Certified Reference Material Fertilizer A
High-analysis Compound Fertilizer

FAMIC-A-17

No. +++

Certificate（Sample）

This reference material is produced by grinding a compound 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 in compound fertilizers or similar fertilizers analyzed by the Testing Method for Fertilizers.

[Certified value]
The certified values (wet concentration) and uncertainty, expressed as mass fraction, are as shown in the following Table 1. 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 ($k = 2$).

Table 1 Certified Value

Component	Content (μ) Mass Fraction (%)	Expanded Uncertainty ($U_{95\%}$) Mass Fraction (%)
Total nitrogen (T-N)	14.08	0.06
Ammonia nitrogen (A-N)	11.72	0.08
Citric soluble phosphate (C-P_2O_5)	13.32	0.04
Citric soluble potassium oxide (C-K_2O)	13.96	0.10
Citric soluble magnesium oxide (C-MgO)	3.54	0.04
Citric soluble manganese oxide (C-MnO)	0.313	0.006
Citric soluble boron oxide (C-B_2O_3)	0.55	0.01
Water soluble boron oxide (W-B_2O_3)	0.45	0.01
Urea nitrogen (U-N)	2.26	0.08

[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 of Fertilizers	Minimum amount of Analytical Sample for 1 Analysis
Moisture	3.1.a Loss on drying method with drying apparatus(75 ℃± 2 ℃, 4 hours.) However, volatile matter correction is not performed.	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
Ammoniacal nitrogen (A-N)	4.1.2.b Formaldehyde method	5 g
	4.1.2.a Distillation method	0.5 g
Citric acid-soluble phosphoric acid ($C\text{-}P_2O_5$)	4.2.3.a Ammonium vanadomolybdate absorptiometric analysis	1 g
Citric acid-soluble potassium ($C\text{-}K_2O$)	4.3.2.a Flame atomic absorption spectrometry or flame photometry	1 g
Citric acid-soluble magnesia (C-MgO)	4.6.2.a Flame atomic absorption spectrometry	1 g
Citric acid-soluble manganese (C-MnO)	4.7.2.a Flame atomic absorption spectrometry	1 g
Citric acid-soluble boron ($C\text{-}B_2O_3$)	4.8.1.a Azomethine-H method	1 g
Water-soluble boron ($W\text{-}B_2O_3$)	4.8.2.a Azomethine-H method	2.5 g
Urea nitrogen (U-N)	6.3.b High-Performance Liquid Chromatography	1 g
Biuret nitrogen (B-N)	5.10.a High-Performance Liquid Chromatography	1 g

For details of the analytical methods for components shown above, see the “Testing Methods for Fertilizers” disclosed in the website of the Food and Agricultural Materials Inspection Center (FAMIC).

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URLs for the above mentioned methods:Testing Methods for Fertilizers
http://www.famic.go.jp/ffis/fert/obj/shikenho/shikenho_2022.pdf

[Method to determine the certified value]
A collaborative study by 16 laboratories was conducted to determine the certified value of the reference material.[3)4)]
At each laboratory, each component was tested in triplicate over two separate days, totally in six test results, and the certified value was determined as the mean of the quantitation value in the collaborative study. 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, although a collaborative study was conducted for moisture and biuret nitrogen, the relative standard deviation between rooms exceeded the Criteria of precision shown in the "Test Method for Fertilizers", and therefore these were not certified.

[Traceability]
The certified value of this reference material is determined by using a reference material and standard solution that are traceable to the specified reference material (national standard) based on Article 134 of the Measurement Law, or by the "Fertilizer Test Method" that has been confirmed to be valid. It is calculated by averaging the quantitative values obtained in the joint study conducted by the same test method using the agreed standard. The joint laboratory is a laboratory that participated in the interlaboratory comparison program sponsored by the Fertilizer Quality Conservation Council "Analysis with Common Samples in 2015" and reported satisfactory results.

[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 obtained by multiplying the standard uncertainty (u) by the coverage factor (k) (formula (b)), and rounding the product off to within two significant digits. The coverage factor (k) here is 2, which corresponds to the approximately 95 % confidence interval for the normal distribution.[5)]

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

Expanded uncertainty ($U_{95\%}$) = $k \times u$ …… (b)

[Attestation date] March 20, 2018

[Expiration date]
The expiration date of the reference material is end of June 2027 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 informed to users by publishing on the FAMIC website etc.

[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 140 g.

[Homogeneity]
From 400 vials of reference material candidates, 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 conducted for duplicate × 10 samples.[6] As a result, no significant difference was observed between samples at the one-sided significance level of 5 %. The repeatability relative standard deviation was 0.5to 4.6 %.

[Storage precautions]
Store the reference material at 20 ℃±10 ℃ protected 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 for test purpose 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]
The reference material was prepared by the following processes using commercially available high-analysis compound fertilizer produced using ammonium phosphate,ammonium sulfate, urea, potassium chloride, magnesium hydroxide fertilizers, borate fertilizers, fritted micronutrient mixture. Eighty (80) kg of the high-analysis compound fertilizer was crushed until it passed through a sieve of 500 μm aperture to be homogenized, and was dispensed into amber glass bottles by approximately 140 g to be sealed.

[Reference information]
The standard deviation of reproducibility, the standard deviation of repeatability, 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). Water and biuret nitrogen whose inter-room reproducible relative standard deviation exceeded the Criteria of precision shown in the “Test Methods for Fertilizers” were used as reference values (Table 4). The certified values or reference values for this reference material are all figures per product, and the dry matter equivalent calculated from the moisture reference value is also shown for reference.

Table 3 Reproducibility Standard Deviation, Repeatability Standard Deviation, and Certified Values on a Dry Moisture Basis

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)	18 (4)	14.08	0.14	0.05	14.29
Ammonia nitrogen (A-N)	21 (2)	11.72	0.19	0.06	11.89
Citric soluble phosphate (C-P_2O_5)	15 (1)	13.32	0.10	0.07	13.52
Citric soluble potassium oxide (C-K_2O)	16 (0)	13.96	0.24	0.13	14.17
Citric soluble magnesium oxide (C-MgO)	16 (0)	3.54	0.08	0.04	3.60
Citric soluble manganese oxide (C-MnO)	14 (2)	0.313	0.013	0.004	0.318
Citric soluble boron oxide (C-B_2O_3)	15 (1)	0.55	0.02	0.01	0.56
Water soluble boron oxide (W-B_2O_3)	15 (1)	0.45	0.01	0.01	0.46
Urea nitrogen (U-N)	10 (0)	2.26	0.14	0.06	2.30

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

Table 4 Reproducibility Standard Deviation, Repeatability Standard Deviation, and Reference Values on a Dry Moisture Basis

Component	Number of laboratories (p (q))*	Reference 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 (%)
Moisture (H_2O)	15 (1)	1.47	0.27	0.08	-
Biuret nitrogen (B-N)	10 (0)	0.009	0.002	0.001	0.009

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

[Laboratories in the collaborative study (in the Japanese syllabary order)]
Iwaki plant, MC Ferticom Co., Ltd.
Ube plant, MC Ferticom Co., Ltd.
Niigata plant, Onoda Chemical Industry Co., Ltd.
Kansai branch Himeji plant , Katakura & Co-op Agri Co.

Niigata analysis center, CO-OP ENG.Co., Ltd.
Headquarters, Japan Fertilizer and Feed Inspection Association
Kobe Regional, Japan Fertilizer and Feed Inspection Association
Fuji plant, JCAM AGRI.Co., Ltd.
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
Nagoya plant, Nitto FC Co., Ltd.
Muroran plant, Hokkaidohiryo Co., Ltd.

[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) Notification from 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/shikenho_2022.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) 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]
Analysis Fertilizer and Soil Amendments Division, Fertilizer and Feed Inspection Department, Headquarters, Food and Agricultural Materials Inspection Center
Saitama New Urban Center, 2-1 Shin-toshin, Chuo-ku, Saitama City, Saitama (330-9731) Japan
TEL: (81) 50-3797-1856, FAX: (81) 48-601-1179
Website: http://www.famic.go.jp

[Full name of certification director]
Food and Agricultural Materials Inspection Center
Administrative director Takeshi Kiuchi

Revision history

March 27, 2020

・[Certified value] The number of laboratories was added to Table 1.

・[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".

March 6, 2023

・[Certified value] The number of laboratories was deleted from Table 1.

・[Expiration date] Based on the results of the stability monitoring, the expiration date was extended from June 2023 to the end of June 2027.

・[Reference information] Added the description of the number of outliers to Tables 3 and 4.