



**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 *rev01* TestQual 125**  
***Dithiocarbamates in Strawberry***

LABORATORY:	AGQ MAROC
LABORATORY CODE:	TQ20-0125-015
ISSUE DATE OF THE REPORT:	03/ <i>Apr</i> /2020
<b><i>ISSUE DATE OF THE REPORT REV01:</i></b>	<b><i>06/Apr/2020</i></b>

***This revision replaces the report rev00 from 03/Apr/2020***

***Ana María Moreno López***  
***TestQual, S.L. Quality manager***

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

## SUMMARY

The samples from this proficiency test were sent on February of 2020 to 21 participant laboratories and 20 sent their results.

Summary TestQual 125-strawberry results:

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)
CS <sub>2</sub>	17	1344,05	61,41	30	403,21	253,20

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

Summary TestQual 125-strawberry z-scores:

ANALITE	NUMBER OF Z-SCORES*	% SATISFACTORY	% QUESTIONABLE	% UNSATISFACTORY
CS <sub>2</sub>	20	90	5	5

*\*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. SUMMARY .....	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
CS <sub>2</sub> .....	11
7. RESULTS DISTRIBUTION (KERNEL DENSITY):.....	11
8. HOMOGENEITY AND STABILITY OF THE TEST MATERIAL .....	12
HOMOGENEITY (µg/Kg): .....	12
STABILITY (µg/Kg): .....	12
9. ANALYTICAL METHODS USED BY THE LABORATORIES .....	13
CS <sub>2</sub> .....	13
10. REFERENCES.....	15

## 1. SUMMARY

The aim of the **TestQual 125 Strawberry** 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 Strawberry**. After the evaluation of the applications (depending on the LOQ of the laboratory and its geographical location), **21** laboratories were accepted, and the test material was sent in **February** 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
17/Feb/20 (Week 8)	Closing date for applications	Participants
18/ Feb /20 (week 8)	Sample shipment	TestQual
13/Mar/20 (Week 11)	Closing date to send results	Participants
20/ Mar /20 (week 12)	Extraordinary date to submit results	TestQual
27/ Mar /20 (Week 13)	Final report publication	TestQual
<b>06/Apr/20 (week 15)</b>	<b>Final report revision 01 publication</b>	<b>TestQual</b>

Some participants informed that they could not log into their client area, after checking that this was an error from TestQual website the deadline to submit results was increased one week for all participants.

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 **24 Kg** of ecological **Strawberry** 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 **Strawberry** 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, which was poured into a homogenizer to ensure complete homogeneity.

Then, **350 g** portions of frozen powder 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, 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](http://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 ( $u_x$ )** 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 ( $\hat{\sigma}$ )**, comes from following 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 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  $V_s$  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|.

LABORATORY CODE	CS <sub>2</sub> ( $\bar{X}$ = 1344,05 µg/Kg) ( $U_x$ = 61,41 µg/Kg)		
	$X_i$ (µg/Kg)	LOQ (µg/Kg)	z-score
TQ20-0125-001	1445	10	0,3
TQ20-0125-002	1140	20	-0,5
TQ20-0125-003	1170	100	-0,4
TQ20-0125-004	1068	10	-0,7
TQ20-0125-005	1180	10	-0,4
TQ20-0125-006	-	50	-
TQ20-0125-007	1841	50	1,2
TQ20-0125-008	1584,92	50	0,6
TQ20-0125-009	1396	100	0,1
TQ20-0125-011	750	50	-1,5
TQ20-0125-012	<b>2542,3*<sup>A</sup></b>	<b>10</b>	<b>3,0</b>
TQ20-0125-013	<b>3380*<sup>A</sup></b>	<b>10</b>	<b>5,0</b>
TQ20-0125-014	1453	1	0,3
TQ20-0125-015	1364	50	0,0
TQ20-0125-016	686* <sup>A</sup>	50	-1,6
TQ20-0125-017	1582	10	0,6
TQ20-0125-018	1677	10	0,8
TQ20-0125-019	1107,8	5	-0,6
TQ20-0125-020	1443	10	0,2
TQ20-0125-021	1339	10	0,0
TQ20-0125-022	1211	50	-0,3

## 5.2. PARTICIPANTS COMMENTS

TQ20-0125-003: Sample was slightly thawed upon receipt in the laboratory. The sample was still cool, but not completely frozen. DHL courier slightly delayed – sample picked up on 18/02/2020 and delivered on 21/02/2020

## 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	17	1344,05	61,41	30	403,21	253,20

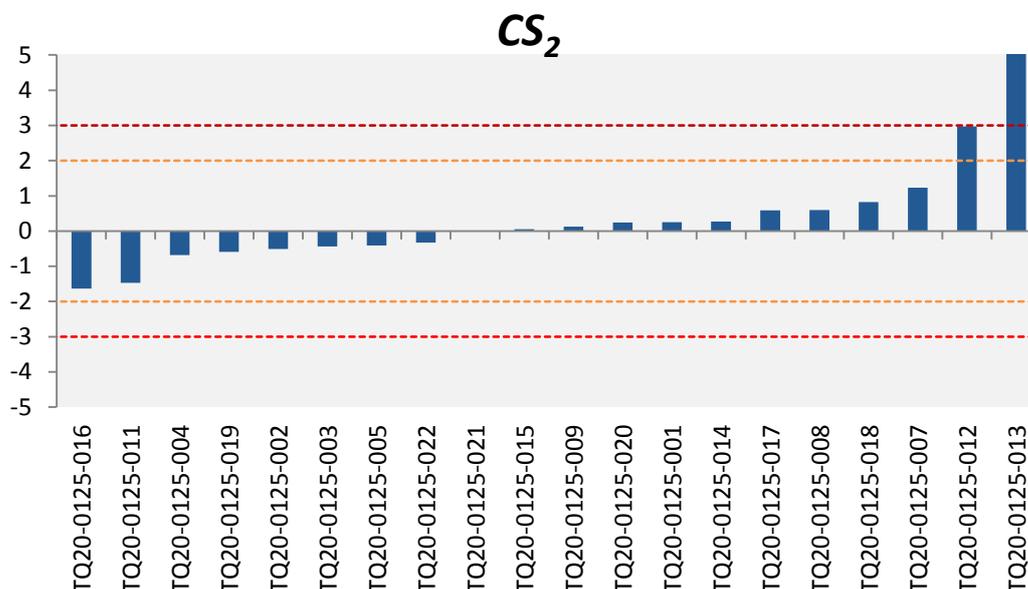
*\*Results considered extreme outliers have not been considered*

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

ANALYTE	NUMBER OF Z-SCORES*	% SATISFACTORY	% QUESTIONABLE	% UNSATISFACTORY
CS2	20	90	5	5

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

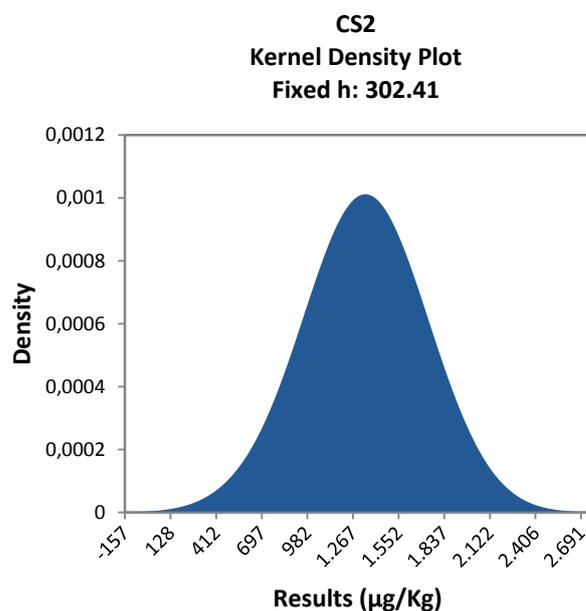
## 6. GRAPHICAL REPRESENTATION OF ASSIGNED Z-SCORES VALUES



## 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  $h=0.75 \cdot (\text{target standard deviation})$  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.**



## 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	1110	1000
SAMPLE 2	1193	954
SAMPLE 3	1075	1030
SAMPLE 4	1144	1218
SAMPLE 5	1068	1210
SAMPLE 6	1224	1133
SAMPLE 7	1287	1458
SAMPLE 8	1252	1300
SAMPLE 9	1262	1212
SAMPLE 10	1258	1695
Acceptance criteria*	<i>Satisfies criteria</i>	

\*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>	1068	1210
t <sub>2</sub>	1203	922
t <sub>3</sub>	1216	958
Acceptance criteria* (Difference $\leq$ 10%)	<i>Satisfies criteria</i>	

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
TQ20-0125-001	YES	50	-	-	Solvent matched - External standard	GC-ECD.
TQ20-0125-002	YES MP-02117-NL in house method	-	-	-	-	Headspace GCMS
TQ20-0125-003	YES	1	Tin Chloride/Hydrochloric acid Water Diethanolamine	Acid Hydrolysis	Solvent matched - External standard	GC-HS with MS Detection
<i>TQ20-0125-004</i>	<i>YES</i>	<i>-</i>	<i>-</i>	<i>-</i>	<i>-</i>	<i>HS-GC-MS/MS</i>
TQ20-0125-005	<i>YES</i>	<i>-</i>	<i>-</i>	<i>-</i>	<i>-</i>	<i>GC-HS</i>
TQ20-0125-006	<i>-</i>	<i>-</i>	<i>-</i>	<i>-</i>	<i>-</i>	
TQ20-0125-007	<i>YES</i>	<i>50</i>	<i>Isooctane</i>	<i>Solvent extraction</i>	<i>Solvent matched</i>	<i>GC-MS/MS</i>
TQ20-0125-008	<i>NO.</i>	<i>10</i>	<i>Isooctane</i>	<i>Acid extraction</i>	<i>MATRIX MATCHED - External standard</i>	<i>GC-MSD-HS</i>
TQ20-0125-009	<i>YES</i>	<i>1</i>	<i>1.5% Tin(II) chloride in 5M HCL</i>	<i>-</i>	<i>Solvent matched - External standard</i>	<i>Other. GC-FPD</i>
TQ20-0125-011	<i>YES</i>	<i>50</i>	<i>isooctane</i>	<i>Solvent extraction isooctane</i>	<i>Solvent matched - External standard</i>	<i>GC MS/MS. MS-mode</i>
TQ20-0125-012	<i>YES IAS</i>	<i>2</i>	<i>Isooctane</i>	<i>Solvent extraction</i>	<i>MATRIX MATCHED - External standard</i>	<i>GC-MSD.</i>
TQ20-0125-013	<i>YES</i>	<i>5</i>	<i>Tinn(II)-chloride solution in water</i>	<i>automated Shaking and heating by agitator, headspace analysis</i>	<i>-</i>	<i>HS-GC-MS</i>
TQ20-0125-014	<i>YES</i>	<i>-</i>	<i>HCl and Tin(II)chlorid solution</i>	<i>Solvent extraction</i>	<i>MATRIX MATCHED - External standard</i>	<i>GC-HS.</i>

LABORATORY CODE	ACREDITATED METHOD?	WEIGHT (g)	EXTRACTION SOLVENT	EXTRACTION TECHNIQUE	CALIBRATION	ANALYSIS TECHNIQUE
TQ20-0125-015	YES	300	ETHANOL	Solvent extraction	Solvent matched - External standard	UV-Vis.
TQ20-0125-016	YES DM0409	2	tin(II)chloride	Solvent extraction Reduction SnCl <sub>2</sub> /HCl;	MATRIX MATCHED - External standard	GC-ECD.
TQ20-0125-017	SI	50	-	Solvent extraction	Solvent matched	GC-MSD.
TQ20-0125-018	YES DIN EN 12396-2	-	-	-	-	-
TQ20-0125-019	YES ME.Q.141 (HS-GC-MS)	3	NO EXTRACTION	HEAD-SPACE	Solvent matched - External standard	GC-MSD. HS-GC-MSD
TQ20-0125-020	YES	5	HCL, H2O	Solvent extraction	Solvent matched - Internal standard	GC-MSD.
TQ20-0125-021	YES	5	Tin solution	Solvent/solvent	Solvent matched - Internal standard	GS-MSMS
TQ20-0125-022	YES	50	HCl/SnCl <sub>2</sub> _Isooctane	-	Solvent matched - External standard	Other. GC-pFPD

## 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

