



Association of German Agricultural Analytic and Research Institutes

## EU FERTILISER RING TEST Q3/2011: NPK-SLOW RELEASE FERTILISER 15+9+15 (+ 2 MgO + 9 S)

In 2011, the Association of German Analytical and Research Institutes (VDLUFA e. V.) carried out an international fertiliser ring test to determine major and minor components in a NPK-Slow Release Fertiliser 15+9+15 (+2 MgO + 9 S). Purpose of this fertiliser ring test was to offer a platform for testing and documenting the analytical quality of laboratories in all EU countries. 28 laboratories from 10 European countries took part in the ring test with the designation EU Q3/2011.

The analytes to be reported by the participating laboratories had to be determined by various official or standardised methods (see Table 1). Laboratories were asked to prepare the samples for analysis according to Annex IV, Section B, Method 1 (sample preparation) of the Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13th October 2003 relating to fertilisers. Four aliquots of the sample material of the ring test EU Q3/2011 were prepared in order to be analysed. The results obtained for each individual determination (n=4) were reported in the units (mass % resp. mg/kg) given in Table 1, based on fresh mass (fm) and, with respect to the elements Cd, Pb, Ni and As, on dry mass (dm).

**Table 1: Analytes to be determined and methods used**

No	Analyte	Method Digestion/ Extraction	Method Final Determination	Unit	Comments
1	N-total-VDLUFA	VDLUFA*) 3.5.2.7	Elemental Analysis	mass % fm	reported as N
2	N-total-EU	EU**) 2.6	EU 2.6	mass % fm	reported as N
3	N-NO <sub>3</sub> -EU	EU 2.2	EU 2.2	mass % fm	reported as NO <sub>3</sub> -N
4	N-NH <sub>4</sub> -EU	EU 2.2	EU 2.2	mass % fm	reported as NH <sub>4</sub> -N
5	P <sub>2</sub> O <sub>5</sub> -water-EU	EU 3.1.6	EU 3.2	mass % fm	reported as P <sub>2</sub> O <sub>5</sub>
6	P <sub>2</sub> O <sub>5</sub> -nac-EU	EU 3.1.4	EU 3.2	mass % fm	reported as P <sub>2</sub> O <sub>5</sub>
7	K <sub>2</sub> O-water-EU	EU 4.1	EU 4.1	mass % fm	reported as K <sub>2</sub> O
8	MgO-EU	EU 8.1	EU 8.7, EU 8.8	mass % fm	reported as MgO
9	CaO-EU	EU 8.1	EU 8.6	mass % fm	reported as CaO
10	S-water-EU	EU 8.3	EU 8.9	mass % fm	reported as S
11	S-HCl-EU	EU 8.1	EU 8.9	mass % fm	reported as S
12	B-HCl-EU	EU 9.1	EU 9.5	mg/kg fm	reported as B
13	Zn-HCl-EU	EU 9.1	EU 9.11	mg/kg fm	reported as Zn
14	Cu-HCl-EU	EU 9.1	EU 9.7	mg/kg fm	reported as Cu
15	Mn-HCl-EU	EU 9.1	EU 9.9	mg/kg fm	reported as Mn
16	Fe-HCl-EU	EU 9.1	EU 9.8	mg/kg fm	reported as Fe
17	Cd-aqua regia	ISO 11466	ICP-OES	mg/kg dm	reported as Cd
18	Pb-aqua regia	ISO 11466	ICP-OES	mg/kg dm	reported as Pb
19	Ni-aqua regia	ISO 11466	ICP-OES	mg/kg dm	reported as Ni
20	As-aqua regia	ISO 11466	HG-AAS	mg/kg dm	reported as As

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

\*\*) Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13<sup>th</sup> October 2003 relating to Fertilisers

Concerning the analysis of P, K, Mg, S, B, Cu, Mn, Fe and Zn, final determination by ICP-OES (inductive coupled plasma optical emission spectrometry) was accepted as an alternative to the official methods. Element determination by means of ICP-OES is an official method of German National Fertiliser Regulation, but not of the EU Regulation 2003/2003. It is reported in the VDLUFA METHODS BOOK, Volume II.1, Fertiliser Analysis (Ed. 1995-2012).

Sample extraction according to ISO 11466 (aqua regia extraction in an open system) was strongly recommended for the analysis of Cd, Pb, Ni, and As. For the final determination, ICP-OES (inductively coupled plasma optical emission spectrometry) was recommended. Any other instrumental method (e.g. AAS, ICP-MS) could be used.

For the final determination of As, hydride generation AAS (HG-AAS) was recommended.

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 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).

### Mean, Standard Deviation, HorRat and Tolerance Limits

Method DIN38402 A45  
 Criterion Zu-Score <= 2

#### VDLUFA Fertilizer Ring Test EU Q3/2011

Sample Measurand	Unit	Mean	Reprod.S.D.		Repeat.S.D.		HorRat	Limit of Tolerance		Number of Laboratories	Values
			Abs.	Rel.	Abs.	Rel.		Lower	Upper		
NPK... N_TOT_L · N-total-VDLUFA	masse%	14,787	0,173	1,17 %	0,073	0,49 %	0,4	14,440	15,130	16	64
N_TOT_EU · N-total-EU 2.6	masse%	14,517	0,390	2,69 %	0,094	0,64 %	1,0	13,750	15,310	20	79
NO3_N · N-NO3-EU 2.2	masse%	2,641	0,262	9,93 %	0,049	1,87 %	2,9	2,141	3,195	22	88
NH4_N · N-NH4-EU 2.2	masse%	7,304	0,349	4,78 %	0,063	0,86 %	1,6	6,621	8,021	23	92
P2O5_W · P2O5-water-EU 3.1.6	masse%	7,705	0,418	5,42 %	0,070	0,91 %	1,8	6,891	8,564	28	112
P2O5_N · P2O5-nac-EU 3.1.4	masse%	9,804	0,188	1,91 %	0,077	0,79 %	0,7	9,430	10,180	27	108
K2O_W · K2O-water_EU 4.1	masse%	15,017	0,301	2,01 %	0,096	0,64 %	0,8	14,430	15,630	29	116
MgO · MgO-EU 8.1	masse%	2,741	0,193	7,03 %	0,035	1,29 %	2,0	2,368	3,141	29	115
CaO_EU · CaO-EU 8.1	masse%	3,519	0,241	6,85 %	0,037	1,06 %	2,1	3,052	4,018	28	111
S_W · S-water-EU 8.3	masse%	9,010	0,351	3,90 %	0,080	0,89 %	1,4	8,321	9,726	28	112
S_HCL · S-HCl-EU 8.1	masse%	9,284	0,371	4,00 %	0,080	0,87 %	1,4	8,555	10,042	27	107
B_HCL · B-HCl-EU 9.1	mg/kg	117,526	19,508	16,60 %	4,459	3,79 %	2,1	81,200	160,400	26	104
Zn_HCL · Zn-HCl-EU 9.1	mg/kg	43,916	5,439	12,39 %	0,827	1,88 %	1,4	33,630	55,560	27	107
Cu_HCL · Cu-HCl-EU 9.1	mg/kg	28,460	3,687	12,96 %	1,228	4,31 %	1,3	21,504	36,377	27	107
Mn_HCL · Mn-HCl-EU 9.1	mg/kg	98,735	11,893	12,04 %	2,010	2,04 %	1,5	76,216	124,133	27	107
Fe_HCL · Fe-HCl-EU 9.1	mg/kg	3597,784	419,053	11,65 %	48,544	1,35 %	2,5	2803,013	4490,637	27	107
CD · Cd-aqua regia	mg/kg dm	0,936	0,141	15,07 %	0,021	2,22 %	0,9	0,672	1,243	24	96
Pb · Pb-aqua regia	mg/kg dm	1,392	0,453	32,58 %	0,078	5,62 %	2,1	0,594	2,499	23	92
Ni · Ni-aqua regia	mg/kg dm	4,405	1,361	30,89 %	0,110	2,49 %	2,4	1,990	7,690	23	92
AS · As-aqua regia	mg/kg dm	1,921	0,396	20,60 %	0,071	3,68 %	1,4	1,196	2,813	22	88

