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 192 PROTOCOL

Metals, anions, contaminants and physicochemical parameters in Table salt

CANCELLED

INDEX

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 192** Proficiency Test (P.T.), belonging to the analysis of **Metals, anions, contaminants and physicochemical parameters** in **Table salt**.

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 192** 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
Cancelled	End of planification and reservation of samples	Participants
Cancelled	Application deadline (acceptance of applications depends on PT availability)	Participants
Cancelled	Sample delivery	TestQual
Cancelled	Final date to submit results	Participants
Cancelled	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.

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 up to 15-16.

5. TEST MATERIAL

TestQual 192 scheme is a proficiency test based in the analysis of **Metals, anions, contaminants and physicochemical parameters** in **Table salt**. The material has been bought in a specialised shop in Spain and analysed by a subcontracted laboratory that holds the standard UNE-EN ISO/IEC 17025 into force.

The material will be poured into a homogenizer at a controlled temperature and then spiked with the analytes selected for this proficiency test. After complete homogenization samples will be packed in vacuumed and thermosealed plastic bags and stored in a cold, dry place, which is temperature-controlled until further shipping to the participants.

Two kinds of samples will be prepared: one with **500g (sample A)** and other with **500g (Sample B).**

Analysis to be carried out in each sample will be specified in the sample instructions that will be sent to inscribed participants before shipping 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. 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 may change from the

scheduled dates of the calendar, but any change will be announced both on the website and by email to the participants.

The test material will be sent by courier (MRW, FedEx or DHL depending on the destination and transit time estimated). The material will be sent in a vacuum packed, heat sealed plastic bag in dark conditions.

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 arrives damaged, defective or not valid the participating laboratory will have to notify this situation to the coordinator before two working days to get another sample.

Before the shipment, TestQual will send the instructions for storage and analysis (which analysis to perform in each sample) via email as well as 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/PARAMETERS.

The **target standard deviation or sigma objective ($\hat{\sigma}$)** which works in this scheme will be the shown in the table below.

The possible **Metals, anions, contaminants and physicochemical parameters** in the Table salt are from the list below:

Analyte	Units	If present, expectable concentration above:	Maximum Standard deviation ($\hat{\sigma}$) (%)	Recommended analysis technique

Calcium	Ca, % (m/m)	0.1	30	Titration
Magnesium	Mg,% (m/m)	0.03	30	Titration

Anions

Analyte	Units	If present, expectable concentration above:	Maximum Standard deviation ($\hat{\sigma}$) (%)	Recommended analysis technique
Chlorides	%, Expressed as NaCl of all the dry matter (m/m)	58.5	30	Titration
Ferrocyanide	mg/Kg Expressed as ferrocyanide anhydre	2.9	30	UV-VIS
Nitrites	mg/Kg	10	30	Titration
Sulphates	%	0.06	30	Gravimetry
	%	0.1	30	Calculated
	%	0.1	30	Calculated
Iodides	mg/kg Iodides expressed as Iodine	10	20	Titration

Physicochemical parameters

Analyte	Units	Maximum Standard deviation ($\hat{\sigma}$) (%)	Recommended analysis technique
Moisture/Humidity at 105ºC	(% (m/m)	30	Gravimetry 105ºC

Insoluble residue in water	%	30	Gravimetry

Metals (some or all might be present/spiked)

Analyte	Units	If present, expectable concentration above:	Maximum Standard deviation ($\hat{\sigma}$) (%)	Recommended analysis technique
Arsenic (As)	Mg/kg	0.25	20	ICP-MS
Cadmium (Cd)	Mg/kg	0.25	20	ICP-MS
Copper (Cu)	Mg/kg	0.25	20	ICP-MS
Lead (Pb)	Mg/kg	0.25	20	ICP-MS
Mercury (Hg)	Mg/kg	0.05	20	AAS
Potassium (K)	Mg/kg	10	20	ICP-MS

Metals less common that might be positive too:

Analyte	Units	If present, expectable concentration above:	Maximum Standard deviation ($\hat{\sigma}$) (%)	Recommended analysis technique
Antimony (Sb)	Mg/kg	0.25	20	ICP-MS
Chorme (Cr)	Mg/kg	0.5	20	ICP-MS
Cobalt (Co)	Mg/kg	0.25	20	ICP-MS
Manganese (Mn)	Mg/kg	0.25	20	ICP-MS
Nickel (Ni)	Mg/kg	0.25	20	ICP-MS

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. 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.

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 evaluation against the characterization is not accredited, analytes evaluated with this assigned value will not be accredited.

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)*** 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 that the uncertainty is not negligible. For the parameters/analytes in which this situation occurs, the evaluation will be issued outside the accreditation as z'-score according to the following calculation:

$$z'\text{-score} = (x_i - X)/\sqrt{\hat{\sigma}^2 + U_x^2}$$

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
	$\lvert z' \rvert$	>3	Unsatisfactory

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.

The target standard deviation will be the robust standard deviation while it is below the maximum target standard deviation stated in section 7 of this protocol for each analyte/parameter.

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

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 (see table from section 7 of this protocol). 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. (see table from section 7 of this protocol).

Testing for sufficient homogeneity:

Ten samples will be chosen at random and sent to be analysed by TestQual's subcontracted laboratory in duplicate in repeatability conditions.

Once received the results, a statistical evaluation will be performed, with the homogeneity evaluation of 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:

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

Being $S_{sam}^2$the estimated sampling standard deviation, obtained from the variance of the results sums and the experimental estimate of analytical standard deviation (S_{an}), which in turn is obtained from the differences between replicates of the same sample. Lastly, c is the limit value, which is obtained as ISO 13528 states, it takes into account two constants, obtained from two significance groups, which are multiplied with a term related to the target standard deviation and the S_{an}.

If $S_{sam}^2 < c$ is true, then the lot prepared will be considered sufficiently homogeneous and only then it would be distributed. With this test what we achieve is to check if the intra-sample deviation is lower than the inter-sample deviation.

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. With these values, a study will be performed according to the guide. The acceptance criteria to ensure the samples have been stable during the whole P.T. 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/S

Upon completion of the analysis period TestQual will conduct a comprehensive statistical evaluation of all participant laboratories' results. Subsequently, TestQual will either issue an individual report, summarizing each participant's performance, or a global report. Regardless of the

type of report, the reports will be sent via email in PDF format or made available for download from the client area on www.TestQual.com.

In the case an individual report is issued, participants are given a 25-day period to review and, if necessary, lodge an appeal against the evaluation of the proficiency program or report any identified mistakes. Following this appeal window, TestQual will proceed to release the global report within the upcoming 5 working days, with the complete performance of all laboratories.

Participants also have the option to request "individual" reports, specific to the groups of analytes given in the proficiency test. It's important to note that these individual reports are not accredited and serve as a summary, cross-referencing the global report to ensure comprehensive information is given. This way, regardless of if an individual report was issued or not, all participants that send results will receive a global report.

All appeals and requests for individual reports must be submitted via email to jpnavarro@testqual.com. The appellation period spans 25 days, allowing participants to communicate concerns or disputes related to results, evaluations received, or any mistakes identified. Reports can be appealed for mistakes found even outside the formal appellation period, ensuring a mechanism for ongoing quality assurance.

This structured process ensures fast reporting, transparency, accountability, and the provision of comprehensive reports tailored to the specific needs and interests of each participant in TestQual's proficiency testing program.

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

END OF DOCUMENT