



Association of German Agricultural Analytic and Research Institutes

EU FERTILISER RING TEST Q9/2017: Calcium ammonium nitrate (CAN 27) and Urea 46

In 2017, the Association of German Agricultural Analytic and Research Institutes (VDLUFA e. V.) carried out an international ring test to determine the major and minor components in a liming material 'magnesium calcium carbonate (dolomitic limestone)'. The purpose of this fertiliser ring test is to offer a platform to laboratories in all EU countries for the testing and documentation of their respective analytical quality. 44 laboratories from 21 European countries took part in this ring test with the designation EU Q9/2017.

The analytes to be reported by the participating laboratories had to be determined using various official or standardised methods (see Tables 1 and 2).

The laboratories were asked to prepare the samples for analysis according to EN 1482-2:2007 'Fertiliser and liming materials - Sampling and sample preparation - Part 2: Sample preparation'.

The results for the individual determination were to be reported in the units given in Tables 1 and 2 based on fresh matter. Particular attention had to be paid to report the results for CO₂ determination as CO₂.

The laboratories were asked to use the official EU-methods as cited in Regulation (EC) No. 2003/2003 of the European Parliament and of the Council of 13th October 2003 relating to fertilisers. It was also possible to use other methods, like various international or national standards, VDLUFA methods (VDLUFA METHODS BOOK Volume II.1) or in-house methods. VDLUFA methods are official methods in the national German fertilizer regulation. Methods had to be reported with the results. Also, participants were asked to give information on the procedure used if more than one procedure was described in a method document of standard for the same analyte. The statistical evaluation of the results from both groups of methods (official EU-methods and the various other methods used) was performed separately.

The statistical evaluation was done by robust methods (DIN 38402 A45, Q-method, HAMPEL estimate). Z_u-scores (tolerance limit $|Z_u| \leq 2,0$) were calculated as a bias estimate using IUPAC guidelines, so that laboratories can evaluate their performance in comparison to other laboratories. HorRat values were calculated for the methods in case a sufficient number of results had been reported. For all statistical calculations, the validated software package ProLab was used.

Table 3 shows all mean values, comparative standard deviations (absolute + relative), repeated standard deviation, tolerance limits and HorRat values.

Interested laboratories can be supplied with material from the tested fertiliser in order to use it as internal reference material (see order form).

Table 1: Parameters to be determined in CAN 27 and methods used

No	Analyte	Method	Unit	Comments
1a	N-total-EN	EN 15476 (EU 2.2.3, Devarda) EN 15558 (EU 2.2.1, Ulsch) EN 15559 (EU 2.2.2, Arnd) EN 15604 (EU 2.6.1)	mass %	reported as N
1b	N-total-others	national or ISO methods, e. g. VDLUFA (II.1) 3.5.2.7 (elemental analysis), VDLUFA (II.1) 3.3.1 (Devarda) in-house methods	mass %	reported as N
2a	NH ₄ -N-EN	EN 15475 (EU 2.1)	mass %	reported as NH ₄ -N
2b	NH ₄ -N-others	national or ISO methods, e. g. VDLUFA (II.1) 3.2 in-house methods	mass %	reported as NH ₄ -N
3a	NO ₃ -N-EN	Calculated as: N total minus NH ₄ -N (EU 2)	mass %	reported as NO ₃ -N
3b	NO ₃ -N-others	national or ISO methods, e. g. VDLUFA (II.1) 3.4 in-house methods	mass %	reported as NO ₃ -N
4a	Ca-EN	EN 15960 (EU 8.1, extraction) and EN 16196 (EU 8.6, oxalate titration)	mass %	reported as Ca
4b	Ca-others	national or ISO methods, e. g. VDLUFA (II.1) 6.2.5 (ICP-OES) in-house methods	mass %	reported as Ca
5a	CO ₂ -EN	EN 14397-1 (EU 5.1)	mass %	reported as CO ₂
5b	CO ₂ -others	national or ISO methods, e. g. VDLUFA (II.1) 6.10 in-house methods	mass %	reported as CO ₂

VDLUFA II.1: VDLUFA (Ed. 1995-2012): VDLUFA METHODS BOOK Volume II.1, Fertiliser Analysis, VDLUFA-Verlag, Darmstadt.

Table 2: Parameters to be determined in Urea 46 and methods used

No	Analyte	Method	Unit	Comments
1a	N-total-EN	EN 15478 (EU 2.2.3)	mass %	reported as N
1b	N-total-others	national or ISO methods, e. g. VDLUFA (II.1) 3.5.2.7 (elemental analysis) in-house methods	mass %	reported as N
2a	Biuret-EN	EN 15479 (EU 2.5, photometry)	mass %	reported as Biuret
2b	Biuret-others	National or ISO methods, e.g. VDLUFA (II.1) 3.9 (photometry or HPLC, please specify!) in-house methods	mass %	reported as Biuret

VDLUFA II.1: VDLUFA (Ed. 1995-2012): VDLUFA METHODS BOOK Volume II.1, Fertiliser Analysis, VDLUFA-Verlag, Darmstadt.

VDLUFA Fertiliser Ring Test EU Q9/2017

Mean, Deviation, HorRat and Tolerance Limits

Method: DIN38402-A45

Criterion: Z_U-Score ≤ 2

Sample	Measurand	Unit	Mean	Reprod. S.D.		Repeat S.D.		HorRat	Limit of Tolerance		Number of Laboratories	Values
				Abs.	Rel.	Abs.	Rel.		Lower	Upper		
CAN_27	N_TOT_EN · N-total EN (as N)	mass%	26,753	0,325	1,21 %	0,145	0,54 %	0,5	26,107	27,407	28	111
	N_TOT_OT · N-total others (as N)	mass%	26,767	0,433	1,62 %	0,148	0,55 %	0,7	25,909	27,640	23	90
	NH4_N_EN · NH4-N-EN (as NH4-N)	mass%	13,421	0,150	1,11 %	0,049	0,37 %	0,4	13,124	13,722	29	114
	NH4_N_OT · NH4-N-others (as NH4-N)	mass%	13,357	0,193	1,45 %	0,099	0,74 %	0,5	12,974	13,746	16	62
	NO3_N_EN · NO3-N-EN (as NO3-N)	mass%	13,376	0,345	2,58 %	0,119	0,89 %	1,0	12,695	14,076	25	98
	NO3_N_OT · NO3-N-others (NO3-N)	mass%	13,345	0,191	1,43 %	0,107	0,80 %	0,5	12,965	13,729	19	73
	Ca_EN · Ca EN (as Ca)	mass%	8,363	0,333	3,98 %	0,089	1,06 %	1,4	7,710	9,043	10	39
	Ca_OT · Ca-others (as Ca)	mass%	8,502	0,284	3,30 %	0,080	0,93 %	1,1	8,044	9,179	34	135
	CO2_EN · CO2 EN (as CO2)	mass%	0,000	-	-	-	-	-	-	-	2	8
	CO2_OT · CO2-others (as CO2)	mass%	9,105	0,867	9,52 %	0,164	1,80 %	3,3	7,446	10,928	9	34
UREA_46	N_TOT_EN · N-total EN (as N)	mass%	46,265	0,392	0,85 %	0,142	0,31 %	0,4	45,484	47,052	23	90
	N_TOT_OT · N-total others (as N)	mass%	46,365	0,375	0,81 %	0,108	0,23 %	0,4	45,618	47,119	23	91
	BIURE_EN · Biuret EN (as Biuret)	mass%	0,804	0,113	14,03 %	0,013	1,53 %	3,4	0,592	1,048	20	80
	BIURE_OT · Biuret-others (as Biuret)	mass%	0,814	0,101	12,40 %	0,011	1,35 %	3,0	0,624	1,031	10	40