Certified Reference Material Fertilizer B
Low-analysis Compound Fertilizer

FAMIC-B-14

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.

[Certified value]
The certified value of the reference material and its uncertainty is as shown below. The quoted uncertainty is the half-width of the expanded uncertainty interval calculated using a coverage factor (k) of 2, which gives a level of confidence of approximately 95 %.

Table 1 Certified Value

Component	Content (μ) Mass Fraction (%)	Expanded Uncertainty ($U_{95\%}$) Mass Fraction (%)
Ammonia nitrogen (A-N)	8.06	0.03
Soluble phosphate (S-P_2O_5)	9.18	0.04
Water soluble phosphate (W-P_2O_5)	6.70	0.03
Water soluble potassium oxide (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	1.7

[Analytical methods]
Analytical methods for respective components are shown below. The symbols for the Sample Preparation Method and the Measurement Method correspond to symbols that show items of the "Testing Methods for Fertilizers (2014 version)" and the "Analytical Methods for Fertilizers (1992 version)[2)]".

Table 2 Analytical Methods

Component	Analytical method	Sample Solution Preparation Method	Measurement Method	Recomended Amount of an Analytical Sample for 1 Analysis
Ammonia nitrogen (A-N)	Testing methods for fertilizers	—	4.1.2.a Distillation method	0.5 g
	Analytical methods for fertilizers	—	4.1.2.1.D Distillation method	
Soluble phosphate ($S\text{-}P_2O_5$)	Testing methods for fertilizers	4.2.2.a Ammonium vanadomolybdate absorption spectrometry	Same as the left	2.5 g
	Analytical methods for fertilizers	4.2.1.C.c.1)	4.2.3.E.b Ammonium vanadomolybdate method	
Water soluble phosphate ($W\text{-}P_2O_5$)	Testing methods for fertilizers	4.2.4.a Ammonium vanadomolybdate absorption spectrometry	Same as the left	5 g
	Analytical methods for fertilizers	4.2.1.C.b	4.2.3.E.a Ammonium vanadomolybdate method	
Water soluble potassium oxide ($W\text{-}K_2O$)	Testing methods for fertilizers	4.3.3.a Flame atomic absorption spectrometry or flame photometry (4.1.2)	4.3.3.a Flame atomic absorption spectrometry or flame photometry	5 g
	Analytical methods for fertilizers	4.3.1.C.b.2) (Note)	4.3.3.E Atomic absorption spectrophotometry	
Arsenic (As)	Testing methods for fertilizers	5.2.a Hydride generation atomic absorption spectrometry	Same as the left	2 g
	Testing methods for fertilizers	5.2.b Silver diethyldithiocarbamate photometric method	Same as the left	
	Analytical methods for fertilizers	5.24.1.D.a.1)	5.24.1.E Silver diethyldithiocarbamate method	
	Analytical methods for fertilizers	5.24.1.D.a.1)	5.24.2.E.2) Atomic absorption spectrophotometry	
Cadmium (Cd)	Testing methods for fertilizers	5.3.a Flame atomic absorption spectrometry (4.1) Remark 1	5.3.a Flame atomic absorption spectrometry	5 g
	Analytical methods for fertilizers	5.6.1.D.a.1)	5.6.1.E.a Atomic absorption spectrophotometry	
Nickel (Ni)	Testing methods for fertilizers	5.4.a Atomic absorption spectrophotometry (4.1) Remark 1	5.4.a Flame atomic absorption spectrometry	5 g
	Analytical methods for fertilizers	5.1.1.D.a.1)	5.21.2.E Atomic absorption spectrophotometry	

For details of the analytical methods for components shown above, see the "Testing Methods for Fertilizers" or "Analytical Methods for Fertilizers" disclosed in the website of the Food and Agricultural Materials Inspection Center.

URLs for the above mentioned methods:
Testing Methods for Fertilizers
http://www.famic.go.jp/ffis/fert/obj/shikenho_2014.pdf
Analytical Methods for Fertilizers (1992)
http://www.famic.go.jp/ffis/fert/sub6_data/sub6_analyze.html

In the establishment of the "Testing Methods for Fertilizers," the analytical methods are validated and care is taken to maintain integrity to the Analytical Methods for Fertilizers.

[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 sextuplicate, 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 3, 2015

[Expiration date]
The expiration date of the reference material is June 2019 under the storage conditions shown below. 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, ten (10) 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 room temperature 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 shown in Table 2 is recommended as the amount to be used in one analysis.

[Handling precautions]
Use for test purposes only. Care should be taken to avoid injury when opening.
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 Data (p)	Certified Value (μ) Mass Fraction (%)	Reproducibility Standard Deviation (s_R) Mass Fraction (%)	Repeatability Standard Deviation (s_r) Mass Fraction (%)	Certified Value on a Dry Moisture Basis Mass Fraction (%)
Ammonia Nitroge (A-N)	15	8.06	0.07	0.04	8.11
Soluble Phosphate (S-P_2O_5)	15	9.18	0.09	0.04	9.25
Water Soluble Phosphate (W-P_2O_5)	15	6.70	0.06	0.03	6.74
Water Soluble Potassium Oxide (W-K_2O)	14	8.32	0.13	0.06	8.38

Component	Number of Data (p)	Certified Value (μ) (mg/kg)	Reproducibility Standard Deviation (s_R) (mg/kg)	Repeatability Standard Deviation (s_r) (mg/kg)	Certified Value on a Dry Moisture Basis (mg/kg)
Arsenic (As)	13	2.87	0.24	0.15	2.89
Cadmium (Cd)	14	4.23	0.28	0.09	4.26
Nickel (Ni)	12	37.9	3.0	0.8	38.1

[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
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".

[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) National Institute for Agro-Environmental Sciences: Analytical Methods for Fertilizers (1992 version), Japan Fertilizer and Feed Inspection Association, Tokyo, 1992.
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
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 Makoto Kimura

March 26, 2015

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