



# **TESTQUAL**

## **PROFICIENCY TESTING SCHEMES**

**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 181 PROTOCOL**

## ***Alcohols in Water***

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## SUMMARY OF CHANGES

Changes from previous revision are marked in blue or highlighted blue.

Rev01 → Calendar updated, improved comment and example of qualitative evaluation, updated bibliography ISO standard 13528 to 2022 edition.

Rev02 → Calendar updated

## 0. GLOSARY AND ABBREVIATIONS

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

## 1. INTRODUCTION

This document describes the **protocol** of the **TestQual 181** Proficiency Test (P.T.), belonging to the analysis of the following analytes in **Water**.

Group of analytes	Name
1	Alcohols

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 181** 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 (YYYY/mm/dd)	Activity	Carried out by
-	Deadline to reserve PT sample.	Participants
2023/09/13	Deadline to request participation*	Participants

Date (YYYY/mm/dd)	Activity	Carried out by
2023/09/ 18-20	Sample delivery	TestQual
2023/10/06	Final date to submit results	Participants
2023/10/13	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](http://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 be consulted by email to [jpnavarro@testqual.com](mailto: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 using 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. 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 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.

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 compounds 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 **3-12**, being 3 the minimum participants for the proficiency test to take place.

## **5. TEST MATERIAL. CONTROL AND DISTRIBUTION.**

TestQual **181** scheme is a proficiency test based in the analysis of Alcohols in Water 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 spiked with a solution with the analytes of the P.T., homogenised at a controlled temperature and stored in amber flasks, then stored in a dry, fresh place without light until further distribution to participants.

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 **200-250 ml** 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:

ROOM TEMPERATURE, The material will be sent in a vacuum packed, heat sealed plastic bag in dark conditions (opaque and padded envelope).

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 will be subcontracted to a courier previously homologated by TestQual.

The main criteria being the courier's delivery time to ensure the receipt of the sample is correct in the participant's facilities.

In addition to this, TestQual established 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. Acceptance of a second test material is dependant on the PT availability.

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 **1** and **30 mg/kg approximately**.

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

The list of possible alcohols in the matrix will be:

Methanol	2-Butanone	n-Butyl Acetate
Ethanol	sec-Butanol	n-Pentanol
Acetone	Iso-Butanol	Tetra Hydro
iso-Propanol	Tertiary Butanol	Furan
n-Propanol	n-Butanol	2-Furaldehyde
Methyl Acetate	iso-Propyl	n-Hexanol
Di-isopropyl-	Acetate	n-Heptanol
Ether	n-Propyl	
Ethyl Acetate	Acetate	

## 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](http://www.TestQual.com) with just one value per analyte/parameter.

The results should be expressed in **mg/kg**. The number of significant figures and the units are to be chosen by laboratories and will be displayed in the report as received by the participant.

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. 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.

## 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 values by Kernel test, 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.

In case of having a lower number of results than expected, the participants would be evaluated against an independent value from their own results, since the lower the number of results is used to obtain the assigned value, the higher is the chance of not identify necessary action signals in case the participants have/had an unknown bias. For this reason, both the assigned value obtained from robust statistic and the characterization value are compared between them, this way we check that there are not sustainable differences and depending on the number of results available and the uncertainty of the assigned value, TestQual will chose according to our internal procedure how the assigned value will be determined and evaluate participants, accordingly, showing it in the report.

If the consensus value is not used, then the characterization of the spiking and the uncertainty will be calculated based in a suitable model and according to ISO 13528 into force.

The **assigned value from characterization (X)** is derived by calculation of the following model:

$$X_{pt} = X_{char} + \delta_{hom} + \delta_{trans} + \delta_{instab}$$

Being  $X_{char}$  derived by calculation from the masses of solvent and solute,  $\delta$  denotes an error term due to ( $hom$ =homogeneity of test materials,  $trans$ =transport,  $stab$ =instability).



The **standard uncertainty ( $u_x$ )** is calculated by combination of uncertainties using the following model:

$$u(x) = \sqrt{u_{char}^2 + u_{hom}^2 + u_{trans}^2 + u_{instab}^2}$$

being  $u_{char}$  the standard uncertainty due to characterization,  $u_{hom}$  the standard uncertainty due to the differences between proficiency test items,  $u_{trans}$  the standard uncertainty due to the transport and  $u_{instab}$  the standard uncertainty due to the instability of the parameter during the proficiency test.

Contributions due to inhomogeneity, stability and transportation will be considered negligible if:

- Lot of samples is not inhomogeneous (statistical check described below).
- Samples are stored in freezer and sent in the lowest transit time (1-3 days).
- Lot of samples is stable, or instability is acceptable (see stability check below).

If some of these contributions could not be considered negligible, they will be calculated and accounted in the assigned value and its uncertainty.

Likewise, and as mentioned, the characterization value will be compared to the participants' consensus and only used if there are not sustainable differences between assigned values. If the assigned values are too different, no evaluation or informative evaluation would be issued, explaining the reason in the report.

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.

The relative standard deviation will be obtained from the Horwitz-Thomson equation and can estimate to be around 10%. See below evaluation for qualitative results.

**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 $	$\leq 2$	Satisfactory
$2 <$	$ z $	$\leq 3$	Questionable
	$ z $	$> 3$	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  $U_x$  is the uncertainty of the assigned value.

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

	$ z' $	$\leq 2$	Satisfactory
$2 <$	$ z' $	$\leq 3$	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.

The evaluation 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.

For participants that send their results in **quantitative format** the previous scores will be calculated to evaluate the performance (z-score or z'-score).

For participants that send their results in **qualitative format** the following evaluation\* will be used:

Concentration\_1<Concentration\_2<Concentration\_N<Concentration\_N+1

score	Present concentration					
Reported result by participant	Concentration_1	Concentration_2	Concentration_3	Concentration_4	Concentration_5	Concentration_6
Concentration_1	0,0	-1,9	-3,3	-4,3	-5,0	-5,6
Concentration_2	1,5	0,0	-1,7	-2,9	-3,8	-4,4
Concentration_3	1,9	-1,9	0,0	-1,4	-2,5	-3,3
Concentration_4	7,5	4,0	1,7	0,0	-1,3	-2,2
Concentration_5	10,0	6,0	3,3	1,4	0,0	-1,1
Concentration_6	12,5	8,0	5,0	2,9	1,3	0,0

\*Each concentration (or range) will be obtained taking into account experience, knowledge and the relative standard deviation. Tables might be modified to procure the fitness for purpose.

Example: If participant sends result "<Concentration\_2" and the assigned value is closer to Concentration\_1 than Concentration\_2, then the evaluation of aforementioned participant would be: score=1,5

(Present concentration=Concentration\_1; Reported concentration=Concentration\_2)

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 (**1 mg/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. (**1 mg/kg**).

**Testing for sufficient homogeneity:**

Once the samples are prepared a number of them will be chosen at random and sent to be analysed by TestQual’s collaborator laboratory in duplicate in repeatability conditions. The number of samples analysed will be chosen based on: TestQual’s experience homogenizing this or similar matrixes, the number of samples analysed is representative to the number of samples prepared in the lot, as well as other factors that, if taken into account, would be mentioned in the final report along the number of samples analysed. Once received the results, a statistical evaluation will be performed, with a modified calculation from 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:

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

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.

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 obtained according to ISO 13528 into force. For example:  $F_1$  equals to 1.88 and  $F_2$  to 1.01 for 10 samples, while it would be 2.1 and 1.43 respectively for  $F_1$  and  $F_2$  with 7 samples. The less samples analysed the higher  $c$  will be, making harder the criteria to consider the lot homogeneous.

$S_{an}^2$  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:

$$\hat{\sigma} = (0.1 / 100) \cdot \bar{X}$$

Being  $\bar{X}$ , the mean of the 20 values from the homogeneity and the 0.1 an approximation of the relative standard deviation obtained from the Horwitz-Thomson equation considering the expected possible concentrations.

If  $S_{sam}^2 < c$  is true, then the lot prepared will be considered sufficiently homogeneous and only then it would be distributed. 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.

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

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

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 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](http://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](mailto: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:	<a href="#">Contact</a>
Email:	<a href="mailto:jpnavarro@testqual.com">jpnavarro@testqual.com</a>
Office phone:	+34 868 94 94 86
Mobile phone:	+34 676 367 555

**11. 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.

ISO13528:2022, 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

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