Certified Reference Material Fertilizer A
High-analysis Compound Fertilizer

FAMIC-A-13

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 values and uncertainty, expressed as mass fraction, are given in the following table. 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 (%)
Total nitrogen (T-N)	14.83	0.09
Ammonia nitrogen (A-N)	10.36	0.13
Citric soluble phosphate (C-P_2O_5)	10.79	0.03
Water soluble potassium oxide (W-K_2O)	13.07	0.08
Citric soluble magnesium oxide (C-MgO)	3.18	0.08
Citric soluble manganese oxide (C-MnO)	0.356	0.009
Citric soluble boron oxide (C-B_2O_3)	0.203	0.005

[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 "Analytical Methods for Fertilizers (1992 version)[2)]" and the "Testing Methods for Fertilizers."

Table 2 Analytical Methods

Component	Analytical method	Sample Solution Preparation Method	Measurement Method	Recomended Amount of an Analytical Sample for 1 Analysis
Total nitrogen (T-N)	Analytical methods for fertilizers	4.1.1.1.C Sulfuric acid method	4.1.1.1.D	2.5 g
	Testing methods for fertilizers	4.1.1.a Kjeldahl method	Same as the left	
	Testing methods for fertilizers	4.1.1.b Combustion method	Same as the left	0.1-0.5 g
Ammonia nitrogen (A-N)	Analytical methods for fertilizers	4.1.2.3.C.3) Formaldehyde method	4.1.2.3.D	5 g
	Testing methods for fertilizers	4.1.2.b Formaldehyde method (4.1.2) Remark 4	4.1.2.b Formaldehyde method	
Citric soluble phosphate (C-P_2O_5)	Analytical methods for fertilizers	4.2.1.C.d	4.2.3.E.c Vanadomolybdate absorption spectrometry	1 g
	Testing methods for fertilizers	4.2.3.a Vanadomolybdate absorption spectrometry	Same as the left	
Water soluble potassium oxide (W-K_2O)	Analytical methods for fertilizers	4.3.1.C.b.2) (Note)	4.3.3.E Atomic absorption spectrophotometry	5 g
	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	
Citric soluble magnesium oxide (C-MgO)	Analytical methods for fertilizers	4.2.1.C.d	4.6.2.E Atomic absorption spectrophotometry	1 g
	Testing methods for fertilizers	4.6.2.a Flame atomic absorption spectrometry	Same as the left	
Citric soluble manganese oxide (C-MnO)	Analytical methods for fertilizers	4.2.1.C.d	4.7.3.E Atomic absorption spectrophotometry	1 g
	Testing methods for fertilizers	4.7.2.a Flame atomic absorption spectrometry	Same as the left	
Citric soluble boron oxide (C-B_2O_3)	Analytical methods for fertilizers	4.2.1.C.d	4.8.3.E Azomethine H method	1 g
	Testing methods for fertilizers	4.8.1.a Azomethine H method	Same as the left	

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

URLs for the above mentioned methods:

Analytical Methods for Fertilizers (1992)	http://www.famic.go.jp/ffis/fert/sub1.html
Testing Methods for Fertilizers	http://www.famic.go.jp/ffis/fert/sub9.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 10 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 official method "Analytical Methods for Fertilizers," or "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. A certified value thus obtained is traceable to the International System of Units (SI).

[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)]

$$u = \sqrt{\frac{s_R{}^2 - \left(1 - \frac{1}{n}\right) s_W{}^2}{p}} \quad \cdots\cdots\cdots\cdots\cdots\cdots \text{(a)}$$

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

[Attestation date] March 3, 2014

[Expiration date]
The expiration date of the reference material is June 2018 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 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 160 g.

[Homogeneity]
From 320 vials of reference material candidates, ten (10) were sampled randomly to quantitate the content of the certified component randomly 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 2.5%.

[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 commercially available high-analysis compound fertilizer produced using urea, ammonium sulfate, ammonium phosphate, calcined phosphate, potassium chloride, magnesium hydroxide fertilizers, borate fertilizers, sulfuric acid. 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 160 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 (75°C, 4 hours) was a 1.43% mass fraction (nine 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_W) Mass Fraction (%)	Certified Value on a Dry Moisture Basis Mass Fraction (%)
Total nitrogen (T-N)	8	14.83	0.14	0.06	15.05
Ammonia nitrogen (A-N)	9	10.36	0.21	0.07	10.75
Citric soluble phosphate (C-P_2O_5)	10	10.79	0.09	0.08	11.20
Water soluble potassium oxide (W-K_2O)	10	13.07	0.16	0.10	13.57
Citric soluble magnesium oxide (C-MgO)	9	3.18	0.12	0.04	3.30
Citric soluble manganese oxide (C-MnO)	10	0.356	0.018	0.012	0.370
Citric soluble boron oxide (C-B_2O_3)	10	0.203	0.009	0.004	0.211

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

Kanto plant, Asahi Industries Co., Ltd.
Niigata plant, Onoda Chemical Industry Co., Ltd.
Tsukuba plant , Co-op Chemical Co., Ltd.
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

[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) 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]

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Food and Agricultural Materials Inspection Center
Administrative director Makoto Kimura

March 12, 2014

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

Appendix: Use of certified reference materials

ISO/IEC 17025:2005 (JIS Q 17025:2006)[1)] recommends to conduct routine internal quality control of laboratories and validation of test methods developed by laboratories using certified reference materials. As an example of trueness evaluation of test results using a certified reference material, this section presents the internal quality control method and a method presented by the ERM application note.[4)]

I. Validation using alert line and action line

The number of replicates (n) in a reproducibility test conducted for internal quality control, the certified value (μ) in Table 1, repeatability standard deviation (s_W) and reproducibility standard deviation (s_R) in Table 3 are used to obtain the standard deviation, alert line and action line for proficiency evaluation from the formulas (a), (b1) and (c1).[2)] Additionally, when test values (or control values) of a repeatability test are used, the number of replicates (n) is $n = 1$, and calculate the alert line (formula (b2)) and the action line (formula (c2)).

When the quality control result is outside the range of the action line, it is desirable to consider the series of the test do not conform, and conduct re-testing. When two consecutive quality control results are outside the range of the alert line, it is desirable to consider the second test do not conform and conduct re-testing.[3)]

Standard deviation for proficiency evaluation (σ)

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

Alert line to the mean = $\mu \pm 2\times\sigma$ $\cdots\cdots\cdots\cdots\cdots\cdots$ (b1)
Alert line to a single test value = $\mu \pm 2\times s_R$ $\cdots\cdots\cdots\cdots$ (b2)

Action line to the mean = $\mu \pm 3\times\sigma$ $\cdots\cdots\cdots\cdots\cdots\cdots$ (c1)
Action line to a single test value = $\mu \pm 3\times s_R$ $\cdots\cdots\cdots\cdots$ (c2)

II. Validation by comparison between measured values and certified value

If formula (d) holds using the number of repetitions (n) for a repeatability test conducted for internal quality control, the certified value (μ) in Table 1 and expanded uncertainty ($U_{95\%}$), no significant difference between the mean of measured values and the certified value is assumed.

$$|\mu - X_{\text{meas}}| \quad \leq \quad 2\sqrt{\left(\frac{U_{95\%}}{2}\right)^2 + {u_{\text{meas}}}^2} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \text{(d)}$$

X_{meas}: Mean of measured values
u_{meas}: Uncertainty of measurement = Standard deviation of measurement /$\sqrt{n}$

To estimate uncertainty (u_{meas}) of measurement, the following approximate methods of standard deviations of measurement are available.

(1) A rough estimation value is applicable to the standard deviation of reproducibility.

(2) A repeatability standard deviation (s_W) obtained using results of the collaborative study in Table 3 can be used if it is confirmed that a testing laboratory has a similar competence that the laboratory participants of the collaborative study of the certified reference material have.

(3) A rough estimate value is applicable to a standard deviation obtained by prolonged measurement. However, an estimate value thus obtained underestimates measurement uncertainty, so it is a tough method to confirm a test result that always has a deviation in one direction.

[Reference specifications and literature]

1) ISO/IEC 17025 (2005): "General requirements for the competence of testing and calibration laboratories"（JIS Q 17025 :2006, *Shikenjo oyobi kouseikikan no nouryoku ni kansuru ippan youkyujikou*）
2) ISO 13528 (2005): "Statistical method for use in proficiency testing by inter laboratory comparisons"（JIS Z 8405 : 2008, *Shikenjokanhikaku niyoru ginoushiken notameno toukeitekihouhou*）
3) Thompson, M. Wood, R.: Harmonized Guidelines for Internal Quality Control in Analytical Chemistry Laboratories, *Pure & Appl. Chem.*, **67** (4), 649~666 (1995)
4) Thomas Linsinger: "Comparison of a measurement result with the certified value", European Reference Materials' application note 1, European Commission - Joint Research Centre Institute for Reference Materials and Measurements (IRMM)