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Reference Material
Polar pesticides and amino alcohols in chia seeds
P2211-RMCh

Specification

The specification related to the reference material was authorised on behalf of PROOF-ACS GmbH by

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Specification

Reference material P2211-RMCh is a validated control material and not a certified reference material. The reference material is validated in ring test P2211-RT, which is organised, performed and evaluated according to the requirements of DIN EN ISO/IEC17043 and the “International Harmonized Protocol” (1,2). DIN ISO13528 is considered during the evaluation of the submitted results and during homogeneity testing. Details related to the applied statistics are provided in the section statistical evaluation. 16 laboratories took part in P2211-RT.

Reference material P2211-RMCh consists of whole, non-milled chia seeds (200 g), which are spiked with polar pesticides and amino alcohols (see table 1).

The corresponding unspiked non-milled chia seeds (150 g) is available as blank material P2211-BLCh (see table 2). The blank material is free from incurred residues of all spiked parameters (< 0.01 mg/kg).

Table 1. Reference material P2211-RMCh - specification

Parameter	Spiked level [mg/kg]	x_{pt} [mg/kg]	x_{pt} in % of the spiked level	$u(x_{pt})$ [mg/kg]	σ_H [mg/kg]	No. of results considered for the calculation of x_{pt}	Accepted range (trueness) [mg/kg]		Accepted range (comparability) [mg/kg]	
							Min	Max	Min	Max
Chlorate	0.11	0.109	99	0.00503	0.0241	14	0.077	0.14	0.061	0.16
Perchlorate	0.083	0.0667	80	0.00341	0.0147	14	0.058	0.10	0.037	0.096
Glyphosate	0.057	0.0418	73	0.00485	0.00920	12	0.039	0.069	0.023	0.060
Phosphonic acid	0.077	0.0635	82	0.00541	0.0140	14	0.053	0.093	0.036	0.091
Nicotine	0.083	0.0853	103	0.00705	0.0188	12	0.058	0.10	0.048	0.12
Diquat	0.039	0.0326	84	0.00507	0.00717	9	0.027	0.047	0.018	0.047
Paraquat	0.051	0.0452	89	0.00337	0.00993	11	0.035	0.062	0.025	0.065
Morpholine	0.079	0.0765	97	0.00885	0.0168	7	0.055	0.095	0.043	0.11
Diethanolamine	0.033	-	-	-	-	-	0.023	0.040	-	-
Triethanolamine	0.042	-	-	-	-	-	0.029	0.051	-	-
BAC C-10	0.031	0.0263	85	0.00125	0.00578	8	0.021	0.038	0.015	0.038
BAC C-12	0.023	0.0214	93	0.00149	0.00471	8	0.016	0.028	0.012	0.031
BAC C-14	0.041	0.0342	84	0.00335	0.00753	8	0.028	0.050	0.019	0.049
DDAC C-8	0.061	0.0547	90	0.00593	0.0120	8	0.042	0.074	0.031	0.079
DDAC C-12	0.035	0.0270	77	0.00352	0.00594	8	0.024	0.042	0.015	0.039

Table 2. Blank material P2211-BLCh - specification

Parameter	Reporting limit [mg/kg]	Result [mg/kg]
Chlorate	0.010	Not detected
Perchlorate	0.010	Not detected
Glyphosate	0.010	Not detected
Phosphonic acid	0.010	Not detected
Nicotine	0.010	Not detected
Diquat	0.010	Not detected
Paraquat	0.010	Not detected
Morpholine	0.010	Not detected
Diethanolamine	0.010	Not detected
Triethanolamine	0.010	Not detected
BAC C-10	0.010	Not detected
BAC C-12	0.010	Not detected
BAC C-14	0.010	Not detected
DDAC C-8	0.010	Not detected
DDAC C-12	0.010	Not detected

Storage conditions and shelf-life

Please store the reference material at -18°C in the dark. The reference material is dispatched in frozen condition.
The minimum shelf-life is one year after preparation (04/2023).

Preparation of the reference material

14 kg of organic chia seeds are utilised as raw material for the preparation of the reference materials and the blank materials. The chia seeds are homogenised in a blender. Subsamples of 150 g of the whole, non-milled and non-ground chia seeds are bottled as blank material P2211-BLCh. An analysis confirms the absence of incurred residues of all spiked parameters in the blank material (see homogeneity testing, “blank”).

Certified reference standards are used for the preparation of the reference material. For that purpose, 8 kg of the chia seeds are stirred in a blender. A mix solution of all parameters, solved in methanol, is added dropwise in order to spike the material. Stirring is continued for another 3 h after spiking in order to ensure a homogeneous distribution of the analytes in the reference material. Subsamples of 200 g are bottled as reference material P2211-RMCh thereafter.

During bottling, eight bottles of the reference material are randomly chosen for homogeneity testing and stability testing. Homogeneity testing is performed before the dispatch of the samples of P2211-RT (April 2022, see homogeneity testing). Stability testing is performed after the receipt of the results of the participants of P2211-RT (June 2022, see stability testing).

The reference materials and the blank materials are stored at -18°C in the dark.

Statistical evaluation

The reference material is prepared and validated according to the requirements of DIN EN ISO/IEC17043 and the “International Harmonized Protocol” (1,2) in a closed scheme. DIN ISO13528 is considered during the evaluation of the submitted results and during homogeneity testing (3). Details related to the applied statistics are provided in sections 1. to 4. below.

1. Assigned value

The assigned value x_{pt} is the statistical average (consensus) value of the results of the participants of the closed scheme. The assigned value is derived according to DIN ISO13528 (3), algorithm A as a robust mean of the results of the participants and represents the consensus of participants` results. The Winsorisation algorithm is applied to minimise the influence of outliers.

The assigned values are presented with an accuracy of three significant figures.

2. Uncertainty of the assigned value

The standard uncertainty of the assigned value $u(x_{pt})$ is calculated of the robust standard deviation s^* and the number of results p (3):

$$u(x_{pt}) = \frac{1.25 \times s^*}{\sqrt{p}}$$

3. Target standard deviation

The target standard deviation σ_H is derived of the assigned value x_{pt} according to DIN ISO13528 (3).

The term to be applied is:

$$\sigma_H = 0.22 \times x_{pt}$$

The target standard deviation according to Horwitz σ_H predicts a statistically expected standard deviation for a given concentration level (4).

4. Accepted ranges

The accepted ranges indicate the ranges within which results would have been accepted as satisfying in P2211-RT either with respect to the trueness criterion or with respect to the comparability criterion.

4.1. Trueness criterion

The trueness criterion considers the correct quantification of the actual analyte concentration in the sample. The trueness of the results is assessed as the coverage of the spiked level in %. The coverage of the spiked level is calculated of the result of each participant x_i according to the equation below:

Coverage of the spiked level [%] = $\frac{x_i}{spiked\ level} \times 100$

Accepted range:

Results, which correspond to a recovery of 70 to 120 % of the spiked level, are considered satisfying with respect to the trueness criterion. A non-commercial rounding is applied during the calculation of the accepted ranges (two significant figures). The figures in table 1 (“accepted range trueness”) correspond to 70 % (“min”) resp. 120 % (“max”) of the spiked level.

4.2. Comparability criterion (z-score)

The distance between the results of the laboratories and the assigned value describes the *comparability* of the results. The more the results differ from the assigned values the lower the comparability of the results.

The z-score is applied to evaluate the comparability of the results. It is derived of the result x_i of each participant, the assigned value x_{pt} and the target standard deviation σ_H:

$$z - score = \frac{x_i - x_{pt}}{\sigma_H}$$

Accepted range:

Results, which correspond to z-scores ≤ |2| are considered satisfying with respect to the comparability criterion. z-scores > |2| represent dissatisfactory results. The figures in table 1 ("accepted range comparability") correspond to z-scores of -2 ("min") resp. +2 ("max").

Homogeneity testing

Homogeneity testing is subcontracted to a lab, which holds an accreditation according to DIN EN ISO 17025.

The blank material was analysed in duplicate in order to confirm the absence of incurred residues of the spiked parameters in the blank material (see “blank” in tables 3 to 5). Seven samples of the reference material were analysed in duplicate for chlorate and perchlorate in order to confirm the homogeneity of the reference material (see “subsample No. 1-7” in table 3). The reference material is analysed in duplicate for all further parameters in order to confirm the spiked levels (tables 4 and 5). Spiked levels are confirmed.

Table 3. Results of the homogeneity testing

Subsample No.	Extraction No.	Chlorate [mg/kg]	Perchlorate [mg/kg]
Reporting limit [mg/kg]		0.01	0.01
blank	1	n.d.	(0.001)
	2	n.d.	(0.001)
1	1	0.10	0.059
	2	0.10	0.057
2	1	0.10	0.060
	2	0.11	0.064
3	1	0.10	0.059
	2	0.11	0.063
4	1	0.10	0.062
	2	0.11	0.065
5	1	0.096	0.060
	2	0.10	0.061
6	1	0.10	0.062
	2	0.11	0.064
7	1	0.10	0.058
	2	0.094	0.055
Mean [mg/kg]		0.103	0.0611
Standard deviation [mg/kg]		0.00312	0.00250
Coefficient of variation [%]		3.0	4.1
Spiked level [mg/kg]		0.11	0.083
Recovery of the spiked level [%]		93	74

n.d.: not detected (< 0.01 mg/kg)

Table 4. Results of the confirmation of the spiked level (part 1)

Subsample No.	Extraction No.	Glyphosate [mg/kg]	Phosphonic acid [mg/kg]	Nicotine [mg/kg]	Diquat [mg/kg]	Paraquat [mg/kg]	Morpholine [mg/kg]	Diethanol-amine [mg/kg]	Triethanol-amine [mg/kg]
blank	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<0.010	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<0.010	n.d.
1	1	0.041	0.075	0.067	0.031	0.041	0.062	0.030	0.034
	2	0.040	0.077	0.075	0.031	0.043	0.059	0.034	0.032
Mean [mg/kg]		0.0405	0.0760	0.0710	0.0310	0.0420	0.0605	0.0320	0.0330
Spiked level [mg/kg]		0.057	0.077	0.083	0.039	0.051	0.079	0.033	0.042
Recovery of the spiked level [%]		71	99	86	79	82	77	97	79

n.d.: not detected (RL: 0.01 mg/kg)

Table 5. Results of the confirmation of the spiked level (part 2)

Subsample No.	Extraction No.	BAC C-10 [mg/kg]	BAC C-12 [mg/kg]	BAC C-14 [mg/kg]	DDAC C-8 [mg/kg]	DDAC C-12 [mg/kg]
blank	1	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.
1	1	0.026	0.021	0.035	0.057	0.034
	2	0.025	0.022	0.037	0.055	0.037
Mean [mg/kg]		0.0257	0.0214	0.0361	0.0560	0.0355
Spiked level [mg/kg]		0.031	0.023	0.041	0.061	0.035
Recovery of the spiked level [%]		83	93	88	92	101

n.d.: not detected (RL: 0.01 mg/kg)

Stability testing

A sample of the reference material was stored for stability testing at -18°C in the dark. After the receipt of the results of the participants of P2211-RT (June 2022), the sample was analysed in duplicate for all spiked parameters (table 6). The results confirm the stability of all parameters throughout the whole testing period.

Table 6. Results of the stability testing

Parameter	Spiked level [mg/kg]	Result stability testing subsample 1 [mg/kg]	Result stability testing subsample 2 [mg/kg]	Mean (stability testing subsample 1/2) [mg/kg]	Mean before shipment [mg/kg]	Recovery compared to the mean before shipment [%]
Chlorate	0.11	0.13	0.12	0.124	0.103	122
Perchlorate	0.083	0.070	0.075	0.0725	0.0611	120
Glyphosate	0.057	0.049	0.051	0.0500	0.0405	123
Phosphonic acid	0.077	0.065	0.062	0.0635	0.0760	84
Nicotine	0.083	0.079	0.077	0.0780	0.0710	110
Diquat	0.039	0.031	0.032	0.0315	0.0310	102
Paraquat	0.051	0.038	0.040	0.0390	0.0420	93
Morpholine	0.079	0.068	0.072	0.0700	0.0605	116
Diethanolamine	0.033	0.040	0.040	0.0400	0.0320	125
Triethanolamine	0.042	0.036	0.037	0.0365	0.0330	111
BAC C-10	0.031	0.025	0.026	0.0255	0.0257	99
BAC C-12	0.023	0.022	0.024	0.0230	0.0214	108
BAC C-14	0.041	0.034	0.035	0.0345	0.0361	96
DDAC C-8	0.061	0.054	0.056	0.0550	0.0560	98
DDAC C-12	0.035	0.033	0.032	0.0325	0.0355	92

References

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