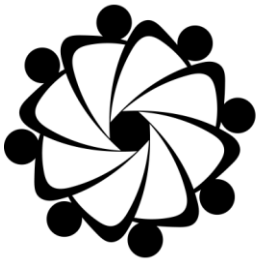

TESTQUAL
PROFICIENCY TESTING SCHEMES

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(Proficiency Testing Schemes)

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TestQual 186 PROTOCOL

Wastewater in situ and Continental water in situ

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 186** Proficiency Test (P.T.), belonging to the analysis of the following analytes of physicochemical parameters and sampling analysis in **Wastewater in situ and Continental water in situ**.

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 186** 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
2023/10/14	Deadline to request participation*	Participants
(in situ) 2023/10/19	PT Takes place	TestQual & participants
2023/11/03	Final date to submit results	Participants
2023/12/15	Final report (Email and/or client area)	TestQual

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 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 ***7-11***, being 11 the minimum participants for the proficiency test to take place.

5. LOCATION, MATRIX, CONDITIONS, PROCEDURE

In case of doubt, contact with the coordinator.
Coordinator mobile phone: +34- 676 367 555

5.1. Meeting point and time.

In order to participate, it will be necessary to have provided the organizer with a list with the full name and ID of those attending the exercise (only 2 people may attend the exercise from each laboratory). Aforementioned list must be provided at least 48 hours before the day of the exercise.

Participants can go directly to the analysis/sampling point or contact the coordinator to establish a meeting point and go together in different cars.

ADDRESS:

The addresses and times will be provided by email to the participants and in the exercise instructions.
All analysis and sampling points are within the **Murcia region (Southeast SPAIN).**

We will distribute by email to the registered participants the instructions with photographs, indications and location on Google maps, both to reach the sampling and analysis points and the procedure that will be followed in the proficiency test.

An email reminder with the date, time and location of the start of the exercise will be sent a few days before the exercise takes place.

EXERCISE DURATION

The proficiency test will begin at 9:30 a.m. with the wastewater module, at the end of which the coordinator and participants will move (using their own vehicles) to the next sampling and analysis point, where food will be offered (examples: Spanish omelets, cold meats like serrano ham, pizzas, some local food, etc. similar to a Spanish brunch without hot meals. For drinking: cola, still water. Plates, cardboard cutlery, toothpick, cardboard glass, etc. will be provided), after resting, the proficiency test will resume before 12:00 to finish the proficiency test between 13:00 and 14:00 (estimate based on experience).

Proficiency test PLAN

1st in situ analysis and on-site sampling of wastewater
2º Go to the next sampling point.
3rd Rest with food offered by the organizer (no extra cost).
4º In situ Analysis of parameters and sampling in situ continental waters.

5.2. PROCEDURE

Before the start of the exercise, the organizer will give a brief explanation of how it will proceed and provide each participant with an opaque TestQual folder with the protocol, the results' form (Annex I), a pen, a "satisfaction survey + feedback" , delivery notes and adhesive stickers with a laboratory identification code (it will be a different code from the participation code so that only the organizer is able to identify the laboratories) that will be used to label the samples taken.

The satisfaction survey must be turned in at the end of the proficiency test. The survey is anonymous and is a very useful tool for improving our services, we thank being as honest as possible. Upon receiving the final report, the results of the satisfaction survey can be modified, although in this case it would not be possible to maintain the anonymity of the answers.

If the situation requires it, to ensure the safety and well-being of all participants, the mask might be mandatory along gloves. The need or relevant protection measures will be indicated in the instructions that will be provided to the participants.

A copy of the current protocol and instructions with the exercise protocol will be provided to be shared by participants.

The analysis may be timed by the coordinator. The coordinator might take photos during the proficiency test, all faces will be blurred/edited to now show participants faces nor their laboratory. The results delivery form (Annex I) must indicate the sampling point (if applicable) and the corresponding analysis/measurement hours.

5.3. ON-SITE ANALYSIS CONDITIONS.

As indicated by the coordinator and reflected in the instructions provided before the proficiency test, the participant will analyze the following parameters in situ:

- Temperature (ºC)
- pH. (pH units)
- Conductivity at 25ºC. (mS/cm)
- Dissolved Oxygen Saturation (mg O2/L)
- Turbidity (Nephelometric Turbidity Units)

The participant will use the equipment, containers and other material necessary to carry out the measurements.
Note: The sample volume to be taken will depend on the participant and the equipment available. A minimum of 500ml is required.

5.4. CONDITIONS OF SAMPLE TAKING.

The sampling will be carried out by the participants using their own means, so each participant must provide all the necessary material, containers (minimum 500ml) and preservatives that are necessary. As a guide, TestQual recommends following the indications of the ISO 5667-3 Standard.

Note: The sampling item will be available to be carried out manually or by telescopic pole. From TestQual we recommend bringing a pole in case it is necessary.

Participants will be able to choose between carrying out a sampling plan or taking a specific sample, so that the sampling is evaluated together/through the evaluation of the parameters:

- Chemical Oxygen Demand (COD) (mg/L)
- Solids in suspension (mg/L)

All laboratories that carry out a sample collection must carry out a second one, using the same procedure, said sample will be delivered to the coordinator.

The sample that will be provided to the coordinator must have at least the identifying adhesive label delivered by the coordinator at the beginning of the proficiency test, although it may carry more stickers or notes from the laboratory, as long as they allow correct reading of the TestQual sticker (if they are identifying, these will be removed prior to analysis except for the TestQual sticker, to guarantee the confidentiality of the samples).

All correctly labeled samples will be properly stored until their subsequent analysis by the collaborating laboratory. All samples delivered to the coordinator will remain together until their subsequent delivery to the collaborating laboratory (accredited according to ISO 17025 in force for the tests in question).

5.5 END OF THE EXERCISE

The exercise will conclude when all the modules proposed for the exercise have been completed.
The labeled samples must have been delivered to the coordinator and the delivery note must be signed as proof of his participation and that the sample/s have been delivered. TestQual ensures that the samples will be analyzed respecting the anonymity of the participating laboratories, in such a way that only TestQual can know which sample belongs to which participant.
Participants will keep a copy of the delivery note signed by the coordinator. In the same way, the anonymous satisfaction survey must be handed to the coordinator (or later sent via email, but losing the anonymity).
The results may be delivered on site (except for the tests carried out in each laboratory) to be delivered later, via email, within the period stipulated in this protocol.

6. RESULTS EXPRESSION

The results will be reported in the result's form using the requested units.
Results will be displayed in the report as received by the participant.
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.

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.

In this case, the assigned relative standard deviation can be seen in the table below.
This value is fixed by relevant normative, however, in case the evaluation is not useful, an alternative evaluation can be requested by the participant, where the assigned relative standard deviation will be equal to the experimental standard deviation.

PARAMETER	UNITS	Relative standard deviation (Normative)
pH	*pH units*	*0,1 (BOJA 109/2015)*
Conductivity (at 25ºC)	*mS/cm*	*20% (BOJA 109/2015)*
Dissolved oxygen	*mg O_2/L*	*20% (BOJA 109/2015)*
Temperature	*ºC*	*0,5 ºC (BOJA 109/2015)*
Turbidity	*NTU (Nephelometric Turbidity Units)*	*25% (BOJA 109/2015)*
COD	*mg O_2/L*	*30% (BOJA 109/2015)*
Solids in suspensión	*mg/L*	*25% (BOJA 109/2015)*

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 <	$\lvert z' \rvert$	≤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.

Evaluation of the site

The analysis will be carried out by TestQual's collaborator laboratory in duplicate in repeatability conditions. The number of analysis will be chosen based on: TestQual's experience with this or similar matrixes, as well as other factors that, if taken into account, would be mentioned in the final report along the number of analysis carried out. 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:

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

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.

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: F1 equals to 1.88 and F2 to 1.01 for 10 samples, while it would be 2.1 and 1.43 respectively for F1 and F2 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 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:

$$\hat{\sigma} = (\%_{tRSD} / 100) \cdot \bar{X}$$

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

If $S_{sam}^2 < c$ is true, then the site will be considered sufficiently homogeneous. If the results from the homogeneity test does not meet the criteria TestQual would evaluate the participants with informative purposes.

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.
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, 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

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