Certified Reference Material Fertilizer C
Composted Sludge Fertilizer

FAMIC-C-12-2

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. In addition, the values of mercury and lead are the results of the collaborative study in 2015 and the values of the other components are the results of the collaborative study in 2012.

Table 1 Certified Value

Component	Content (μ) Mass Fraction (%)	Expanded Uncertainty ($U_{95\%}$) Mass Fraction (%)
Total nitrogen (T-N)	4.70	0.04
Total phosphorus (T-P_2O_5)	8.62	0.04
Total potassium (T-K_2O)	0.58	0.02
Total calcium (T-CaO)	5.82	0.16
Organic carbon (O-C)	20.2	0.2

Component	Content (μ) (mg/kg)	Expanded Uncertainty ($U_{95\%}$) (mg/kg)
Total copper (T-Cu)	583	12
Total zinc (T-Zn)	992	18
Arsenic (As)	21.4	0.8
Cadmium (Cd)	1.8	0.1
Mercury (Hg)	0.49	0.01
Nickel (Ni)	73	2
Chromium (Cr)	82	4
Lead (Pb)	36	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	Sample Solution Preparation Method	Measurement Method	Recommended Amount of Analytical Sample for 1 Analysis
Total nitrogen (T-N)	4.1.1.a Kjeldahl method	Same as on the left	5 g
	4.1.1.c Devarda's alloy –Kjeldahl method	Same as on the left	
	–	4.1.1.b Combustion method	100 - 500 mg
Total phosphorus ($T-P_2O_5$)	4.2.1.a Ammonium vanadomolybdate absorptiometric analysis	4.2.1.a Ammonium vanadomolybdate absorptiometric analysis	5 g
	4.9.1.a Flame atomic absorption spectrometry (4.1) a) - h)*		
Total potassium ($T-K_2O$)	4.9.1.a Flame atomic absorption spectrometry (4.1) a) - h)*	4.3.1.a Flame atomic absorption spectrometry or flame photometry	5 g
	4.3.1.a Flame atomic absorption spectrometry or flame photometry (4.1) (Incineration-hydrochloric acid boiling)		
Total calcium (T-CaO)	4.9.1.a Flame atomic absorption spectrometry (4.1) a) - h)*	4.5.1.a Flame atomic absorption spectrometry	5 g
	4.5.1.a Flame atomic absorption spectrometry (4.1) (Incineration-hydrochloric acid boiling)		
Organic carbon (O-C)	4.11.1.a Dichromate oxidation	Same as on the left	50 mg
	—	4.1.1.b Combustion method	
Total copper (T-Cu)	4.10.1.a Flame atomic absorption spectrometry*	Same as on the left	5 g
Total zinc (T-Zn)	4.9.1.a Flame atomic absorption spectrometry*	Same as on the left	5 g
Arsenic (As)	5.2.b Silver diethyldithiocarbamate absorption spectrometry	Same as on the left	2 g
	5.2.a Hydride generation atomic absorption spectrometry	Same as on the left	
Cadmium (Cd)	5.3.a Flame atomic absorption spectrometry*	Same as on the left	5 g
Mercury (Hg)	5.1.a Cold vapor atomic absorption spectrometry	Same as on the left	1 g
Nickel (Ni)	5.4.a Flame atomic absorption spectrometry*	Same as on the left	5 g
Chromium (Cr)	5.5.a Flame atomic absorption spectrometry (fertilizers containing organic matters)*	Same as on the left	5 g
Lead (Pb)	5.6.a Flame atomic absorption spectrometry*	Same as on the left	5 g

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_2014.pdf

[Method to determine the certified value]
A collaborative study by 12 laboratories was conducted to determine the certified value of the reference material in August, 2012.[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)]
In addition, as there was concern of the underestimation of the uncertainty and difficulty of use regarding mercury and lead, they were re-certified under a collaborative study by 12 laboratories in July, 2015.

[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)]

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

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

[Attestation date] November 30, 2012 except for mercury and lead
January 29, 2016 for mercury and lead

[Expiration date]
The expiration date of the reference material is June 2020 under the storage conditions shown below. Moreover, when change arises in the certified value by deterioration unexpected in the term of validity etc., it is published on this center's 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 400 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 for the respective 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 0.46 % to 5.3 %.

[Storage precautions]
Store the reference materials at room temperature 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 deteriorates, it cannot be used as a certified reference material.

[Manufacturing method]
The reference material was prepared by the following processes using commercially available composted sludge fertilizer which was fermented for 45 days by mixing the sewage sludge from multiple sewage treatment plants, food industry sludge and animal material. 90 kg of composted sludge fertilizer was dried at 65 ºC for 24 hours using a temperature-controlled dryer. It was then crushed until it passed through a sieve of 500 μm aperture using an ultra-centrifugal mill. After homogenization, it was dispensed to be sealed in 120 g batches into amber glass bottles. Then, as an anti- mold measure, the bottles were subjected to gamma irradiation sterilization. Gamma irradiation sterilization was carried out by Japan Irradiation Service Co., Ltd.

[Reference information]
All of the certified value was for wet concentration. 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 conducted, was 11.7 % mass fraction (11 laboratories, the mean of n = 6). Additionally, the moisture content at the time of re-certification was 11.6 % mass fraction (11 laboratories, the mean of 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 (Reference Information)

Component	Number of Data (p)	Reference Value (μ) Mass Fraction (%)	Reproducibility Standard Deviation (s_R) Mass Fraction (%)	Repeatability Standard Deviation (s_W) Mass Fraction (%)
Moisture(H_2O) [1)]	11	11.7	0.81	0.17
Moisture(H_2O) [2)]	12	11.6	0.7	0.2

1) Collaboration study in 2012
2) Re-collaboration study in 2015

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

Component	Number of Data (p)	Certified Value (μ) Mass Fraction (%)	Reproducibility Standard Deviation (s_R) Mass Fraction (%)	Repeatability Standard Deviation (s_W) Mass Fraction (%)	Drying Matter Conversion Factor of Certified Value Mass Fraction (%)
Total nitrogen (T-N) [1)]	11	4.70	0.08	0.03	5.32
Total phosphorus (T-P_2O_5) [1)]	9	8.62	0.08	0.03	9.76
Total potassium (T-K_2O) [1)]	11	0.58	0.04	0.01	0.66
Total calcium (T-CaO) [1)]	11	5.82	0.29	0.10	6.59
Organic carbon (O-C) [1)]	12	20.2	0.6	0.4	22.9
Component	Number of Data (p)	Certified Value (μ) (mg/kg)	Reproducibility Standard Deviation (s_R) (mg/kg)	Repeatability Standard Deviation (s_W) (mg/kg)	Drying Matter Conversion Factor of Certified Value (mg/kg)
Total copper (T-Cu) [1)]	11	583	22	10	660
Total zinc (T-Zn) [1)]	12	992	32	15	1123
Arsenic (As) [1)]	10	21.4	1.4	0.5	24.2
Cadmium (Cd) [1)]	10	1.8	0.1	0.04	2.0
Mercury (Hg) [2)]	12	0.49	0.03	0.02	0.56
Nickel (Ni) [1)]	11	73	5	1	83
Chromium (Cr) [1)]	10	82	7	2	93
Lead (Pb) [2)]	12	36	1	0.5	41

Footnotes: See Table 3

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

Niigata Environment Hygiene Central Laboratory Co. (Participated in only 2015)
Japan Food Research Laboratories
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
NAITOH Environmental Science Co., Ltd. (Participated in only 2015)
Heisei Riken Co., Ltd.

[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_2014.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 Makoto Kimura

March 24, 2016

Fertilizer Technique Review Meeting,
Certified Reference Material Fertilizer Preparation Committee
Food and Agricultural Materials Inspection Center

Revision History

January 29, 2016

- [Certified Value]: It was described that the collaboration studies for mercury and lead were carried out on a different time from other components. In Table 1, numerical values regarding cadmium, mercury and lead were corrected. The rounding method of the numerical value of expanded uncertainty was changed.
- [Analytical Method]: Analytical methods were unified to the Testing Methods for Fertilizers.
- [Method to determine the certified value]: The collaborative study in 2015 was described.
- [Traceability]: The description about “Analytical Methods for Fertilizers” was deleted and the description about “Standard Solution” was added.
- [Calculation of uncertainty]: The rounding method of the numerical value for the calculation of expanded uncertainty was changed. In addition, omission marks used were corrected.
- [Attestation date]: The attestation dates of recertified components were listed.
- [Expiration date]: Extended from June, 2016 to June, 2020.
- [Reference information]: Information about a moisture content rate, mercury and lead in the collaboration study of the re-certificate was added. The maximum number of display digits was changed. In addition, omission marks used were corrected.
- [Reference specifications and literature]: The description about “Analytical Methods for Fertilizers” was replaced with the “Testing Methods for Fertilizers”.
- [Full name of certification director]: The full name was changed.
- “Appendix: Use of certified reference materials” was made into a separate volume.