



Association of German Agricultural Analytic and Research Institutes

EU FERTILISER RING TEST Q1/2009: NPK-FERTILISER 12+12+17 (+2MgO+8S)

In 2009, the Association of German Analytical and Research Institutes (VDLUFA e. V.) carried out an international fertiliser ring test to determine major and minor components of NPK-fertiliser 12+12+17 (+2 MgO + 8 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. 29 laboratories from 10 European countries took part in the ring test with the designation EU Q1/2009.

The analytes to be reported by the participating laboratories had to be determined by various official or standardized 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 Q1/2009 were prepared in order to be analysed. (mass % resp. mg/kg) given in Table 1, based on fresh mass (fm).

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-NO3-EU	EU 2.2	EU 2.2	mass % fm	reported as N (nitric nitrogen)
4	N-NH4-EU	EU 2.2	EU 2.2	mass % fm	reported as N (ammoniacal nitrogen)
5	P2O5-water-EU	EU 3.1.6	EU 3.2	mass % fm	reported as P2O5
6	P2O5-nac-EU	EU 3.1.4	EU 3.2	mass % fm	reported as P2O5
7	K2O-water-EU	EU 4.1	EU 4.1	mass % fm	reported as K2O
8	MgO-EU	EU 8.1	EU 8.7, EU 8.8	mass % fm	reported as MgO
9	S-water-EU	EU 8.3	EU 8.9	mass % fm	reported as S
10	S-HCl-EU	EU 8.1	EU 8.9	mass % fm	reported as S
11	B-water-EU	EU 9.2	EU 9.5	mg/kg fm	reported as B
12	B-HCl-EU	EU 9.1	EU 9.5	mg/kg fm	reported as B
13	Zn-water-EU	EU 9.2	EU 9.11	mg/kg fm	reported as Zn
14	Zn-HCl-EU	EU 9.1	EU 9.11	mg/kg fm	reported as Zn
15	Cd-aqua regia	ISO 11466	ICP-OES	mg/kg fm	reported as Cd
16	Pb-aqua regia	ISO 11466	ICP-OES	mg/kg fm	reported as Pb
17	Ni-aqua regia	ISO 11466	ICP-OES	mg/kg fm	reported as Ni
18	Hg-aqua regia	ISO 11466	CV-AAS or AFS	mg/kg fm	reported as Hg
19	As-aqua regia	ISO 11466	ICP-OES	mg/kg fm	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 13th October 2003 relating to Fertilisers

Concerning the analysis of P, K, Mg, S, B 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).

Currently no EU regulation for analysing As, Cd, Pb, Ni and Hg in fertilizers exists. Therefore, sample extraction due to ISO 11466 (aqua regia extraction in an open system) was recommended. The method for final determination of As, Cd, Pb, Ni and Hg had to be chosen by the participants. ICP-OES was recommended for As, Cd, Pb and Ni and cold vapour atomic absorption spectrometry (CV-AAS) or atomic fluorescence spectrometry (AFS) was recommended for Hg, respectively.

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).

EU Fertilizer Ringtest Q1/2009

Mean, Standard Deviation, HorRat and Tolerance Limits

Sample	Measurand	Unit	Mean Value	Reprod.S.D.	Rel.Reprod.S.D.	Repeat.S.D.	Rel.Repeat.S.D.	HorRat	Lower Tol.	Upper Tol.	Laboratories	Values	Stat.Meth.
NPK	N_TOT_L	mass%	11,881	0,126	1,06	0,035	0,29	0,383	11,600	12,100	16	63	DIN38402
NPK	N_TOT_E	mass%	11,874	0,191	1,61	0,061	0,52	0,585	11,500	12,300	23	91	DIN38402
NPK	N03_N	mass%	4,678	0,217	4,64	0,060	1,27	1,464	4,250	5,120	23	92	DIN38402
NPK	NH4_N	mass%	7,192	0,118	1,64	0,034	0,48	0,551	6,960	7,430	26	104	DIN38402
NPK	P2O5_W	mass%	9,894	0,238	2,41	0,065	0,66	0,851	9,420	10,380	27	104	DIN38402
NPK	P2O5_N	mass%	12,470	0,207	1,66	0,061	0,49	0,607	12,100	12,900	28	110	DIN38402
NPK	K2O_W	mass%	17,148	0,318	1,86	0,103	0,60	0,712	16,500	17,800	27	107	DIN38402
NPK	MGO	mass%	2,003	0,099	4,94	0,019	0,94	1,370	1,810	2,210	27	106	DIN38402
NPK	S_W	mass%	8,745	0,265	3,03	0,045	0,52	1,050	8,220	9,280	22	88	DIN38402
NPK	S_HCL	mass%	9,018	0,311	3,45	0,063	0,70	1,201	8,410	9,650	24	96	DIN38402
NPK	B_W	mg/kg	173,840	19,593	11,27	2,269	1,31	1,531	137,000	215,000	22	88	DIN38402
NPK	B_HCL	mg/kg	240,928	44,040	18,28	5,069	2,10	2,609	160,000	339,000	23	92	DIN38402
NPK	ZN_W	mg/kg	1,511	0,785	51,96	0,108	7,16	3,456	0,340	3,580	15	60	DIN38402
NPK	ZN_HCL	mg/kg	89,984	6,568	7,30	0,817	0,91	0,898	77,300	103,600	25	100	DIN38402
NPK	CD	mg/kg	5,700	0,395	6,92	0,071	1,24	0,563	4,940	6,520	24	96	DIN38402
NPK	PB	mg/kg	1,602	0,616	38,44	0,060	3,76	2,580	0,550	3,160	20	80	DIN38402
NPK	NI	mg/kg	9,544	1,146	12,01	0,174	1,82	1,054	7,370	11,990	23	91	DIN38402
NPK	HG	mg/kg	0,011	0,006	53,43	0,001	7,86	1,693		0,030	13	52	DIN38402
NPK	AS	mg/kg	4,451	1,255	28,20	0,111	2,50	2,207	2,210	7,430	21	84	DIN38402