



Association of German Agricultural Analytic and Research Institutes

EU FERTILISER RING TEST Q8/2016: MAGNESIUM CALCIUM CARBONATE (DOLOMITIC LIMESTONE)

In 2016, 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. 45 laboratories from 18 European countries took part in this ring test with the designation EU Q8/2016.

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

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 Table 1 based on original matter as analysed except for the determination of heavy metals (Cd, Pb, Cr, Ni, Hg, As, Tl) which were to be reported based on dry matter.

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. 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 1: Analytes to be determined and methods used

Analyte	Method Digestion / Extraction	Method Final determination	Unit	Comments
Calcium	Acid digestion (HCl): EN 12946 VDLUFA II.1 6.1.1	Complexometry (e.g. EN 12946) Oxalate titration (EN 13475) F-AAS (e.g. VDLUFA II.1 6.2.4) ICP-OES (e.g. VDLUFA II.1 6.2.5)	mass %	reported as Ca
Magnesium	Acid digestion (HCl): EN 12947 EN 12946 VDLUFA II.1 6.1.1	F-AAS (EN 12947, VDLUFA II.1 7.2.3) Complexometry (e.g. EN 12946) ICP-OES (e.g. VDLUFA II.1 7.2.4)	mass %	reported as Mg
size distribution	EN 12948 VDLUFA II.1 6.5.1	EN 12948 VDLUFA II.1 6.5.1	mass %	reported as 3.15 mm and 1.00 mm screened fraction after dry sieving
moisture content	EN 12048	EN 12048	mass %	reported as moisture content
dry matter content	VDLUFA II.1 15.2.1	VDLUFA II.1 15.2.1	mass %	reported as dry matter content
reactivity	EN 13971 VDLUFA II.1 6.4	EN 13971 VDLUFA II.1 6.4	%	reported as reactivity
neutralisation value	EN 12945 VDLUFA II.1 6.3.1	EN 12945 VDLUFA II.1 6.3.1	mass %	reported as CaO
Cadmium	ISO 11466	ICP-OES AAS ICP-MS	mg/kg d.m.	reported as Cd
Lead	ISO 11466	ICP-OES AAS ICP-MS	mg/kg d.m.	reported as Pb
Chromium	ISO 11466	ICP-OES AAS ICP-MS	mg/kg d.m.	reported as Cr
Nickel	ISO 11466	ICP-OES AAS ICP-MS	mg/kg d.m.	reported as Ni
Mercury	ISO 11466	CV-AAS AFS	mg/kg d.m.	reported as Hg
Arsenic	ISO 11466	HG-AAS ICP-MS	mg/kg d.m.	reported as As
Thallium	ISO 11466 pressure digestion	GFS-AAS ICP-MS GF-AAS	mg/kg d.m.	reported as Tl

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

Table 2 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).

VDLUFU Fertiliser Ring Test EU Q8/2016

Mean, Standard Deviation, HorRat and Tolerance Limits

Method: DIN38402 A45

Criterion: Zu-Score <= 2

Sample	Measurand	Unit	Mean	Reprod. S.D.		HorRat	Limit of Tolerance		Number of Laboratories	Values
				Abs.	Rel.		Lower	Upper		
MG_CA_	CA_EU · Ca EU (as Ca)	mass%	17,806	0,369	2,07 %	0,8	17,057	18,571	19	76
	CAVDLUFU · Ca VDLUFU (as Ca)	mass%	18,185	1,126	6,19 %	2,4	15,944	20,569	34	136
	MG_EU · Mg EU (as Mg)	mass%	10,867	0,368	3,39 %	1,2	10,125	11,634	20	80
	MGVDLUFU · Mg VDLUFU (as Mg)	mass%	10,745	0,481	4,48 %	1,6	9,780	11,755	33	132
	SIZE315 · size distribution < 3.15 mm	mass%	98,064	1,158	1,18 %	-	95,704	100,451	31	124
	SIZE100 · size distribution < 1.00 mm	mass%	86,245	1,956	2,27 %	-	82,280	90,300	32	128
	MOISTURE · moisture content	mass%	12,837	0,280	2,18 %	-	12,270	13,418	40	160
	DRY · dry matter content	mass%	87,109	0,210	0,24 %	-	86,679	87,540	26	101
	REACT_EN · reactivity EN	%	17,107	5,930	34,66 %	13,3	6,516	32,153	15	53
	REACT_VD · reactivity VDLUFU	%	18,804	4,777	25,40 %	9,9	9,966	30,196	12	48
	NEUTRAL · neutralisation value (as CaO)	mass%	49,776	1,675	3,36 %	1,5	46,399	53,268	30	117
	CD · Cd aqua regia (as Cd)	mg/kg dm	0,328	0,096	29,17 %	1,5	0,153	0,561	37	143
	PB · Pb aqua regia (as Pb)	mg/kg dm	52,033	8,096	15,56 %	1,8	36,536	70,135	36	139
	CR · Cr aqua regia (as Cr)	mg/kg dm	4,531	1,204	26,57 %	2,1	2,312	7,426	35	135
	NI · Ni aqua regia (as Ni)	mg/kg dm	4,209	1,263	30,02 %	2,3	1,907	7,319	37	142
	HG · Hg aqua regia (as Hg)	mg/kg dm	0,011	0,006	58,95 %	1,9	0,002	0,028	30	117
	AS · As aqua regia (as As)	mg/kg dm	7,979	1,091	13,67 %	1,2	5,875	10,391	31	124
	TL · Tl (as Tl)	mg/kg dm	0,080	0,037	45,90 %	2,0	0,020	0,178	19	76