



TestQual, S.L.
(Proficiency Testing Schemes)

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FINAL REPORT TestQual 92
Dithiocarbamates in potato

LABORATORY:

AGQ MAROC

LABORATORY CODE:

TQ17-092-015

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1. SUMMARY

The aim of the **TestQual 92 potato** proficiency test (PT) is to obtain information about the quality and accuracy of the results sent by the participating laboratories.

This proficiency test is based on the analysis of **dithiocarbamates** in **potato**. After the evaluation of the applications (depending on the LOQ of the laboratory and its geographical location), **fifteen laboratories** were accepted, and the test material was sent in **November 2017**. The assigned concentration value (X) for the analyte present in the sample was calculated by consensus among participating laboratories.

The laboratory results were considered satisfactory if the z-score parameter was $|z| \leq 2$, questionable if $2 \leq |z| \leq 3$ and unsatisfactory if $|z| > 3$.

The most important dates of the proficiency test have been:

DATE	ACTIVITY	CARRIED OUT BY
06/11/2017	Closing date for applications	Participants
07/11/2017	Sample shipment	Organizer
07/12/2017	Closing date to send results	Participants
December	Provisional and final report publication	Organizer

Program coordinator: María Ángeles Garrido (magarrido@testqual.com)

Each laboratory was assigned a unique code to participate in the Proficiency Test. These codes were only known by the laboratory and the organizer (TestQual), and they were confidential during and after the PT.

If any participant wants to appeal against the evaluation of their performance, their allegations must be sent by mail to magarrido@testqual.com.

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2. TEST MATERIAL

About **15 Kg** of **potato** were bought to a local provider in Murcia and were spiked with a solution containing the following commercial product:

COMMERCIAL PRODUCT	ACTIVE COMPONENT
Thiram 80 GD (Adama)	Thiram

Potato was cut into small pieces, contaminated with the previous solution and then submerged into liquid nitrogen. Once fully frozen it was ground into a fine powder and poured into a homogenizer to ensure complete homogeneity

Then, **350 g** portions of frozen powder were packaged in plastic bottles with pressure seal and screw cap before labelling them. Each packaged sample was stored at a temperature below -20 ° C until further delivery to each participating laboratory.

Ten of these samples were analyzed by our collaborating laboratory to check their homogeneity, and two more were analyzed for stability tests. These tests were performed by a subcontracted laboratory (Laboratorio Químico Microbiológico, S.A.) that holds the ISO standard UNE-EN ISO/IEC 17025:2005.

Once ensured the homogeneity of the samples, these were sent to the participants by courier, under the proper conditions for their conservation.

3. ANALYSIS

Each participant had to analyse the sample, detect and quantify the presence of **dithiocarbamates** in the test material according to their own procedures. Then, fill in with just one result the Results Form of its private area of the website www.testqual.com, expressing the results in **µg/Kg**.

The techniques and analysis method used were chosen by the laboratories, and they are shown later in this report.

4. STATISTICAL RESULTS EVALUATION

The number of significant figures and the units are shown as they were sent by the laboratories.

The **assigned value (X)** was 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.

TestQual considers as an **extreme outlier** any data which differs more than **50%** to the median of all results reported by the laboratories. These extreme values are not included in the calculation of the assigned value.

The **standard uncertainty (u_x)** was calculated using robust statistics from the following formula:

$$u_x = 1,25 \cdot (s^*/\sqrt{p})$$

Being s^* the robust standard deviation of the data and p the number of results considered.

The **standard deviation for proficiency assessment**, also named **target standard deviation ($\hat{\sigma}$)**, comes from this formula:

$$\hat{\sigma} = b_i \cdot X$$

Being $b_i = \%_{\text{DSRA}}/100$, and $\%_{\text{DSRA}}$ is the assigned **relative standard deviation**.

In this case, the assigned relative standard deviation is **30%**. This value was chosen based on the European rule N°519/2014 of May 16th of 2014.

Proficiency assessment (z-score): This parameter shows the competence and accuracy of the laboratory. It is calculated using the following formula:

$$z = (x - X) / \hat{\sigma}$$

Where x 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 were:

$$\begin{aligned} |Z| \leq 2 & \text{ Satisfactory} \\ 2 < |Z| \leq 3 & \text{ Questionable} \\ |Z| > 3 & \text{ Unsatisfactory} \end{aligned}$$

False negatives: are results that show the presence of analytes in the sample over the quantitation limit of the proficiency test previously established by the organization (**10 µg/Kg**), that have not been informed as quantitated by the participant laboratory. To these results a z-score is assigned derived of the assignment as result its LOQ/2.

False positives: are results that show the presence of analytes that were not present in the test material, and reported by the participant at concentrations higher than the limit of quantification of the PT (**10 µg/Kg**).

Testing for sufficient homogeneity: Ten of the samples were analysed by the collaborating laboratory. Once received the results, a statistical evaluation according to the IUPAC Harmonic Protocol was performed.

The acceptance criterion to ensure that the randomly chosen samples are homogeneous was that:

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

Where S_{sam} is the estimated sampling standard deviation, and

$$c = F_1 \cdot \sigma_{\text{all}}^2 + F_2 \cdot S_{\text{an}}^2,$$

being $F_1 = 1,88$ and $F_2 = 1,01$ (for 10 samples) and

$$\sigma_{\text{all}}^2 = (0,3 \hat{\sigma})^2$$

where $\hat{\sigma}$ is the target standard deviation, and $\hat{\sigma} = 0.30 \cdot \bar{X}$ (\bar{X} is the average of the values).

Testing for sufficient stability: three samples were analysed, in duplicate, before, during and at the end (once all laboratories had sent the results) of the PT. With these values, a study was performed according the SANCO guide into force (SANCO/12571/2013 Guidance document on analytical quality control), referred to analysis under repeatability conditions. The acceptance criteria to ensure the samples have been stable during the PT are the following:

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

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

Being $|(X_{t1} - X_{tn}) / X_{t1}|$ the difference between the average of the samples analysed before (X_{t1}), during (X_{t2}) and at the end (X_{t3}) of the PT.

*The results of both tests are shown later in this report.

5. RESULTS

The results sent by the laboratories and their proficiency assessment are shown below:

CARBON DISULFIDE*¹ (X= 734,53µg/Kg) (u _x = 85,17µg/Kg)			
LABORATORY CODE	X(µg/Kg)	LOQ (µg/Kg)	z-score
TQ17-092-001			
TQ17-092-002	1039	10	1,4
TQ17-092-003	789	50	0,2
TQ17-092-004	700	10	-0,2
TQ17-092-005	1654* ^A	10	4,2
TQ17-092-006	1462* ^A	100	3,3
TQ17-092-007	587	10	-0,7
TQ17-092-008	1622,8* ^A	50	4,0
TQ17-092-009	710	40	-0,1
TQ17-092-010	899,3	20	0,7
TQ17-092-011	885	0,05	0,7
TQ17-092-012	1390* ^A	50	3,0
TQ17-092-013	810	100	0,3
TQ17-092-015	426	50	-1,4
TQ17-092-016	500	10	-1,1

Legend:

LOQ: Limit of quantification.

NA: Analyte not analyzed by the laboratory.

NO: Analyte not informed (i.e. not detected) by the laboratory.

***A:** Result considered as an extreme outlier. Extreme outliers are not included in the statistical calculations of the assigned value.

***1:** This proficiency test has been performed by **15** laboratories, the minimum required to consider valid the statistics applied. Nonetheless, 1 of the laboratory has not sent their results (TQ16-092-001). In addition, not all laboratories have reported acceptable values for the calculation of the assigned value; because of that, **the uncertainty of the assigned value cannot be considered negligible**. Still, TestQual has decided to statistically evaluate all the laboratories and provide them a **z-score for information purposes only**.

TABLE 1: ASSIGNED VALUE AND TARGET STANDARD DEVIATION

ANALYTE	NUMBER OF DATA*	ASSIGNED VALUE (µg/Kg)	UNCERTAINTY (µg/Kg)	%DSR _A	TARGET SD (µg/Kg)	ROBUST SD (µg/Kg)
CARBON DISULFIDE	10	734,53	85,17	25	220,36	215,46

**Results considered extreme outliers have not been considered.*

TABLE 2: SATISFACTORY, QUESTIONABLE AND UNSATISFACTORY Z-SCORES

ANALYTE	NUMBER OF Z-SCORES*	% SATISFACTORY	% QUESTIONABLE	% UNSATISFACTORY
CARBON DISULFIDE	14	71,43	7,14	21,43

**Every result has been assigned with a z-score, including the results considered as extreme outliers.*

TABLE 3: FALSE POSITIVES AND FALSE NEGATIVES

FALSE POSITIVES:

No false positives have been reported for this proficiency test.

FALSE NEGATIVES:

No false positives have been reported for this proficiency test.

NOTES FROM PARTICIPANTS:

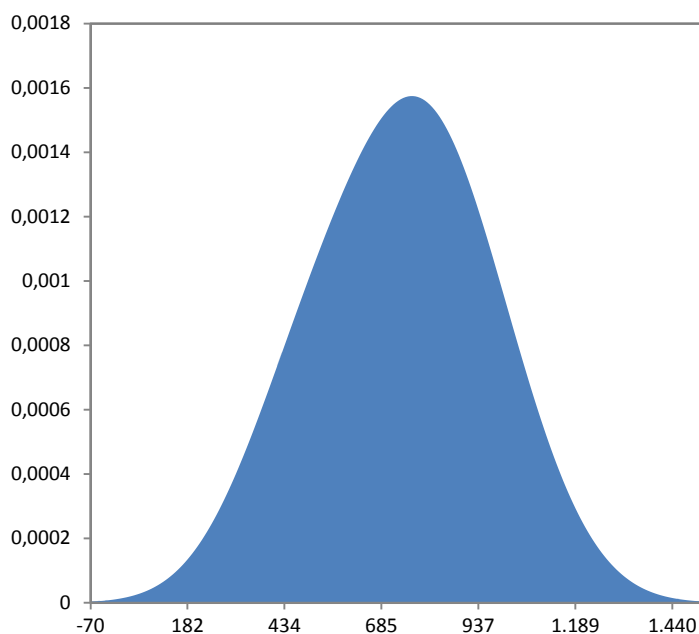
TQ17-092-001 Informed that they will not submit any results.

DISTRIBUTION OF RESULTS (KERNEL DENSITY):

Distribution of all the results sent by the laboratories, not including the results considered as extreme outliers.

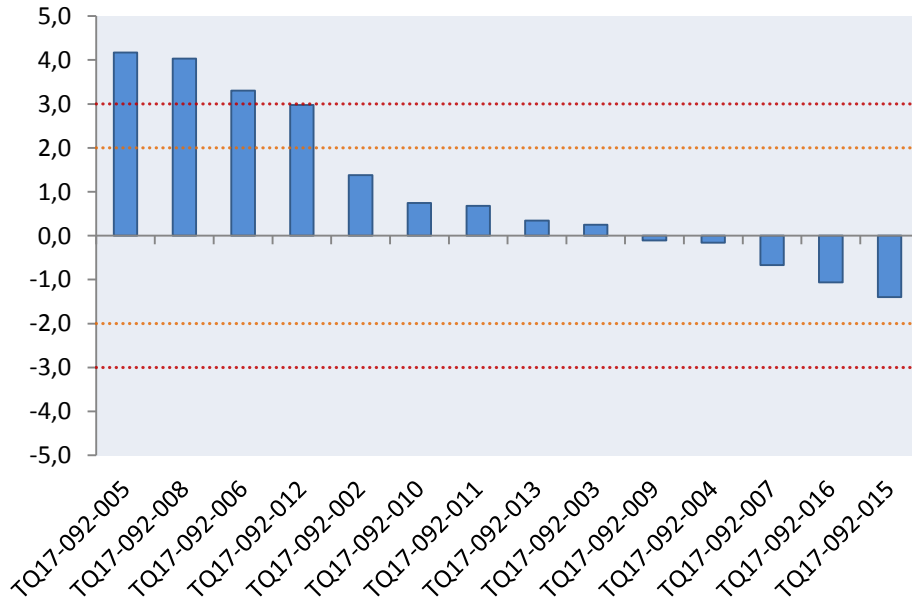
CARBON DISULFIDE

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6. ASSIGNED Z-SCORES VALUES GRAPHICAL REPRESENTATION

CARBON DISULFIDE



7. HOMOGENEITY AND STABILITY OF THE TEST MATERIAL

The results expressed here will not be taken into account as absolute concentrations, only as relative data, not used for any calculations.

HOMOGENEITY ($\mu\text{g/Kg}$):

	CARBON DISULFIDE	
	A ₁	A ₂
SAMPLE 1	768	963
SAMPLE 2	996	886
SAMPLE 3	993	962
SAMPLE 4	909	915
SAMPLE 5	1039	926
SAMPLE 6	1076	940
SAMPLE 7	795	843
SAMPLE 8	912	862
SAMPLE 9	1129	1095
SAMPLE 10	632	939
Acceptance criteria*	Accept	

*The acceptance criteria are described in the Harmonized Protocol of the IUPAC (see pg.8 of this report).

STABILITY ($\mu\text{g/Kg}$):

	CARBON DISULFIDE	
	A ₁	A ₂
t ₁	1039	926
t ₂	1000	1070
t ₃	1030	990
Acceptance criteria* (Differences \leq 10%)	Accept	

t₁: sample analyzed before the PT.

t₂: sample analyzed during the PT.

t₃: sample analyzed after the PT.

*The acceptance criteria are described in the SANCO/12571/2013 guide (see pg. 9 of this report).

8. ANALYTICAL METHODS USED BY THE LABORATORIES

CARBON DISULFIDE

LABORATORY CODE	ACREDITATED METHOD?	WEIGHT (g)	EXTRACTION SOLVENT	EXTRACTION TECHNIQUE	CALIBRATION	ANALYSIS TECHNIQUE
TQ17-092-001						
TQ17-092-002						
TQ17-092-003	NO	2	Acid mixture	Head-Space	Matrix matched-External standard	GC-MSD
TQ17-092-004	SI	50			Solvent - External standard	GC-FDD
TQ17-092-005	YES	2	SnCl ₂	Extraction with solvents	Solvent - Internal standard	GC-MS/MS
TQ17-092-006	YES	500		Extraction with solvents	Matrix matched-Internal standard	UV-Vis
TQ17-092-007	YES	20	Ethyl Acetate	Extraction with solvents	Matrix matched	GC-MSD
TQ17-092-008	NO	2	Isooctane	Extraction with solvent	Solvent - External standard	GC-PFPD
TQ17-092-009	NO	50	Isooctane	Extraction with solvent	Solvent	GC-MSD
TQ17-092-010	YES	4	Isooctane	Extraction with solvent	Solvent - External standard	GC-FDD
TQ17-092-011	YES	2	Isooctane	Extraction with solvent	Solvent	GC-HS
TQ17-092-012	YES	2	Isooctane		Solvent - External standard	GC-FDD
TQ17-092-013	YES	200		Extraction with solvent	Solvent - External standard	UV-Vis
TQ17-092-015	YES	250	Ethanol	Extraction with solvent	Solvent - External standard	UV-Vis
TQ17-092-016	YES	3	Water and HCl with SnCl ₂ for the derivatization	Acid digestion	Solvent - External standard	GC-MSD

9. REFERENCES

TestQual Proficiency Testing Schemes are based on the following standards:

- *UNE-EN ISO/IEC 17043*
- *ISO 13528*
- *THE INTERNATIONAL HARMONIZED PROTOCOL FOR THE PROFICIENCY TESTING OF ANALYTICAL CHEMISTRY LABORATORIES*
- *SANCO 12571/2013, Guidance document on analytical quality control.*

END OF REPORT

