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Fertilizers — Comparison of the CEN/TC 260/WG 7 ring test results with tolerances given in the Regulation (EC) Nr 2003/2003 Annex II and conclusions

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Fertilizers - Comparison of the CEN/TC 260/WG 7 ring test results with tolerances given in the Regulation (EC) Nr 2003/2003 Annex II and conclusions

Engrais - Comparaison des résultats des essais interlaboratoires menés par le CEN/TC 260/WG 7 avec les tolérances données dans le règlement (CE) n°2003/2003 Annexe II et conclusions

Düngemittel - Vergleich der Ringversuchsergebnisse der CEN/TC 260/WG 7 mit den in der Verordnung (EG) Nr. 2003/2003 Anhang II angegebenen Toleranzen und Schlussfolgerungen

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Foreword

This document (CEN/TS 16490:2013) has been prepared by Technical Committee CEN/TC 260 “Fertilizers and liming materials”, the secretariat of which is held by DIN.

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Introduction

Following a request from the European Commission (Mandate M/418), an evaluation was done of the existing tolerances as per Regulation (EC) No. 2003/2003. Input for this evaluation was derived from the precision data obtained via the several ring tests that have been made according to Mandate M/335.

As to exclude eventual interference from effects due to inhomogeneity of physically blended grades, no blends have been included in the ring tests; test samples have been limited and chosen as to be representing some main product grades sold within the EU.

The statistical evaluation has been done in line with ISO 5725-2 and whenever deemed necessary for appropriate evaluation and interpretation of the test results, some extra statistical evaluation was made on the test data.

As to judge to what extent problems arise in case of enforcement controls, some field data have been analysed as to verify to what extent actual conflicts exist in between test results from official controls and applied tolerances.

The evaluation revealed no real need for adjustments to tolerances as they relate to analytical variability. However, it should be emphasised that the tolerances given in Regulation 2003/2003 relate not only to analytical variability but to the total variability including allowances for sampling error and product variability.

Finally if the European Commission sees the necessity of further method improvements, then one could consider a project entitled to develop an alternative method. Only following a full evaluation including ring testing, a final judgment can be made if the newly developed method could be a candidate for replacement of the existing one(s) assuming better accuracy data.

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1 Scope

In Regulation (EC) No. 2003/2003 [2] tolerance limits are mentioned for nutrient contents in mineral fertilizers (Annex II of Regulation (EC) No. 2003/2003) as well as prescribed methods for control purposes (Annex IV of Regulation (EC) No. 2003/2003).

Prior to the work done by CEN/TC 260 following Mandate M/335, no statistical data were available for the official analytical methods to be applied. Due to the standardization work done for this mandate, statistical data have been generated as ring testing was a major topic in this mandate.

This Technical Specification describes to what extent the presently applied tolerances are in line with the obtained precision data from the analytical methods studied.

The purpose of this document is to give feedback on the applied tolerances within Regulation (EC) No. 2003/2003 based on the method evaluation done as an outcome of the work executed by CEN/TC 260/WG 7 according to Mandate M/335. This evaluation of the tolerances was part of Mandate M/418.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
tolerance (T)
variation including manufacturing, raw materials, sampling and analytical methods

3.2
repeatability limit (r)
the value less than or equal to which the absolute difference between two test results obtained under repeatability conditions may be expected to be with a probability of 95 %

[SOURCE: ISO 5725-1:1994]

Note 1 to entry: In other words, r is the minimum difference between two results in order to be statistically different, under repeatability conditions, at a 95 % probability level.

3.3
reproducibility limit (R)
the value less than or equal to which the absolute difference between two test results obtained under reproducibility conditions may be expected to be with a probability of 95 %

[SOURCE: ISO 5725-1:1994]

Note 1 to entry: In other words, R is the minimum difference between two results in order to be statistically different, under reproducibility conditions, at a 95 % probability level.

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4 Statistical method validation

4.1 General

European laboratories were involved, including as well private, industry, official as commercial laboratories.

ISO 5725-2 was applied as standard for ring testing and statistical evaluation of its results.

In general, legislative tolerances are given to accommodate variability in raw materials, manufacturing, sampling and analytical routines.

4.2 Approach taken by CEN/TC 260/WG 7

4.2.1 Product selection

The European market is characterised by a broad portfolio of different types of fertilizer grades, Hence there was a need for selection of a limited number of products to be tested for the ring-test(s). Aim during the selection process was to get fertilizer samples tested reflecting some main grades sold in the EEC.

4.2.2 Samples and their preparation

In order to be able to evaluate the precision data of the method as such, samples have been taken to the utmost extent as a spot (not agglomerated) sample out of a bulk production. This was done on purpose as to reduce the possible variation originating from raw materials, manufacturing and sampling procedure. Furthermore, all samples have been ground before distribution to the participating labs. Only solid, homogeneous samples and liquid samples have been used; no blends. The aim was to work with a limited number of samples, representing the main fertilizer grades applied.

4.2.3 Laboratories involved

The participation of the laboratories was on a voluntary basis, enabling as well private and industry, official and commercial laboratories to contribute. As far as the lab proficiency concerns, the ring test set-up did not require a familiarisation step for each of the individual participating laboratories nor for the methods evaluated. The chosen approach does not imply any assurance on the degree of experience and routine of the labs involved with the method under investigation and reflects the day-to-day situation as is.

4.2.4 Data evaluation

As already stated, ISO 5725-2 has been applied as the standard for the statistical data evaluation. However, for some methods a more in depth approach has been made, with the support of an expert statistician, due to the fact that the reproducibility parameters seemed to be in conflict with the existing tolerances. Based on this refined statistical analysis, it has been the intention to come up with adequate tolerances.

As stated in [1], R should be ≤ 0,7 T. In case this condition is not fulfilled, one should from a theoretical perspective considering the following alternative options:

— improve the method of analysis;

— propose an alternative method with better performance;

— increase the tolerances.

4.3 Statistical data: results versus tolerances

The ring test data and findings are given in the informative Annex A.

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4.4 Refined statistical analysis

Despite the method refinements to the determination of water soluble sulfur and water soluble calcium, reproducibility figures could not be improved substantially. Therefore, a more in-depth statistical analysis has been performed by an expert statistician. The main principles are described below; the detailed information can be consulted in Annex B.

In a first step, after applying the classical criteria for removing outliers of a population of data (see ISO 5725-2), it could be concluded that the reproducibility data were in conflict with the existing tolerances.

A substantial number of test results show high R values which implies that the methods only comply with tolerance substantially higher than the existing ones. In order to improve these reproducibility data, data sets outside the 99,9 % confidence interval (after removal of outliers according to Grubb's and Cochran's tests) have been removed. The s_R calculated from the remaining data is used to find a more adequate tolerance value and at the same time comply with the performance of the method.

The same exercise has been performed for the total sulfur content.

Further, the remaining data population has been crosschecked with the official tolerances. However, still conflicts were observed.

In a final step, it has been attempted to derive, based on statistical principles, reasonable tolerances for the concerned nutrients.

4.5 Field data

In order to cross-check the outcome of the statistical evaluation of official methods versus tolerances in place and verify the necessity for eventual adjustment of the existing tolerance limits, a population of obtained anonymised test results have been evaluated. The test results submitted were data derived from official controls (enforcement) and covering data from nutrient analysis on various fertilizer types such as: calcium ammonium nitrate (CAN), CAN+MgO and NPK. In total about 450 analyses were presented, covering analysis of Nitrogen, Sulfur, Magnesium and Phosphorus.

Sampling as well as analyses has been conducted according to EC methods.

These data have only been used to check whether problems arise in case of enforcement controls or not. The enforcement data have not been evaluated statistically on repeatability or reproducibility. Neither have they been used to evaluate the precision or correctness of the data obtained with CEN methods.

Tables 1 to 3 summarise data for fertilizer types that were numerously represented.

Table 1 — Product type: CAN27

Component	Declared value %	Number of analyses	Deviation from declaration %	Out of tolerance
N total	27	30	-0,4 to +0,6	No
N NH_4	13,5	30	-0,4 to +0,5	No

Table 2 — Product type: CAN27 + MgO

Component	Declared value %	Number of analyses	Deviation from declaration %	Out of tolerance
N total	27	20	-0,5 to +0,6	No
N NH_4	13,5	20	-0,6 to +0,5	No
MgO	4	20	-0,04 to +0,4	No
MgO (ws)	1 to 1,8	20	-0,96 to +1,0	Yes

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Table 3 — Product type: NPK containing sulfur

Component	Declared value %	Number of analyses	Deviation from declaration %	Out of tolerance
N total	15 to 16	12	-0,2 to +0,8	No
S	2 to 4	9	+0,3 to 2,31	No
S (ws)	1,6 to 3,2	10	-0,3 to +1,4	No
P_2O_5 (citrate)	15	10	-1,3 to +0,7	No

As can be seen from Tables 1 to 3, about 30 samples of CAN have been analysed and no exceeding of the tolerances was detected for the nitrogen content.

For the 20 samples of CAN + MgO that have been analysed no exceeding of tolerances for nitrogen and magnesium was found, except for MgO water soluble where a few deviations were identified.

About 15 samples of S containing NPK showed no exceeding of tolerances, neither for nitrogen, sulfur or phosphorus.

Based on these data, one can conclude that there is no urgent need for adjustments to tolerances, however it is obvious that deviation from declared values are larger for MgO and S compared to those for nitrogen.

5 Conclusions

In the frame of the mandate from the European Commission, and given the working conditions of WG 7, ring tests have been performed using a limited number of samples, representing the main fertilizer grades on the market. However, no physically blended grades have been used in the ring tests. Possible effects due to inhomogeneity of physically blended grades are therefore not reflected in the statistical evaluation of the various methods.

Based on evaluation of precision data there is in general no direct need for adaption of the existing tolerances as they relate to analytical variability (see Introduction). However, some discrepancy between the tolerances and the statistical data of the ring tests has been revealed. It concerns mainly the determination of calcium and magnesium, in particular related to the water soluble part. To a lesser extent also the determination of sulfur and more specifically the water soluble (ws) part, is concerned.

Therefore we do not recommend changing the applied tolerance limits from Regulation (EC) No 2003/2003 to the methods that have been evaluated, with exception of the nutrients mentioned above. The evaluation of a data set of enforcement controls seems to support this conclusion. However, since analytical variability is shown to account for the entire tolerances in Regulation 2003/2003, consideration must be given to increasing the individual tolerances to take account of sampling and product variability.

Regarding the method for determination of water soluble calcium, WG 7 has been exploring several possibilities to improve the accuracy of this method. Nevertheless, no major progress has been achieved in improving especially the reproducibility. Also a bench-mark with other legislative frames did not reveal better and alternative methods, as the water soluble calcium is not incorporated in non-European regulation.

As far as the nutrients water soluble calcium and magnesium, total sulfur and water soluble sulfur are concerned, a more in depth statistical evaluation has been made revealing that there are still conflicts between the analytical results and the official tolerances.

Nonetheless, based on the refined data population and the back calculation of reasonable tolerances, it is recommended to introduce the following adjustments to the officially applied tolerance limits:

— Sulfur (total and water soluble): 1,2 to 1,5;

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— Calcium and Magnesium (water soluble): 1,2 to 1,5.

Although the proposal above is an improvement to the existing situation, and given the inherent problems of the method of analysis and certain matrices, the proposed tolerance still does not cover completely the variability originating from sampling, manufacturing and analysis. Nevertheless, considering the cross-check with the field data, the proposed tolerance levels should be capable to take into account the full variability.

The proposed adjustment to the calcium tolerance still reveals possible conflicts for products with high calcium content, i.e. CAN 27.

Method 2.6.2 (EN 15750) for the determination of different forms of nitrogen in fertilizers containing nitrogen only as nitric, ammoniacal and urea nitrogen, such as UAN + S, does not perform well enough. Therefore, two alternative methods have been tested and have been proposed to replace method 2.6.2. It is also recommended to adjust the existing tolerance levels from 0,6 % up to 1,0 %.

However, an extra option could be to consider some further evaluation and development work regarding an alternative method for determination of the concerned nutrients, i.e. water soluble sulfur, calcium and magnesium. The nature of this work would be more in the field of method development at first instance, whereas a next step would be the launch of a ring test to define its precision data. Based on the evaluation of its statistical data, it should be possible to judge whether the alternative method is suitable for integration in the EU regulatory frame.

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Annex A
(informative)

Statistical data of the inter-laboratory tests and findings

A.1 General

Tables A.1 to A.32 show the accuracy data compared to tolerances for the methods given in Annex IV of the Regulation (EC) No. 2003/2003,

where

$\bar{x}$ is the mean value (mass fraction);

s_r is the repeatability standard deviation (mass fraction);

RSD_r is the relative repeatability standard deviation;

r is the repeatability limit (mass fraction);

s_R is the reproducibility standard deviation (mass fraction);

RSD_R is the relative reproducibility standard deviation;

R is the reproducibility limit (mass fraction).

A.2 Nitrogen

Table A.1 — Determination of ammoniacal nitrogen (EC method 2.1, EN 15475)

Sample	Sample type	Number of labs	Number of labs retained after elimination of outliers	$\bar{x}$	s_r	RSD_r	r	s_R	RSD_R	R	Current EC Tole-rance
AN 33,5	Solid	22	18	16,67	0,05	0,29	0,13	0,23	1,36	0,63	0,6
CAN 27	Solid	24	24	13,53	0,05	0,36	0,14	0,14	1,02	0,39	0,8
NPK1 (14-8-24+8S)	Solid	24	23	8,38	0,03	0,38	0,09	0,12	1,43	0,34	1,1
NPK2 (16-16-8+4S)	Solid	24	21	10,02	0,03	0,28	0,08	0,16	1,59	0,45	1,1
NP (DAP)	Solid	24	21	17,64	0,04	0,20	0,10	0,23	1,31	0,65	1,1

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