

# TESTQUAL

## PROFICIENCY TESTING SCHEMES

### TestQual, S.L. (Proficiency Testing Schemes)

*Pol.Industrial Oeste,  
Av.Principal, Parcela 21/1  
C.P. 30169 San Ginés, Murcia  
Telephone: 868 949 486 / 676 367 555*



## FINAL REPORT TestQual 133

### *Dithiocarbamates in Apple*

LABORATORY:	AGQ MAROC
LABORATORY CODE:	TQ20-0133-007
ISSUE DATE OF THE REPORT:	19/11/2020

José Pedro Navarro Vicente  
TestQual, S.L. Technical manager

## SUMMARY

The samples from this proficiency test were sent on October of 2020 to 29 participant laboratories and 27 of them sent their results.

Summary TestQual 133-Apple results:

ANALYTE	NUMBER OF DATA*	ASSIGNED VALUE (µg/Kg)	UNCERTAINTY (µg/Kg)	%DSR <sub>A</sub>	TARGET	ROBUST
					STANDARD DEVIATION (µg/Kg)	STANDARD DEVIATION (µg/Kg)
CS <sub>2</sub>	21	795,74	56,14	30	238,72	257,25

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

Summary TestQual 133-Apple z-scores:

ANALITE	NUMBER OF Z-SCORES*	% SATISFACTORY	% QUESTIONABLE	% UNSATISFACTORY
CS <sub>2</sub>	27	85	7	7

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

There are PT items available from this PT as Quality Control Material and can be acquired from TestQual's website.

# INDEX

SUMMARY .....	2
1. OBJECTIVE AND CALENDAR.....	4
2. TEST MATERIAL.....	5
3. ANALYSIS .....	5
4. STATISTICAL RESULTS EVALUATION .....	6
5. RESULTS.....	9
5.1. RESULTS, LIMITS OF QUANTIFICATION AND Z-SCORE.....	9
5.2. PARTICIPANTS COMMENTS.....	10
5.3. FALSE POSITIVES AND FALSE NEGATIVES .....	10
5.3.1. FALSE POSITIVES:.....	10
5.3.2. FALSE NEGATIVES:.....	10
5.4. ASSIGNED VALUE AND TARGET STANDARD DEVIATION .....	10
5.5. SATISFACTORY, QUESTIONABLE AND UNSATISFACTORY Z-SCORES.....	10
6. GRAPHICAL REPRESENTATION OF ASSIGNED Z-SCORES VALUES .....	11
7. RESULTS DISTRIBUTION (KERNEL DENSITY):.....	12
8. HOMOGENEITY AND STABILITY OF THE TEST MATERIAL .....	13
HOMOGENEITY ( $\mu\text{g}/\text{Kg}$ ): .....	13
STABILITY ( $\mu\text{g}/\text{Kg}$ ): .....	13
9. ANALYTICAL METHODS USED BY THE LABORATORIES .....	14
10. REFERENCES.....	16

## 1. OBJECTIVE AND CALENDAR

The aim of the **TestQual 133 Apple** Proficiency Test (PT) is to gather information about the quality and accuracy of the results sent by the participating laboratories and helps them to ensure quality results and allows detecting any possible error or bias.

This proficiency test is based on the analysis of **Dithiocarbamates (Expressed as CS<sub>2</sub>)** in **Apple**. After the evaluation of the applications (depending on the LOQ of the laboratory and the transit time estimated by our homologated couriers), **29** laboratories were accepted, and the test material was sent in **October** of **2020**. The assigned concentration value ( $\mu$ ) 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
30/Sep/20 (Week 40)	Closing date for applications	Participants
13/Oct/20 (Week 42)	Sample shipment	TestQual
06/Nov/20 (Week 45)	Closing date to send results	Participants
20/Nov/20 (Week 47)	Final report publication	TestQual

Program coordinators: José Pedro Navarro

Each laboratory was assigned a unique code to participate in the proficiency test. These codes were only known by the laboratory and TestQual, and they were confidential during and after the proficiency test.

If any participant wants to appeal against the evaluation of their performance, their allegations must be sent by mail to [jpnavarro@testqual.com](mailto:jpnavarro@testqual.com).

## 2. TEST MATERIAL

About **18 Kg** of ecological **Apple** were bought to a specialized provider in Murcia (Spain). All of it was spiked with a solution containing the following commercial product:

COMMERCIAL PRODUCT	ACTIVE COMPONENT
Thiram 80 GD (Adama)	Thiram

The **Apple** was chopped, contaminated with the solution and then submerged in liquid N<sub>2</sub>. Once fully frozen, it was grounded into a fine powder and sieved to keep only <6mm pieces, which was poured into a homogenizer to ensure complete homogeneity and equal distribution of the matrix.

Then, portions of approximately **300 g** were packaged in previously labelled cylindrical jars with pressure seal and screw cap. Each packaged sample was stored at a temperature below -20 °C until further delivery to each participating laboratory.

Ten of these samples were chosen randomly and analysed by our collaborating laboratory to check their homogeneity before sending the samples to the participants; in addition, two more samples were saved for stability tests, one after distributing the samples, during the period of analysis and the last one after the deadline for returning results. These tests were performed by a subcontracted laboratory that holds the ISO standard UNE-EN ISO/IEC 17025 into force.

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

## 3. ANALYSIS

Each participant had to analyse the sample, detect and quantify the presence of in the test material according to their own procedures. Then, fill in with just one result in the “Results Form” that could be found in the client area of the website *www.testqual.com*, the results were expressed as **µg/Kg** of **CS<sub>2</sub>** (Including maneb, mancozeb, metiram, propineb, thiram and ziram), as stated in the EU legislation covered in the Commission Regulation 2016/1 amending Annexes II and III to Regulation (EC) No 396/2005 regards maximum residue levels for Dithiocarbamates.

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 submitted by the laboratories.

The **assigned value (X)** was determined using the robust average of the results considered valid for statistical computing (after removing extreme outliers), according to the standard ISO/IEC 13528 into force.

TestQual consider 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 taken into account for the calculation of the assigned value.

The **standard uncertainty (u<sub>x</sub>)** was 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 not considered as extreme outliers.

The **standard deviation for proficiency assessment**, also named **target standard deviation (σ̂)**, comes from following formula:

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

Being b<sub>i</sub> = %<sub>DSRA</sub>/100, and %<sub>DSRA</sub> is the assigned **relative standard deviation**.

In this case, the assigned relative standard deviation is **30 %**. This value was previously set by the organizer and informed in the protocol of the proficiency test, based on the extensive experience of TestQual organizing these and similar proficiency tests.

**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 each of the laboratories,  $X$  is the assigned value, and  $\hat{\sigma}$  is the target standard deviation for each analyte.

The criterion for defining the z-score values are:

$ Z  \leq 2$	Satisfactory
$2 <  Z  \leq 3$	Questionable
$ Z  > 3$	Unsatisfactory

**False negative:**

Is a result, for an analyte present in the sample over the limit of quantification of the proficiency test previously established by the organization (**10µg/Kg**), which has not been informed by the laboratory. To these results the z-score is obtained from assigning as a returned result half of its Limit of Quantification (LOQ).

**False positive:**

Is a submitted result for an analyte which was not present in the test material, but it was reported by the participant at a concentration higher than the limit of quantification of the proficiency test. (**10µg/Kg**).

**Testing for sufficient homogeneity:**

Once the samples were prepared ten of them were chosen at random and sent to be analysed by TestQual's collaborator laboratory. Once received the results, a statistical evaluation was performed, according to the IUPAC Harmonic Protocol.

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

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

Firstly  $Vs$  is the variance of the sums  $S_i$  (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)), secondly  $S_{an}^2$ , which is the experimental estimate of analytical standard deviation, is obtained following the next formula:

$$V_s = \sum \frac{(S_i - \bar{S})^2}{(m - 1)} \qquad S_{an}^2 = \frac{\sum D_i}{2m}$$

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  $\sigma_{all}^2$  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:

$$\hat{\sigma} = 0.3 \cdot \bar{X}$$

Being  $\bar{X}$ , the mean of the 20 values from the homogeneity.

#### Testing for sufficient stability:

Three samples were analysed, in duplicate, before, during and at the end (once all laboratories have submitted their results) of the proficiency test. The acceptance criteria to ensure the samples have been stable during the proficiency test are the following:

$$\left| \frac{X_{t1} - X_{t2}}{X_{t1}} \right| \cdot 100 \leq 10\%$$

$$\left| \frac{X_{t1} - X_{t3}}{X_{t1}} \right| \cdot 100 \leq 10\%$$

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

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



## 5. RESULTS

### 5.1. RESULTS, LIMITS OF QUANTIFICATION AND Z-SCORE

**Legend:**

- X: Assigned value.
- $U_x$ : Uncertainty of the assigned value.
- $X_i$ : Participant's reported value.
- LOQ: Participant's Limit of quantification.
- NA: Analyte not analysed by the participant.
- NO: Analyte no informed (not detected) by the participant (false negative).
- <LOQ: Analyte in a concentration lower than the participant's limit of quantification.
- \*<sup>A</sup>: Result considered as statistically aberrant and not taken into account to calculate the assigned value.
- Bold** Results that obtained a z-score > |2|.
- \*<sup>1</sup> Uncertainty of the assigned value not negligible. Evaluation issued with informative purposes.
- (C)** Comment related in section 5.2..

LABORATORY CODE	CS <sub>2</sub>		
	$X_i$ (µg/Kg)	LOQ (µg/Kg)	z-score
		( $X= 795,74$ µg/Kg)	
		( $U_x= 56,14$ µg/Kg)	
TQ20-0133-001	831	10	0,1
TQ20-0133-002	470	10	-1,4
TQ20-0133-003	540	10	-1,1
TQ20-0133-004	1100	100	1,3
TQ20-0133-005	1044	50	1,0
TQ20-0133-006	1004	5	0,9
TQ20-0133-007	1082	50	1,2
TQ20-0133-008	724	50	-0,3
TQ20-0133-009	983,7	50	0,8
TQ20-0133-010	1142,8	10	1,5
TQ20-0133-011	536	10	-1,1
TQ20-0133-012	<b>2006*<sup>A</sup></b>	<b>10</b>	<b>5,1</b>
TQ20-0133-013	692	50	-0,4
TQ20-0133-014	761	10	-0,1
TQ20-0133-015	925	10	0,5
TQ20-0133-016	<b>42*<sup>A</sup></b>	<b>10</b>	<b>-3,2</b>
TQ20-0133-017	675	50	-0,5
TQ20-0133-018	<b>1429,26*<sup>A</sup></b>	<b>50</b>	<b>2,7</b>
TQ20-0133-019	702	10	-0,4
TQ20-0133-020	933	100	0,6
TQ20-0133-021	(C)	10	
TQ20-0133-022	440	200	-1,5
TQ20-0133-023	859	10	0,3
TQ20-0133-024	340* <sup>A</sup>	10	-1,9
TQ20-0133-025	416	100	-1,6
TQ20-0133-026	<b>1436*<sup>A</sup></b>	<b>50</b>	<b>2,7</b>
TQ20-0133-027	(C)	50	
TQ20-0133-028	410* <sup>A</sup>	50	-1,6
TQ20-0133-029	850	10	0,2

## 5.2. PARTICIPANTS COMMENTS

Any comment that was not in English has been translated.

Laboratory	Comment
(C) TQ20-0133-000 TestQual (organizer)	Participants TQ20-0133-021 and TQ20-0133-027 informed the coordinator that they would not be able to submit results.

## 5.3. FALSE POSITIVES AND FALSE NEGATIVES

### 5.3.1. FALSE POSITIVES:

No false positives were reported for this Proficiency Test.

### 5.3.2. FALSE NEGATIVES:

No false negatives were reported for this Proficiency Test.

## 5.4. ASSIGNED VALUE AND TARGET STANDARD DEVIATION

ANALYTE	NUMBER OF DATA*	ASSIGNED VALUE (µg/Kg)	UNCERTAINTY (µg/Kg)	%DSR <sub>A</sub>	TARGET STANDARD DEVIATION (µg/Kg)	ROBUST STANDARD DEVIATION (µg/Kg)
CS2	21	795,74	56,14	30	238,72	257,25

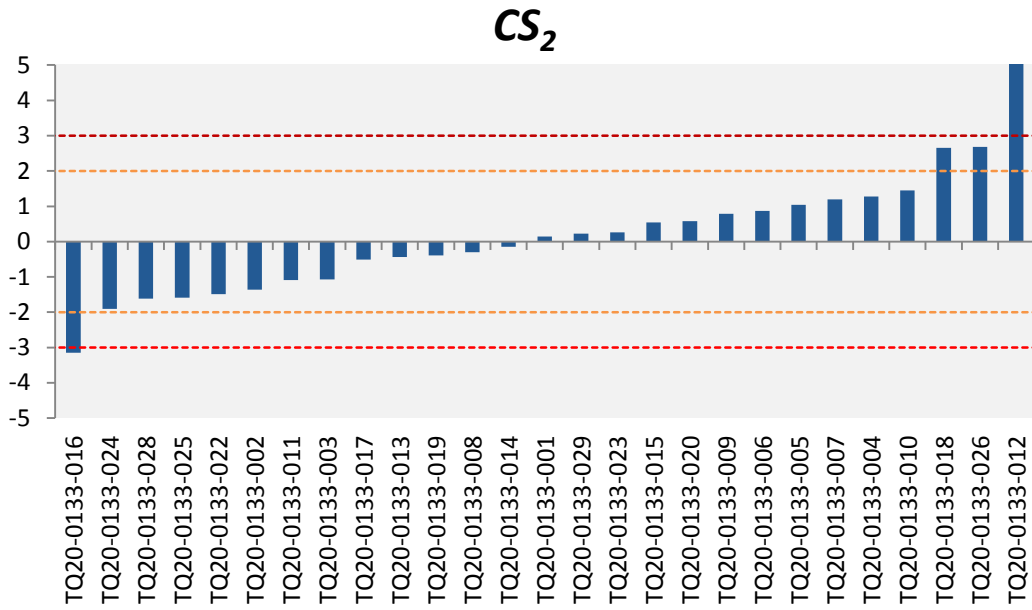
*\*Results considered extreme outliers have not been considered*

## 5.5. SATISFACTORY, QUESTIONABLE AND UNSATISFACTORY Z-SCORES

ANALITE	NUMBER OF Z-SCORES*	% SATISFACTORY	% QUESTIONABLE	% UNSATISFACTORY
CS2	27	85	7	7

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

## 6. GRAPHICAL REPRESENTATION OF ASSIGNED Z-SCORES VALUES

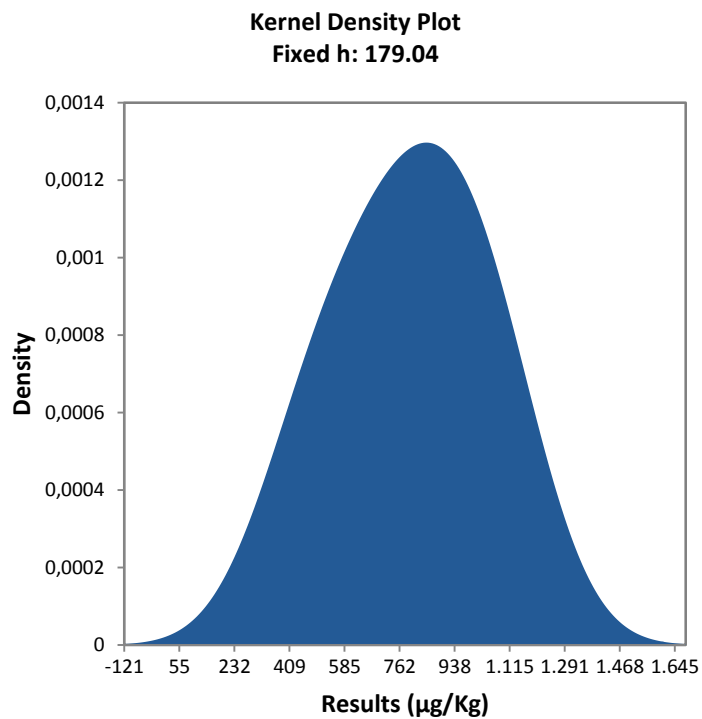


## 7. RESULTS DISTRIBUTION (KERNEL DENSITY):

Here is shown the Kernel density estimate for each analyte with enough available data (8 or more results not outliers), this is a non-parametric estimation that represents the population density function versus the data results not considered as outliers. The smoothing parameter or bin width  $h$  was selected as  $h=0.75*(\text{target standard deviation})$  as referred in ISO 13528 into force. Through the evaluation of the symmetry of this distribution it is possible to evaluate the unimodality of the data set:

**For this proficiency test the CS<sub>2</sub> has shown an adequate symmetry to be considered unimodal.**

**CS<sub>2</sub>**



## 8. HOMOGENEITY AND STABILITY OF THE TEST MATERIAL

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

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

	CS <sub>2</sub>	
	A <sub>1</sub>	A <sub>2</sub>
SAMPLE 1	472	530
SAMPLE 2	410	451
SAMPLE 3	422	429
SAMPLE 4	350	350
SAMPLE 5	470	440
SAMPLE 6	424	475
SAMPLE 7	464	486
SAMPLE 8	530	530
SAMPLE 9	449	408
SAMPLE 10	421	403
Acceptance criteria*	Satisfies criteria	

\*The acceptance criteria are described in the SANCO/12571/2013 guide (see pg. 7 and 8 of this report)

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

	CS <sub>2</sub>	
	A <sub>1</sub>	A <sub>2</sub>
t <sub>1</sub>	470	440
t <sub>2</sub>	412	471
t <sub>3</sub>	420	415
Acceptance criteria* (Difference $\leq$ 10%)	Satisfies criteria	

t<sub>1</sub>: sample analysed before sending the samples.

t<sub>2</sub>: sample analysed during the period of analysis.

t<sub>3</sub>: sample analysed after the deadline for submit results.

\*The acceptance criteria is described in pg. 8 of this report)

## 9. ANALYTICAL METHODS USED BY THE LABORATORIES

CS<sub>2</sub>

LABORATORY CODE	ACREDITATED METHOD?	WEIGHT (g)	EXTRACTION SOLVENT	EXTRACTION TECHNIQUE	CALIBRATION	ANALYSIS TECHNIQUE
TQ20-0133-001	YES	10	-	-	solvent matched - external standard	GC-ECD
TQ20-0133-002	YES	-	-	-	-	GC-HS-MS
TQ20-0133-003	NO	-	-	-	-	GC-HS-MS
TQ20-0133-004	-	-	-	-	-	-
TQ20-0133-005	YES	25	ISOoctane	LIQUID	SOLVENT MATCHED	GC-MS
TQ20-0133-006	YES	5	isooctane	Solvent extraction.	solvent matched - external standard	GC-MSD.
TQ20-0133-007	YES	257	ethanol	Solvent extraction.	solvent matched - external standard	UV-Vis.
TQ20-0133-008	YES	50	Iso-octane	H2O/HCl/SnCl2	solvent matched - external standard	GC-pFPD
TQ20-0133-009	YES	2	isooctane	Solvent extraction.	solvent matched - external standard	GC-MSD.
TQ20-0133-010	YES	4	-	-	matrix matched - external standard	GC MS/MS.
TQ20-0133-011	YES	50	SnCl2 in acid	Solvent extraction	matrix matched - external standard	GC-ECD
TQ20-0133-012	L00.00-49/2 modified	-	-	-	-	GC-ECD
TQ20-0133-013	YES. EN 12396-2:1999	50	-	. head space	solvent matched - external standard	GC-ECD.
TQ20-0133-014	YES. EURL-SRM Dithiocarbamates as CS2 Ver2	20	isooctane	Solvent extraction.	solvent matched - external standard	GC-MSD.
TQ20-0133-015	YES, EN 12396-2 (modified)	2	SnCl2-HCl-solution	Solvent extraction.	matrix matched - Standard addition	GC-MSD. GC Agilent 7890A, MS HP5975
TQ20-0133-016	NO	5	ISOoctane	-	CS2 solvent Isoctane	GC-MSMS

CS<sub>2</sub>, continuation

LABORATORY CODE	ACREDITATED METHOD?	WEIGHT (g)	EXTRACTION SOLVENT	EXTRACTION TECHNIQUE	CALIBRATION	ANALYSIS TECHNIQUE
TQ20-0133-017	-	50	isooctane	Solvent extraction	solvent matched - external standard	GC-ITD.
TQ20-0133-018	YES. IAS. PCO-800	2	Water, Isoctane and acid	Acid hydrolisis at high temperature with HCl and SnCl <sub>2</sub> as catalizer	matrix matched - external standard	Other. GC - MS
TQ20-0133-019	YES	5	tin(II) chloride hydrochloric acid solution	Solvent extraction.	solvent matched - internal standard	GC-HS.
TQ20-0133-020	YES	100	-	-	solvent matched	UV-Vis.
TQ20-0133-021	-	-	-	-	-	-
TQ20-0133-022	YES. TP282	20	40	Solvent extraction. Stanous Chloride	matrix matched - external standard	other. GCMS-HS
TQ20-0133-023	YES	10	iso-C8	Solvent extraction.	matrix matched - external standard	GC-MSD.
TQ20-0133-024	-	-	-	-	-	-
TQ20-0133-025	YES	50	isooctane	Release of carbon disulfide after heating of the sample with aquatic solution of tin (II) chloride	Solvent -isooctane	GC/FPD
TQ20-0133-026	YES	100	H <sub>2</sub> O/HCl	-	solvent matched - external standard	UV-Vis.
TQ20-0133-027	-	-	-	-	-	-
TQ20-0133-028	YES	2	Isooctane	Solvent extraction	solvent matched - Standard addition	GC-MSD
TQ20-0133-029	YES	10	cyclohexane	Solvent extraction	matrix matched	GC-MSD

## 10. REFERENCES

TestQual Proficiency Testing Schemes are based on the following standards:

- *UNE-EN ISO/IEC 17043:2010 Conformity assessment — General requirements for proficiency testing.*
- *ISO 13528:2015 Statistical methods for use in proficiency testing by interlaboratory comparison.*
- *THE INTERNATIONAL HARMONIZED PROTOCOL FOR THE PROFICIENCY TESTING OF ANALYTICAL CHEMISTRY LABORATORIES (IUPAC Technical Report.)*
- *SANTE 12682/2019, 1<sup>st</sup> January 2020, Guidance document on analytical quality control.*
- *Commission Regulation (EU) 2016/1 of 3 December 2015 amending Annexes II and III to Regulation (EC) No 396/2005 of the European Parliament and of the Council (2016) OJ L 70, 16.3.2005, p. 1–16 (ES, CS, DA, DE, ET, EL, EN, FR, IT, LV, LT, HU, MT, NL, PL, PT, SK, SL, FI, SV)*

# END OF THE REPORT

