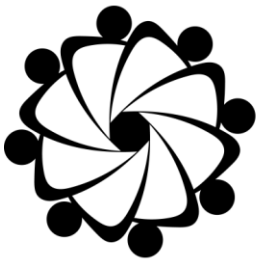

TESTQUAL
PROFICIENCY TESTING SCHEMES

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

PROFICIENCY TEST TestQual 22A
PROTOCOL
Non-volatile matter in Ethanol (solvent)

Summary of changes

Changes marked with blue or highlighted blue.
Rev01 →
·Acceptance deadline of applications updated.
·Text added regarding LOQs and applications acceptance.
·More info added about subcontracting done.
·If z'-score is issued, it will be accredited and the difference against z-score will be included in the report.
·Other minor changes
Rev02 → Calendar updated
Rev03 → Calendar updated

INDEX

0. GLOSARY AND ABREVIATIONS

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 22A** Proficiency Test (P.T.), belonging to the analysis of **Non-volatile matter** in **Ethanol (solvent)**.

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 22A** 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
26/May/22	Deadline to send application (acceptance depends on availability)	Participants
31/May/22	Sample delivery	TestQual
17/Jun/22	Final date to submit results	Participants
30/Jun/22	Final report (Email and/or client area)	TestQual

*Participants are requested in the application to submit their LOQ/LOQs, for PTs with multiple possible analytes, if participants analyse above a certain percentage (as described in our internal

procedure) of present/planned analytes the participation is accepted, a laboratory code is granted and sent by email to confirm the participation acceptance to the user of the TestQual's account.

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. 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 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 those 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 always kept confidential, 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.

TestQual can anticipate that the number of participants of this proficiency test will be around 5, being that the minimum participants for the proficiency test to take place

5. PREPARATION. DISTRIBUTION AND CONTROL

TestQual 22A scheme is a proficiency test based in the analysis of **Non-volatile matter** in **Ethanol (solvent)**, for that a known amount of salt (table salt or any other salt with enough fusion temperature to withstand the analysis) will be dissolved in a known amount of ethanol, then bathed in ultrasounds and homogenised for enough time to ensure complete solution of the chosen salt in the ethanol. No separation will be made as the ethanol will not be oversaturated (see possible concentration ranges in section 7).
Samples of more than 200ml will be prepared in amber flasks and stored in a fresh (temperature controlled), dry place without sunlight until the dispatch.
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.

Before the samples are distributed, random samples will be selected to be analysed in duplicate to assess the homogeneity of the lot, likewise, random samples will be reserved to be analysed in duplicate at different times for stability assessment purpose.

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.

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 **200-250 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:
Room temperature, with enough padding and an padded envelope to ensure the sample arrives without leakage or breaking.

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.

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, if no remaining samples would be available if the participant made any payment in advance TestQual will return the money or reach another agreement with the participant.

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 correctly conserve 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 AND RESULTS EXPRESSION

For this proficiency tests the range of concentration for the target analytes might by between **1** and **5 mg/L .**

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 and the expanded uncertainty of the result.

The results should be expressed in **mg/L**. 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 submitting your results you can contact the coordinator of the PT for guidance or help.

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.

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

Xpt=Xchar+ δhom+ δtrans+ δinstab

Being Xchar derived by calculation from the masses of solvent and solute, δ 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 uchar the standard uncertainty due to characterization, uhom the standard uncertainty due to the differences between proficiency test items, utrans the standard uncertainty due to the transport and uinstab 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.

Proficiency assessment (En-score): it is a proficiency assessment that evaluate results against the claimed uncertainty, and it is calculated using the following formula:

$$En=\frac{x_i-x_{PT}}{\sqrt{U^2(x_i)+U^2(X_{PT})}}$$

The denominator should not be larger than the deviation in the numerator, therefore the criteria for interpretation of En-score results are:

En<-1	Questionable (Need to review uncertainties)
-1<En<+1	Satisfactory results
En>1	Questionable (Need to review uncertainties)

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/L)**. TestQual will qualify this results as insatisfactory.

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 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:

$$\hat{\sigma} = 0.15 \cdot \bar{X}$$

Being $\bar{X}$, the mean of the 20 values from the homogeneity and the 0.15 an approximation of the obtained from the Horwitz-Thomson equation for expected standard deviation for the proficiency test considering the expected possible concentrations.

Testing for sufficient stability:

Three samples will be analysed, in duplicate, before 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:

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

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

Once received and statistically evaluated all 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 or an email notifying that the report is now available to be downloaded from the private area of each participant in.
If desired, the laboratory may request the report in paper, and it will be sent to its laboratory by mail.

If 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.

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

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.

ISO13528:2015, 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

END OF DOCUMENT