Certified Reference Material Fertilizer B
Low-analysis Compound Fertilizer

FAMIC-B-14

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 main components and harmful components of compound fertilizers or similar fertilizers analyzed by the Testing Method for Fertilizers.

[Certified value]
The certified values (wet concentration) of the reference material and its uncertainty is 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 (%)
Ammoniacal nitrogen (A-N)	8.06	0.03
Citrate-soluble phosphoric acid (S-P_2O_5)	9.18	0.04
Water-soluble phosphoric acid (W-P_2O_5)	6.70	0.03
Citric acid-soluble potassium (W-K_2O)	8.32	0.06

Component	Content (μ) (mg/kg)	Expanded Uncertainty ($U_{95\%}$) (mg/kg)
Arsenic (As)	2.87	0.11
Cadmium (Cd)	4.23	0.14
Nickel (Ni)	37.9	1.700

[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	Minimum amount of an Analytical Sample for 1 Analysis
Ammoniacal nitrogen (A-N)	4.1.2.a Distillation method	0.5 g
Citrate-soluble phosphoric acid (S-P_2O_5)	4.2.2.a Ammonium vanadomolybdate absorptiometric analysis	2.5 g
Water-soluble phosphoric acid (W-P_2O_5)	4.2.4.a Ammonium vanadomolybdate absorptiometric analysis	5 g
Water-soluble potassium (W-K_2O)	4.3.3.a Flame atomic absorption spectrometry or flame photometry	5 g
Arsenic (As)	5.2.a Hydride generation atomic absorption spectrometry	2 g
	5.2.b Silver diethyldithiocarbamate absorptiometric analysis	
Cadmium (Cd)	5.3.a Flame atomic absorption spectrometry	5 g
Nickel (Ni)	5.4.a Flame atomic absorption spectrophotometry	5 g

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/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)]

[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 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 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 a 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 26, 2015

[Expiration date]
The expiration date of the reference material is 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 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 0.6 % to 3.4 %.

[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 seal 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 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]
The reference material was prepared by the following processes using a commercially available low-analysis compound fertilizer produced using ammonium sulfate, single superphosphate, and potassium chloride. Eighty (80) kg of the low-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 about 150 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. Because the loss in weight of unopened bottles measured using a dry oven by the heat dry method (100 °C, 3 hours) was a 0.69 % mass fraction (expanded uncertainty 0.04 %,14 laboratory, the mean of $n = 6$), the certified values obtained as moisture contents are converted on a dry moisture basis, and the calculated results are listed below.

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 (%)
Ammoniacal Nitroge (A-N)	15 (1)	8.06	0.07	0.04	8.11
Soluble phosphate (S-P_2O_5)	15 (1)	9.18	0.09	0.04	9.25
Water soluble phosphate (W-P_2O_5)	15 (1)	6.70	0.06	0.03	6.74
Water soluble potassium oxide (W-K_2O)	14 (2)	8.32	0.13	0.06	8.38
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)
Arsenic (As)	13 (0)	2.87	0.24	0.15	2.89
Cadmium (Cd)	14 (0)	4.23	0.28	0.09	4.26
Nickel (Ni)	12 (1)	37.9	3.0	0.8	38.1

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

[Laboratories in the collaborative study (in the Japanese syllabary order)]
Niigata plant, Onoda Chemical Industry Co., Ltd.
Tsukuba Research Institute, Katakura Chikkarin Co.,Ltd.
Kaken Environmental Consulting Inc.
Japan Fertilizer and Feed Inspection Association Kansai Branch
Japan Fertilizer and Feed Inspection Association Headquarters
Hachinohe plant, Co-op Chemical Co.,Ltd.
Kashima plant, Summit Agri-Business Corporation

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
Research and Development Department, Nittofc Co.,Ltd.
Palynosurvey Co.,Ltd.
Obihiro plant, Hokuren Fertilizer 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) JIS Z 8404-2, Measurement uncertainty - Part II: Measurement uncertainty for metrological applications – Repeated measurements and nested experiments.
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
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[Full name of certification director]

Food and Agricultural Materials Inspection Center
Administrative director Takeshi Kiuchi

Revision history

January 26, 2018

・The date of the header was changed from the certification date to the shipping date.

・Clarified the serial number printing location of certified reference materials.

March 27, 2020

・[Certified value] Clarified that the certified value is wet concentration. The number of laboratories was added to Table 1.

・[Expiration date] Added "Unopened" as a condition. Based on the results of the stability monitoring, the expiration date was extended from June 2021 to the end of June 2023.

・[Notes on storage] Added the range of normal temperature.

・[Acquisition of information] The URL of the homepage is described.

・[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 2026.

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