
HCH-Alfa	Metoxuron	pp-TDE(DDD)
HCH-Beta	Metribucina	Procimidona
HCH-Delta	Mevinfos	Procloraz
HCH-Gamma (lindano)	Miclobutanil	Profam
Heptacloro	Molinato	Profenofos
Heptacloro-epoxido	Monocrotofos	Profluralin
Heptenofos	Monolinuron	Promecarb
Hexaclorobenceno	Monuron	Prometrina
Hexaconazol	Napropamida	Propacloro
Hexaflumuron	Neburon	Propamocarb
Hexazinona	Nitenpiram	Propanil
Hexitiazox	Nitrofenol	Propargita
Imazalil	Nitrotal-isopropil	Propetamfos
Imazametabenz-metil	Norflurazon	Propiconazol
Imidacloprid	Nuarimol	Propizamida
Indoxacarbo	Ofurace	Propoxur
Iprobenfos	Ometoato	Prosulfocarb
Iprodiona	op-TDE (DDD)	Protiofos
Iprovalicarbo	Oxadiazon	Quinalfos
Isazofos	Oxadixilo	Quinoxifeno
Isocarbofos	Oxamil	Quintoceno

Rotenona	Terbufos	Tolclofos-metil
Simacina	Terbumeton	Triadimefon
Simetryn	Terbutilacina	Triadimenol
Spinosad A+D	Terbutrina	Triazofos
Sulfotep	Tetraconazol	Tricloronato
Sulprofos	Tetradifon	Tridemorfo
Tebuconazol	Tetrametrina	Trifloxistrobina
Tebufenocida	Tetrasul	Triflumuron
Tebufenpirad	Tiabendazol	Trifluralina
Tebupirimfos	Tiacloprid	Vinclozolina
Tecnaceno	Tiametoxam	Yodofenfos
Teflubenzuron	Tiobencarb	Zoxamida
Teflutrina	Tiodicarb	
Terbacilo	Tiometon	

8. RESULTS EXPRESSION

Each participant laboratory must analyse the sample received according to their routine procedure, and fill up the RESULTS form of its private are of the website www.testqual.com with just one value.

The results should be expressed in $\mu\text{g}/\text{Kg}$. The number of significant figures and the units are shown as they were sent by the laboratories.

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 previously shown deadline for the test.

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 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:

	$ z \leq 2$	<i>Satisfactory</i>
$2 <$	$ z \leq 3$	<i>Questionable</i>
	$ z > 3$	<i>Unsatisfactory</i>

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 proficiency test (**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:

$$S_{sam} = \left(\frac{V_s}{2} - S_{an} \right)$$

Firstly V_s is the variance of the sums S_i :

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

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 σ_{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.

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 will be performed according the SANTE guide (SANTE/12682/2019 *Guidance document on analytical quality control*), referred to analysis under reproducibility 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 tab
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.