Certified Reference Material Fertilizer C
Composted Sludge Fertilizer
FAMIC-C-21
No. +++
Certificate (Sample)

This reference material is produced by grinding composted sludge fertilizer specified in the official specifications of ordinary fertilizers[1)] to be homogenized. It can be used for quality control of the analysis results and for the validation of the analysis method, etc., in the quantitation of the main components, organic carbon, and harmful components of composted sludge fertilizer analyzed by the Testing Method for Fertilizers.

[Certified value]
The certified value (wet concentration) of the reference material and its uncertainty is as shown below. The uncertainty of the certified value is expanded uncertainty multiplying the standard uncertainty, which is obtained in a collaborative study to determine the certified value, by the coverage factor (k = 2). The number of digits to be expressed is up to the order of the minimum limit of quantification in the Testing Methods for Fertilizers, etc.

Table 1 Certified Value

Component	Content (μ) Mass Fraction (%)	Expanded Uncertainty ($U_{95\%}$) Mass Fraction (%)
Total nitrogen (T-N)Combustion method	4.11	0.02
Total nitrogen (T-N)Kjeldahl method	3.8	0.1
Total phosphorus (T-P_2O_5)	5.29	0.04
Total potassium (T-K_2O)	0.53	0.02
Total calcium (T-CaO)	4.16	0.08
Organic carbon (O-C)	27.0	0.20

Component	Content (μ) (mg/kg)	Expanded Uncertainty ($U_{95\%}$) (mg/kg)
Total copper (T-Cu)	447	8
Total zinc (T-Zn)	1340	14
Arsenic (As)	7.3	0.6
Cadmium (Cd)	2.0	0.1
Mercury (Hg)	0.61	0.02
Nickel (Ni)	27	2
Chromium (Cr)	31	2
Lead (Pb)	23	1

[Analytical methods]

Analysis is according to the Testing Methods for Fertilizers [2)]. Analytical methods for respective components are shown below:

Table 2 Analytical Methods

Component	Testing Methods for Fertilizers	Minimum amount of Analytical Sample for 1 Analysis
Total nitrogen (T-N)	4.1.1.b Combustion method	0.05 g - 0.5 g
	4.1.1.a Kjeldahl method	2.5 g
Total phosphorus ($T-P_2O_5$)	4.2.1.a Ammonium vanadomolybdate absorptiometric analysis	2.5 g - 5 g
Total potassium ($T-K_2O$)	4.3.1.a Flame atomic absorption spectrometry or flame photometry	5 g
Total calcium (T-CaO)	4.5.1.a Flame atomic absorption spectrometry	5 g
Organic carbon (O-C)	4.11.1.a Dichromate oxidation	0.05 g
	4.11.1.b Combustion method	0.05 g
Total copper (T-Cu)	4.10.1.a Flame atomic absorption spectrometry	5 g
	4.10.1.b ICP Optical Emission Spectrometry	5 g
Total zinc (T-Zn)	4.9.1.a Flame atomic absorption spectrometry	5 g
	4.9.1.b ICP Optical Emission Spectrometry	5 g
Arsenic (As)	5.2.a Hydride generation atomic absorption spectrometry	1 g - 2 g
	5.2.b Silver diethyldithiocarbamate absorption spectrometry	1 g – 2 g
Cadmium (Cd)	5.3.a Flame atomic absorption spectrometry	5 g
	5.3.b ICP Optical Emission Spectrometry	5 g
Mercury (Hg)	5.1.a Cold vapor atomic absorption spectrometry	1 g
Nickel (Ni)	5.4.a Flame atomic absorption spectrometry	5 g
	5.4.b ICP Optical Emission Spectrometry	5 g
Chromium (Cr)	5.5.a Flame atomic absorption spectrometry (fertilizers containing organic matters)	5 g
	5.5.d ICP Optical Emission Spectrometry	5 g
Lead (Pb)	5.6.a Flame atomic absorption spectrometry	5 g
	5.6.b ICP Optical Emission Spectrometry	5 g
(Reference information) Moisture (H_2O)	3.1.a Loss on drying method with drying apparatus*	5 g
	3.1.b Loss on drying method by moisture analyzers**	5 g

* : 100 ℃ ± 2 ℃, 5hours

** : Dry at 100 ° C until constant weight (mass loss 1 mg / 90 seconds or 1 mg / 140 seconds or less)

For details of analytical methods for components shown above, see the “Testing Methods for Fertilizers” disclosed in the website of the Food and Agricultural Materials Inspection Center.
URL for the above mentioned method: Testing Methods for Fertilizers
http://www.famic.go.jp/ffis/fert/obj/shikenho_2021.pdf

[Method to determine the certified value]
A collaborative study by 14 laboratories was conducted to determine the certified value of the reference material in December, 2021.[3) 4)]
The mean of the quantitation value in the collaborative study was determined as the certified value. In the calculation of the mean, the Cochran test at the one-sided significance level of 1 % and the Grubbs test at the two-sided significance level of 1 % were conducted to exclude outliers.[4)]

[Traceability]
The certified value of the reference material is the mean of the quantitation value in the collaborative study conducted by the “Testing Methods for Fertilizers” , which was validated using a reference material and standard solution traceable to the specified reference material (national standard) based on the Article 134 of the Measurement Law.

[Calculation of uncertainty]
The standard deviation of the total mean of the collaborative study is defined here as standard uncertainty (u), which is calculated according to formula (a) using the repeatability standard deviation (s_W), reproducibility standard deviation (s_R), the number of laboratories (p) and the number of repetitions (n = 6) at each laboratory of the collaborative study. The uncertainty of certified value is expanded uncertainty, which is obtained, after rounding the standard uncertainty (u) to one significant digit, by multiplying the rounded standard uncertainty (u) by the coverage factor (k) (formula (b)), and rounding the product off to the minimum limit of quantification of the “Testing Methods for Fertilizers”. The coverage factor (k) is 2, which corresponds to a 95 % confidence interval for the normal distribution.[5, 6)]

$$\text{Standard uncertainty } (u) = \sqrt{\frac{\left(s_R{}^2 - s_W{}^2\right) + \frac{s_W{}^2}{n}}{p}} \quad \cdots (a)$$

$$\text{Expanded uncertainty } (U_{95\,\%}) = k \times u \quad \cdots (b)$$

[Attestation date] February 25, 2022

[Expiration date]
The expiration date of the reference material is the end of June 2026 under the storage conditions shown below and unopened. Moreover, when change arises in the certified value by deterioration unexpected in the term of validity etc., it will be published on the FAMIC website.

[Form]
The reference material is powder that passed through a sieve of 500 μm aperture, and is sealed in an amber glass vial. The content is about 150 g.

[Homogeneity]
From 320 vials of a reference material candidate, 10 vials were sampled randomly to quantitate the content of the certified component in duplicate using one of the analytical methods listed in Table 2,

and one-way analysis of variance was duplicated × 10 samples.[7] As a result, no significant difference was observed between samples at the one-sided significance level of 5 %. The repeatability relative standard deviation was 0.2 % to 5.9 %.

[Storage precautions]
Store the reference materials at normal temperature (20 ℃±10 ℃) and protect them from direct sunlight, high temperature and high humidity. After opening, make sure to close the inner lid, and store sealed as much as possible.

[Usage precautions]
After using the reference material, do not leave the container open, and immediately close the inner lid.
The amount to be used in one analysis is shown in Table 2.
Moreover, the plants grown using this reference material are not to be served as food.

[Handling precautions]
Use the reference material for test only. Care should be taken to avoid injury when opening the container.
After opening, if the reference material becomes contaminated or deteriorated, it cannot be used as a certified reference material.

[Manufacturing method]
This reference material was prepared in the following process using a commercial composted sludge fertilizer produced by fermenting for 45 - 60 days after mixing human waste sludge, industrial sludge, sewage sludge and food residue.
After drying about 100 kg of composted sludge fertilizer in a constant temperature dryer at 65 ℃ for 5 hours or more, pulverize it with an ultra centrifugal pulverizer until it passes through a sieve with an aperture of 500 μm, homogenize, and then about 150 g brown Subdivided into glass bottles and sealed. Thereafter, sterilization by gamma irradiation was performed as a mold prevention measure.

[Reference information]
All of the certified value was for wet concentration. Moisture is tested by the loss on drying method with drying apparatus (Testing Methods for Fertilizers 3.1.a) and the loss on drying method by moisture analyzer (Testing Method for Fertilizers 3.1.b) , and the moisture content by method is shown in Table 3.
The standard deviation of reproducibility, the standard deviation of repeatability, the drying matter conversion factor of a certified value and the number of effective data calculated from the results of the collaborative study to determine the certified value of the reference material are shown in Table 4 as reference.
In the joint test results, there was a difference in the average value between the Kjeldahl method and the combustion method. Since this difference is that nitrate nitrogen contains a mass fraction of 0.36% (number of test rooms = 1, n = 3, phenolic sulfuric acid method (Testing Method for Fertilizers 4.1.3 .c) in the sample (Table 5), the certification value was set for each analysis method (Table 1) in this certified standard material, so be careful when using this standard substance.

Table 3 Reproducibility Standard Deviation and Repeatability Standard Deviation by method of Moisture (Reference Information)

Component	Numberof laboratories (p (q))*	Reference Value (μ) Mass Fraction (%)	Reproducibility Standard Deviation (s_R) Mass Fraction (%)	Repeatability Standard Deviation (s_W) Mass Fraction (%)
Moisture(H_2O) Loss on drying method with drying apparatus	8 (1)	12.0	0.5	0.2
Moisture(H_2O) Loss on drying method by moisture analyzers	6 (0)	13.2	0.2	0.2

* p=number of laboratories retained after outlier removed and (q)=number of outliers

Table 4 Reproducibility Standard Deviation, Repeatability Standard Deviation and Drying Matter (Loss on drying method with drying apparatus) Conversion Factor of Certified Value

Component	Number of laboratories (p (q))*	Certified Value (μ) Mass Fraction (%)	Reproducibility Standard Deviation (s_R) Mass Fraction (%)	Repeatability Standard Deviation (s_W) Mass Fraction (%)	Certified Value on a Dry Moisture Basis Mass Fraction (%)
Total nitrogen (T-N) Combustion method	9 (1)	4.11	0.02	0.02	4.67
Total nitrogen (T-N) Kjeldahl method	9 (0)	3.8	0.17	0.09	4.32
Total phosphorus (T-P_2O_5)	12 (1)	5.29	0.07	0.04	6.01
Total potassium (T-K_2O)	12 (0)	0.53	0.03	0.01	0.60
Total calcium (T-CaO)	9 (3)	4.16	0.12	0.07	4.7
Organic carbon (O-C)	10 (1)	27.0	0.4	0.2	30.7
Component	Number of laboratories (p (q))*	Certified Value (μ) (mg/kg)	Reproducibility Standard Deviation (s_R) (mg/kg)	Repeatability Standard Deviation (s_W) (mg/kg)	Certified Value on a Dry Moisture Basis (mg/kg)
Total copper (T-Cu)	11 (2)	447	16	9	515
Total zinc (T-Zn)	10 (3)	1340	35	31	1543
Arsenic (As)	11 (0)	7.3	1.1	0.3	8.4
Cadmium (Cd)	11 (2)	2.0	0.06	0.04	2.3
Mercury (Hg)	12 (1)	0.61	0.05	0.03	0.71
Nickel (Ni)	13 (0)	27	3	1	32
Chromium (Cr)	13 (0)	31	3	1	36
Lead (Pb)	11 (2)	23	1	0.4	26

* p=number of laboratories retained after outlier removed and (q)=number of outliers

Table 5 Nitrate nitrogen of this certified standard substance

Component	Reference Value (μ)[a)] Mass Fraction (%)	Standard Deviation (s) Mass Fraction (%)
Nitrate nitrogen (N-N)[b)]	0.36	0.002

a) n=3

b) Testing Method for Fertilizers 4.1.3.c Phenol sulfuric acid method

[Laboratories in the collaborative study (in the Japanese syllabary order)]

Japan Food Research Laboratories
Environment Research Center, Ltd.
Sumika Chemical Analysis Service, Ltd.
Nasu Kankyo Gijutsu Center Co., Ltd.
Hokuriku Environmental Science Institute Inc.
Kansai Branch, Japan Fertilizer and feed Inspection Association
Headquarters, Japan Fertilizer and feed Inspection Association
Kobe Regional Center, Food and Agricultural Materials Inspection Center
Sapporo Regional Center, Food and Agricultural Materials Inspection Center
Sendai Regional Center, Food and Agricultural Materials Inspection Center
Nagoya Regional Center, Food and Agricultural Materials Inspection Center
Fukuoka Regional Center, Food and Agricultural Materials Inspection Center
Headquarters, Food and Agricultural Materials Inspection Center
Nagasaki Agricultural and Forestry Technical Development Center

[Acquisition of information]

Changing the certified value or the like, as well as notify the purchaser if there is significant revision, is posted on the website below.

It should be noted that, with respect to technical information on how such use of this standard is to be referred to Annex "Using this certified reference substance".

URLs for the above website: http://www.famic.go.jp/ffis/fert/sub6.html

[Reference specifications and literature]

1) Public notice of the Ministry of Agriculture, Forestry and Fisheries: Subjects on the establishment of official specifications for ordinary fertilizers based on the Fertilizer Control Law, etc.: February 22, 1986, Notification No. 284 of the Ministry of Agriculture, Forestry and Fisheries, 1986. Final revision: June 14, 2021, Notification No. 1010, 2021.
2) Food and Agricultural Materials Inspection Center (FAMIC): Testing Methods for Fertilizers. <http://www.famic.go.jp/ffis/fert/obj/shikenho_2018.pdf>
3) JIS Q 0035, Reference Materials – General and Statistical Principles for Certification, 2008.
4) JIS Z 8402-2, Accuracy (trueness and precision) of measured methods and values - Part II: Basic methods to determine repeatability and reproducibility of standard measurement methods, 1999.
5) Supervised by Kozo Iizuka: Guides for expression of accuracy in measurement, Japanese Standards Association, 1996.
6) Japan Society for Analytical Chemistry, the supervisor of a translation: Quantifying Uncertainty by Analytical Measurement, Japan Society for Analytical Chemistry (2013)

7) Thompson, M., Ellison, S.L.R., Wood, R.: The International Harmonized Protocol for the Proficiency Testing of Analytical Chemical Laboratories, *Pure & Appl. Chem*., **78** (1), 145~196 (2006)

[Contact center for the certified reference material]

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