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(Proficiency Testing Schemes)

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PROVISIONAL REPORT TestQual 84
Dithiocarbamates in escarole

LABORATORY:

AGQ MAROC

LABORATORY CODE:

TQ17-084-024

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1. SUMMARY

The aim of the **TestQual 84 escarole** proficiency test 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 **dithiocarbamates** in **escarole**. After the evaluation of the applications (depending on the LOQ of the laboratory and its geographical location), **twenty four** laboratories were accepted, and the test material was sent in **March 2017**. The assigned concentration value (μ) 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 $2 < |z| \leq 3$ and unsatisfactory if $|z| > 3$.

The most important dates of the proficiency test have been:

| DATE | ACTIVITY | CARRIED OUT BY |
|------------|-------------------------------|----------------|
| 13/03/2017 | Closing date for applications | Participants |
| 14/03/2017 | Sample shipment | Organizer |
| 06/04/2017 | Closing date to send results | Participants |
| Abril 2017 | Final report publication | Organizer |

Program coordinator: Alberto Martínez (amartinez@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 P.T.

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

2. TEST MATERIAL

About **15Kg** of ecological **escarole** were bought in a shop in Murcia. All of it was spiked with a solution containing the following commercial product.

| COMMERCIAL PRODUCT | ACTIVE COMPONENT |
|----------------------|------------------|
| Thiram 80 GD (Adama) | Thiram |

The test material 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.

After that, **350g** were packed into plastic bottles with pressure seal and screw cap before labeling 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 of temperature and conservation

3. ANALYSIS

Each participant had to analyze 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 their private area on the website www.testqual.com, expressing the results in $\mu\text{g}/\text{Kg}$.

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 ISO13528 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:

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

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:

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

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 P.T., based on the extensive experience of TestQual organizing similar proficiency tests.

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

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

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:

| | |
|------------------|----------------|
| $ z \leq 2$ | Satisfactory |
| $2 < z \leq 3$ | Questionable |
| $ z > 3$ | Unsatisfactory |

False negatives: are results that show the presence of analytes in the sample over the limit of quantification of the proficiency test previously established by the organization (**10 µg/Kg**), that have not been informed as quantified 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 prepared were sent to be analyzed by TestQual collaborator laboratory. Once the results were submitted, a statistical evaluation according to the IUPAC Harmonic Protocol was performed.

The acceptance criteria to ensure that the randomly chosen samples are homogeneous was that $S_{sam}^2 < c$, where S_{sam} is the estimated sampling standard deviation, and $c = F_1 \sigma_{all}^2 + F_2 S_{an}^2$, being $F_1 = 1,88$ and $F_2 = 1,01$ (10 samples). $\sigma_{all}^2 = (0,3 \hat{\delta})^2$, where $\hat{\delta}$ is the target standard deviation, and being $\hat{\delta} = 0,30 \times \bar{X}$ (\bar{X} is the average of the 20 values).

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 P.T. 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, during and at the end 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 (X= 851,31 µg/Kg) (u _x = 70,61 µg/Kg) | | | |
|--|---------------------|--------------------|----------------|
| LABORATORY CODE | X (µg/Kg) | LOQ (µg/Kg) | Z-SCORE |
| TQ17-084-001 | 1575* ^A | 50 | 2,8 |
| TQ17-084-002 | 1025 | 10 | 0,7 |
| TQ17-084-003 | 1092 | 50 | 0,9 |
| TQ17-084-005 | 941 | 50 | 0,4 |
| TQ17-084-006 | 4100* ^A | 10 | 12,7 |
| TQ17-084-007 | 880 | 100 | 0,1 |
| TQ17-084-008 | 817 | 50 | -0,1 |
| TQ17-084-009 | 992 | 10 | 0,6 |
| TQ17-084-010 | 998 | 50 | 0,6 |
| TQ17-084-011 | 1513* ^A | 20 | 2,6 |
| TQ17-084-012 | 312* ^A | 50 | -2,1 |
| TQ17-084-013 | 953 | 10 | 0,4 |
| TQ17-084-014 | 1300 | 10 | 1,8 |
| TQ17-084-015 | 530 | 10 | -1,3 |
| TQ17-084-016 | 853 | 50 | 0,0 |
| TQ17-084-017 | 395* ^A | 10 | -1,8 |
| TQ17-084-018 | 1067 | 100 | 0,8 |
| TQ17-084-019 | 308,5* ^A | 50 | -2,1 |
| TQ17-084-020 | 612 | 50 | -0,9 |
| TQ17-084-021 | 876 | 50 | 0,1 |
| TQ17-084-022 | 772 | 500 | -0,3 |
| TQ17-084-023 | 513 | 10 | -1,3 |
| TQ17-084-024 | 457 | 50 | -1,5 |
| TQ17-084-025 | 700 | 200 | -0,6 |

NA: Analyte no analyzed by the participant

NO: Analyte no informed (no detected) by the participant

LOQ: Quantification limit of the participant

*^AThis result has been considered as an extreme outlier, so it has not been included to calculate the assigned value

TABLE 1: ASSIGNED VALUE AND TARGET STANDARD DEVIATION

| ANALYTE | NUMBER OF DATA* | ASSIGNED VALUE (µg/Kg) | UNCERTAINTY (µg/Kg) | %DSR _A | TARGET STANDARD DEVIATION (µg/Kg) | ROBUST STANDARD DEVIATION (µg/Kg) |
|------------------|-----------------|------------------------|---------------------|-------------------|-----------------------------------|-----------------------------------|
| CARBON DISULFIDE | 18 | 851,31 | 70,61 | 30 | 255,39 | 239,66 |

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

TABLE 2: SATISFACTORY, QUESTIONABLE AND UNSATISFACTORY Z-SCORES

| ANALITE | NUMBER OF Z-SCORES* | % SATISFACTORY | % QUESTIONABLE | % UNSATISFACTORY |
|------------------|---------------------|----------------|----------------|------------------|
| CARBON DISULFIDE | 24 | 80 | 16 | 4 |

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

TABLA 3: FALSE POSITIVES AND FALSE NEGATIVES

FALSE POSITIVES:

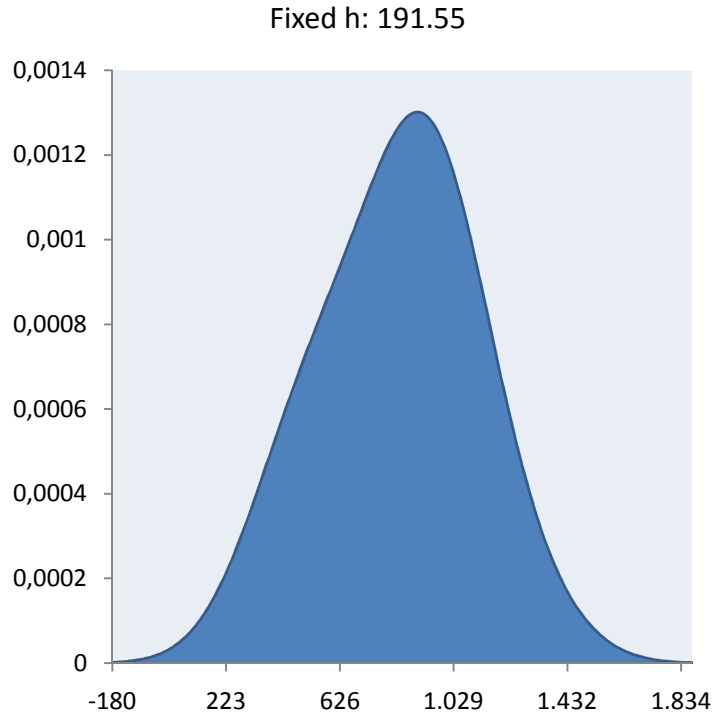
No false positives have been reported for this proficiency test.

FALSE NEGATIVES:

No false negatives have been reported for this proficiency test.

DISTRIBUTION OF RESULTS (KERNEL DENSITY):

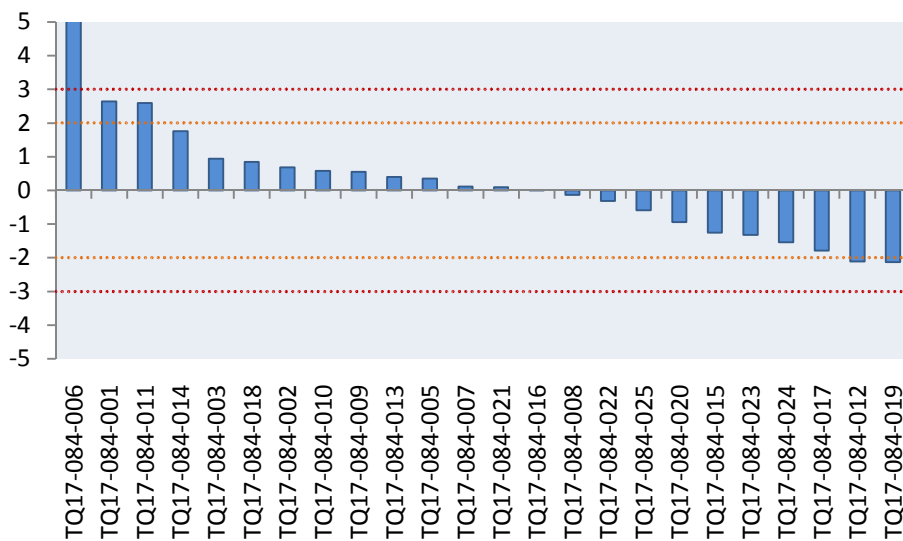
CARBON DISULFIDE:



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

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

| CARBON DISULFIDE | | |
|----------------------|----------------|----------------|
| | A ₁ | A ₂ |
| SAMPLE 1 | 624 | 461 |
| SAMPLE 2 | 557 | 884 |
| SAMPLE 3 | 602 | 650 |
| SAMPLE 4 | 623 | 935 |
| SAMPLE 5 | 953 | 982 |
| SAMPLE 6 | 892 | 904 |
| SAMPLE 7 | 750 | 601 |
| SAMPLE 8 | 912 | 862 |
| SAMPLE 9 | 923 | 945 |
| SAMPLE 10 | 896 | 866 |
| Acceptance criteria* | Accept | |

*The acceptance criteria are described in the Harmonized Protocol of the IUPAC (see pg.6 of this report)

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

| CARBON DISULFIDE | | |
|---|----------------|----------------|
| | A ₁ | A ₂ |
| t ₁ | 953 | 982 |
| t ₂ | 923 | 869 |
| t ₃ | 850 | 910 |
| Acceptance criteria* (difference $\leq 10\%$) | 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. 6 of this report)

8. ANALYTICAL METHODS USED BY THE LABORATORIES

| LABORATORY CODE | ACCREDITED? | WEIGHT (g) | EXTRACTION SOLVENT | EXTRACTION TECHNIQUE | CALIBRATION | ANALYSIS TECHNIQUE |
|-----------------|-------------------|------------|---|--|------------------------------------|--------------------|
| TQ17-084-001 | YES | 2 | Isoctane | Solvent extraction | Solvent – External standard | GC-FDD |
| TQ17-084-002 | YES* ¹ | 50 | - | Head Space | Matrix-matched – External standard | GC-FPD |
| TQ17-084-003 | YES | 50 | Isoctane | Solvent extraction | Matrix-matched – External standard | GC-MS/MS |
| TQ17-084-005 | YES | 50 | Isoctane | SnCl ₂ , HCl, Water | Solvent – External standard | p-FPD |
| TQ17-084-006 | YES | 20 | Isoctane | Solvent extraction | Solvent – External standard | GC-MSD |
| TQ17-084-007 | YES | 200 | SnCl ₂ , HCl, Water | Solvent extraction | Solvent – External standard | UV-VIS |
| TQ17-084-008 | YES | 500 | HCl | Solvent extraction | Solvent | UV-VIS |
| TQ17-084-009 | YES | 50 | Isoctane | Acid hydrolysis and Solvent extraction | Solvent – External standard | GC-ECD |
| TQ17-084-010 | YES | 2 | - | Solvent extraction | Solvent | GC-HS |
| TQ17-084-011 | YES | 4 | Isoctane | Solvent extraction | Matrix-matched – External standard | GC-FDD |
| TQ17-084-012 | YES | 10 | SnCl ₂ , Isoctane | Solvent extraction | Solvent | GC-MS/MS |
| TQ17-084-013 | YES | 2 | SnCl ₂ , HCl, diethanolamine | Head Space | Solvent | GC-MS |
| TQ17-084-014 | YES* ² | 50 | Solution | - | Solvent – External standard | GC-MS/MS |
| TQ17-084-015 | YES | 5 | SnCl ₂ , HCl | Solvent extraction | Matrix-matched – External standard | GC-MSD |
| TQ17-084-016 | NO | 5 | - | Solid phase extraction | Matrix-matched – External standard | GC-MSD Head Space |
| TQ17-084-017 | YES | 50 | SnCl ₂ , HCl | Solvent extraction | Matrix-matched – External standard | GC-ECD |
| TQ17-084-018 | YES | 100 | - | - | Solvent | UV-VIS |
| TQ17-084-019 | YES* ³ | 50 | SnCl ₂ , HCl, Isoctane | Solvent extraction | Solvent – External standard | GC-NPD |
| TQ17-084-020 | NO | 4 | concentrated chlorhydric acid , Thin chloride dyhidrate, Isoctane y distilled water | Solvent extraction | Solvent – External standard | GC-PFPD |
| TQ17-084-021 | YES | 50 | - | - | - | - |
| TQ17-084-022 | YES | 100 | - | - | Solvent – External standard | UV-VIS |
| TQ17-084-023 | YES | 5 | Isoctane | Solvent extraction | Matricial – Estándar interno | GC-MSD. GCMS[EI] |
| TQ17-084-024 | YES | 250 | Ethanol | Solvent extraction | Solvent – External standard | UV-VIS |
| TQ17-084-025 | YES | 100 | - | Distillation | Solvent – External standard | UV-VIS |

*¹ UNI EN 12396-2:1999

*² UNIEN 15396-2:1999

*³ ISO 17025

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 THE REPORT

