



Swedish University of Agricultural Sciences
Dept of Forest Biomaterials and Technology

Certificate

Energy Grass (*Phalaris arundinaceae* L.) Reference Material NJV 94-4

This Reference Material is intended for use in the control of instruments and methods in energy parameter and elemental analysis of energy grass.

Description of material

The reference material consists of reed canary grass (*Phalaris arundinaceae* L.) cultivated at Röbbäcksdalen, Västerbotten, Sweden. The grass was spring harvested in May, 1992.

The energy grass fuel has been chopped in a forage cutter and dried in 60 °C with gradual increase of temperature up to 90 °C during 5 days. The grass was then ground in a knife mill (Retsch) with a 2 mm sieve and finally in the same mill with a 1 mm sieve. The dry matter content is approximately 95 %.

Homogenization and test of homogeneity

The reference material was homogenized by thorough mixing in a large sack. It was then packed in dark 200 mL glass pots with screw lids, using a sample divider (Retsch PTZ).

The reference material was tested for homogeneity by duplicate analyses of 30 randomly chosen samples with respect to the content of ash, carbon, hydrogen and nitrogen. The results were analysed by "Analysis of variation (ANOVA)". The material was considered homogeneous if the variation between units, including inhomogeneity and analytical error, was not significantly larger than the analytical error.

No inhomogeneity was observed with respect to the analysed parameters.

Storage

The reference material should be stored in a dark and dry place in closed containers, preferably below room temperature. A similar material has been stored for over 5 years without any change in composition. Control of this material with respect to degradation will be carried out continuously.

Certifying procedure

The composition of this reference material has been determined in a proficiency test where 13 laboratories from Sweden, Finland and Denmark participated. The laboratories are listed in alphabetic order on page 4. Two randomly chosen samples of the grass material were distributed to the laboratories, together with instructions and report forms. The participants were requested to make duplicate determinations on each sample of the fuel material and report the results on a dry matter basis.

The statistical evaluation procedure was as follows:

1. Laboratory means were calculated on the basis of the reported individual determinations. All laboratories that reported one or more "Less than results" for a parameter were excluded from the statistical treatment of that parameter.
2. The set of data was analysed for technical outliers, which were rejected before the statistical evaluation.
3. The set of data was tested for statistical outliers by using the Dixon outlier test and the outliers were rejected. If several results were suspected as outliers, a consecutive Dixon outlier test was used.
4. The consensus value and its confidence interval at a significance level of 0.05 were calculated using a one-stage nested design according to "Certification of reference materials - General and statistical principles", **ISO GUIDE 35 : 1989**.

Analytical methods

Parameter	Methods of final determination
Ash	SS 18 71 71; ISO 1171 (500 °C); Leco-MAC 400 (550 °C)
Volatile matter	SS-ISO 562; ISO 562; DIN 51720
Calorific value	SS 18 71 82; ISO 1928; DIN 51900; ASTM D 3286
Carbon	CHN-analyzer
Hydrogen	CHN-analyzer
Nitrogen	CHN-analyzer; Kjeldahl
Sulfur	SS 18 71 76; SS 18 71 77; ASTM D 4239; Nefelometry
Chlorine	SS 18 71 54; ASTM D 2361; ASTM D 4208 with Ion Chromatography
Phosphorous	Colorimetry; ICP-AES; XRF
Aluminium	FAAS; ICP-AES; XRF
Calcium	FAAS; ICP-AES; XRF
Iron	FAAS; ICP-AES; XRF
Magnesium	FAAS; ICP-AES; XRF
Manganese	FAAS; ICP-AES; XRF
Potassium	FAAS; FAES; ICP-AES; XRF
Silicon	FAAS; ICP-AES; XRF
Sodium	FAAS; FAES; ICP-AES; XRF
Arsenic	AAS-hydride generation; GFAAS; ICP-MS
Cadmium	GFAAS; ICP-MS
Chromium	FAAS; GFAAS; ICP-MS
Copper	FAAS; GFAAS; ICP-MS
Lead	GFAAS; ICP-MS
Titanium	GFAAS; ICP-AES; XRF
Zink	FAAS; ICP-AES

Instructions for use

Rehomogenisation of the bottle contents prior to sampling is necessary. For the analysis of e.g., calorific value, carbon, hydrogen, nitrogen and sulphur by using high temperature combustion methods, the sample should be pelleted before analysis. For the other methods the sample should be taken as it is. The correction to dry mass should be obtained on a separate portion from the bottle by drying in an oven at 105 ± 2 °C to constant mass.

Certified values

Table Certified values of the composition of Energy Grass (*Phalaris arundinaceae* L.) Reference Material NJV 94-4

Parameter	Concen- ¹ tration	Confidence ² interval	No of ³ labs	No of ⁴ results
Ash, (%)	6,87	± 0,086	12 (0)	43 (0)
Calorific value, (MJ/kg)	18,5	± 0,19	10 (0)	36 (0)
Nitrogen, (%)	1,04	± 0,068	6 (0)	29 (0)
Sulphur, (%)	0,132	± 0,0097	8 (1)	32 (4)
Chlorine, (%)	0,058	± 0,0044	8 (1)	26 (4)
Phosphorous, (%)	0,109	± 0,0090	6 (0)	16 (0)
Aluminium, (%)	0,18	± 0,017	8 (0)	24 (0)
Calcium, (%)	0,21	± 0,018	8 (1)	24 (4)
Iron, (%)	0,106	± 0,0063	8 (1)	25 (2)
Magnesium, (%)	0,088	± 0,0074	9 (0)	28 (0)
Manganese, (%)	0,016	± 0,0016	8 (0)	26 (0)
Potassium, (%)	0,38	± 0,021	7 (2)	20 (8)
Silicon, (%)	2,1	± 0,24	5 (0)	12 (0)
Arsenic, (mg/kg)	0,4	± 0,12	5 (0)	18 (0)
Cadmium, (mg/kg)	0,09	± 0,023	6 (1)	24 (2)
Chromium, (mg/kg)	3,4	± 0,68	5 (0)	18 (0)
Copper, (mg/kg)	6,8	± 0,46	7 (0)	26 (0)
Lead, (mg/kg)	2,1	± 0,43	6 (1)	24 (2)
Zinc, (mg/kg)	42	± 4,2	7 (0)	26 (0)

¹ expressed on dry matter basis

² significance level of 0,05

³ accepted laboratories (eliminated laboratories)

⁴ accepted results (eliminated results)

Information values

Table Information values of the composition of Energy Grass (*Phalaris arundinaceae* L.) Reference Material NJV 94-4

Parameter	Concen- ¹ tration	Confidence ² interval	No of ³ labs	No of ⁴ results
Volatile matter ⁵ , (%)	77,2	± 0,77	9 (0)	36 (0)
Carbon, (%)	46,6	± 0,14	3 (1)	17 (2)
Hydrogen, (%)	5,7	± 0,14	4 (0)	19 (0)
Sodium, (%)	0,03	± 0,016	9 (0)	27 (0)
Titanium, (mg/kg)	128	± 24	4 (0)	10 (0)

¹ expressed on dry matter basis

² significance level of 0,05

³ accepted laboratories (eliminated laboratories)

⁴ accepted results (eliminated results)

⁵ reported as an information value due to the high dependency of experimental conditions on the result for this operationally defined parameter

Participating laboratories

ANALYTICA AB, Täby, Sweden

Central Laboratory Agricultural Research Centre of Finland, Jokioinen, Finland

dk-TEKNIK, Söborg, Denmark

Graf-Analys, Jönåker, Sweden

Helsingborg Energi AB, Helsingborg, Sweden

Hjortens Lab AB, Östersund, Sweden

Dept. of Agricultural Research for Northern Sweden, Swedish University of Agricultural Sciences, Umeå, Sweden

Ljunga Lab AB, Ljungaverk, Sweden

OY Keskuslaboratorio - Centrallaboratorium, Espoo, Finland

SGAB-analys, Luleå, Sweden

SP, Swedish National Testing and Research Institute, Borås, Sweden

VAPO OY, Jyväskylä, Finland

VTT, Combustion and thermal engineering Laboratory, Jyväskylä, Finland

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Robert Samuelsson

Swedish University of Agricultural Sciences
Dept. of Forest Biomaterials and Technology