Certified Reference Material Fertilizer C
Composted Sludge Fertilizer

FAMIC-C-18-2

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 the quality control of analysis results and the validation of analytical methods, etc., in the quantitation of major components, organic carbon and harmful components in composted sludge fertilizers or similar 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 (%)	Number of laboratories (p)
Total nitrogen (T-N)	4.83	0.12	9
Total phosphorus (T-P_2O_5)	4.66	0.07	10
Total potassium (T-K_2O)	0.12	0.01	11
Total calcium (T-CaO)	1.68	0.06	11
Organic carbon (O-C)	37.2	0.2	11

Component	Content (μ) (mg/kg)	Expanded Uncertainty ($U_{95\%}$) (mg/kg)	Number of laboratories (p)
Total copper (T-Cu)	950	30	11
Total zinc (T-Zn)	1560	50	11
Arsenic (As)	12.9	0.8	10
Cadmium (Cd)	1.9	0.02	11
Nickel (Ni)	25	1.4	11
Chromium (Cr)	46	2	11
Lead (Pb)	26	0.6	11

[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	Sample Solution Preparation Method・Measurement Method	Recommended Amount of Analytical Sample for 1 Analysis
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
Total nitrogen (T-N)	4.1.1.a Kjeldahl method	2.5 g
	4.1.1.b Combustion method	0.1 g - 0.5 g
Total phosphorus ($T\text{-}P_2O_5$)	4.2.1.a Ammonium vanadomolybdate absorptiometric analysis (4.1.1) (4.4.2) (4.1.3)	5 g
Total potassium ($T\text{-}K_2O$)	4.3.1.a Flame atomic absorption spectrometry or flame photometry (4.1.1) (4.1.2)	5 g
Total calcium (T-CaO)	4.5.1.a Flame atomic absorption spectrometry (4.1.1) (4.1.2)	5 g
Organic carbon (O-C)	4.11.1.a Dichromate oxidation	0.05 g
	4.11.1.b Combustion method	
Total copper (T-Cu)	4.10.1.a Flame atomic absorption spectrometry*	5 g
	4.10.1.b ICP Optical Emission Spectrometry	
Total zinc (T-Zn)	4.9.1.a Flame atomic absorption spectrometry*	5 g
	4.9.1.b ICP Optical Emission Spectrometry	
Arsenic (As)	5.2.a Hydride generation atomic absorption spectrometry	1 g - 2 g
	5.2.b Silver diethyldithiocarbamate absorption spectrometry	
Cadmium (Cd)	5.3.a Flame atomic absorption spectrometry*	5 g
	5.3.b ICP Optical Emission Spectrometry	
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	
Chromium (Cr)	5.5.a Flame atomic absorption spectrometry (fertilizers containing organic matters)*	5 g
	5.5.d ICP Optical Emission Spectrometry	
Lead (Pb)	5.6.a Flame atomic absorption spectrometry*	5 g
	5.6.b ICP Optical Emission Spectrometry	

The methods specified by "*" are the same sample solution preparation method.

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_2018.pdf

[Method to determine the certified value]

A collaborative study by 11 laboratories was conducted to determine the certified value of the reference material in December, 2018.[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)]

Although distribution started in April 2019, due to doubts about mercury repeatability, a small-scale joint test by 6 laboratories was conducted in March 2020 and calculated again, and it was reference values.

[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) here 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] March 29, 2019

[Expiration date]

The expiration date of the reference material is the end of June 2023 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 120 g.

[Homogeneity]

From 150 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 0.4 % to 7.6 %.

[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 shown in Table 2 is recommended as the amount to be used in one analysis.
Moreover, the plants grown using this reference material are not to be served as food.

[Handling precautions]
Use the reference material for test purposes 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 sludge fermentation fertilizer produced by fermenting for 30 days from human waste sludge generated from an agricultural settlement wastewater treatment facility. After drying about 100 kg of sludge fermentation fertilizer in a constant temperature dryer at 65 ° C 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 120 g brown Subdivided into glass bottles and sealed. Thereafter, sterilization by gamma irradiation was performed as a mold prevention measure. Gamma irradiation sterilization was carried out by Japan Irradiation Service Co., Ltd.

[Reference information]
All of the certified value was for wet concentration. For the moisture content at the time of certification when 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) were carried out. The moisture content 6.8 % by mass (average of 10 test rooms, n = 6).
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 below as reference information.

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

Component	Numberof laboratories (p)	Reference Value (μ)	Reproducibility Standard Deviation (s_R)	Repeatability Standard Deviation (s_W)	Reference Value on a Dry Moisture Basis
Moisture(H_2O)	10	6.8	0.4	0.2	-
Mercury (Hg)	6	0.97	0.14	0.14	1.04

a) Unit：Mass Fraction (%) as Moisture, (mg/kg) as Mercury.

Table 4 Reproducibility Standard Deviation, Repeatability Standard Deviation and Drying Matter Conversion Factor of Certified Value

Component	Number of laboratories (p)	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)	9	4.83	0.2	0.05	5.18
Total phosphorus (T-P_2O_5)	10	4.66	0.1	0.03	5.00
Total potassium (T-K_2O)	11	0.12	0.01	0.004	0.13
Total calcium (T-CaO)	11	1.68	0.09	0.04	1.8
Organic carbon (O-C)	11	37.2	0.5	0.3	40.0
Component	Number of laboratories (p)	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	950	60	20	1019
Total zinc (T-Zn)	11	1560	80	20	1673
Arsenic (As)	10	12.9	1	0.5	13.9
Cadmium (Cd)	11	1.9	0.06	0.04	2.0
Nickel (Ni)	11	25	2	0.6	27
Chromium (Cr)	11	46	4	2	49
Lead (Pb)	11	26	1	0.8	28

[Laboratories in the collaborative study (in the Japanese syllabary order)]
Gifu Prefectural Public Health Inspection Center
Nasu Kankyo Gijutsu Center Co., Ltd.
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
Hokuriku Environmental Science Institute Inc.

[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.
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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[Full name of certification director]

Food and Agricultural Materials Inspection Center
Administrative director Kiuchi Takeshi

Revision history

March 29, 2020

- **[Expiration date] Added "Unopened" as a condition.**
- **[Notes on storage] Added the range of normal temperature.**
- **[Acquisition of information] Described the method of entering information.**
- **[Certification Officer] Deleted the item described as "Signature".**

June 25, 2020

- **[Certified value] Deleted for mercury.**
- **[Method of determining the certified value] The reason of using the reference value for mercury was described.**
- **[Homogeneity] The value of the parallel relative standard deviation was changed.**
- **[Reference information] Mercury is listed as a reference value.**
- **[Full name of certification director] The full name was changed.**