



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material[®] 695

Trace Elements in Multi-Nutrient Fertilizer

This Standard Reference Material (SRM) is intended primarily for use in the evaluation of techniques employed in the analysis of multi-nutrient fertilizer materials and materials of a similar matrix. A unit of SRM 695 consists of approximately 70 g of jet-milled fertilizer.

Certified Values: The certified concentrations for major, minor, and trace elements, expressed as mass fractions [1] on a dry-mass basis, are provided in Table 1. Certified values are based on results from critically evaluated independent analytical techniques. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account [2].

Reference Values: The reference values for selected elements, expressed as mass fractions on a dry-mass basis, are provided in Table 2. The reference values are based on results obtained from a single NIST analytical method. Reference values are non-certified values that are the best estimate of the true value; however, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may not include all sources of uncertainty [2].

Information Values: The values for selected elements, expressed as mass fractions [1] on a dry-mass basis, are provided in Table 3. A NIST information value is a value that may be of interest to the SRM user, but insufficient information is available to assess the uncertainty associated with the value [2]. The information values included in this certificate are based on results from one NIST method. Information values cannot be used to establish metrological traceability.

Expiration of Certification: The certification of **SRM 695** is valid, within the measurement uncertainty specified, until **01 April 2026**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see “Instructions for Use”). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Coordination of technical measurements for the certification of this SRM was performed by E.A. Mackey of the NIST Material Measurement Laboratory.

Statistical consultation for this SRM was provided by S.D. Leigh of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

Analytical measurements were performed by S.E. Long, J.R. Sieber, R. Oflaz, L.J. Wood, A.F. Marlow, L.L. Yu, and K.E. Murphy of the Chemical Sciences Division; M.S. Rearick formerly of NIST; and E.A. Mackey.

Measurements at United States Geological Survey (Denver, CO) were performed by S.A. Wilson, Z.A. Brown, P.H. Briggs, and J. Budahn.

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INSTRUCTIONS FOR USE

Sampling: The SRM should be thoroughly mixed by repeatedly inverting and rotating the bottle horizontally before sampling. A minimum sample mass of 200 mg should be used for analytical determinations to be related to elemental concentration values provided. The SRM should be stored in its original, tightly sealed bottle away from intense sources of heat.

Drying: In order to relate measurements to the certified and reference values that are expressed on a dry mass basis, users should determine a drying correction at the time of each analysis. The recommended drying procedure is desiccator drying of portions with a depth ≤ 0.5 cm, for two weeks, over fresh magnesium perchlorate. The average mass loss measured at NIST using this method for six portions of SRM 695 was 1.34 % (1 s = 0.06 %). Oven drying, even at relatively low temperatures (85 °C), can result in decomposition of the carbonate and ammonium (and possibly other) compounds in this blended fertilizer material. **DO NOT** dry SRM 695 in an oven to determine the dry-mass basis.

SOURCE, PREPARATION, AND ANALYSIS

This multi-nutrient blended fertilizer was developed in collaboration with members of the Association of American Plant Food Control Officials (AAFPCO) and The Fertilizer Institute (TFI). The material used to prepare SRM 695 was provided to NIST by William L. Hall Jr. (The Mosaic Company). The material consists of urea, diammonium hydrogen phosphate, calcium carbonate, potassium chloride, potassium nitrate, and potassium magnesium sulfate, and various other metal sulfates. The material was ground and shipped to NIST where the material was jet-milled, blended, and bottled by C. Fales of the Office of Reference Materials.

Analyses of this material used for certification were performed at NIST (Gaithersburg, MD) and at the United States Geological Survey. The analytical techniques used for each element are listed in Table 4.

Table 1. Certified Values for Selected Elements (Dry-Mass Basis) in SRM 695^(a)

Major and Minor Constituent Elements				
Elements	Mass Fraction (%)		Mass Fraction (%)	
Calcium	2.26	± 0.04	Manganese	0.305 ± 0.005
Iron	3.99	± 0.08	Sodium	0.405 ± 0.007
Magnesium	1.79	± 0.05	Potassium	11.65 ± 0.13
			Zinc	0.325 ± 0.005

Trace Elements				
Elements	Mass Fraction (mg/kg)		Elements	Mass Fraction (mg/kg)
Arsenic	200	± 5	Mercury	1.955 ± 0.036
Cadmium	16.9	± 0.2	Molybdenum	20.0 ± 0.3
Chromium	244	± 6	Nickel	135 ± 2
Cobalt	65.3	± 2.4	Lead	273 ± 17
Copper	1225	± 9	Vanadium	122 ± 3

^(a) Certified values for all elements except arsenic and mercury are the unweighted means of results from two or three analytical methods. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance with a pooled, within method variance [3] following the ISO/JCGM Guide [4]. The certified values for As and Hg are each results from a single NIST method (INAA for As, and CV-ID-ICP-MS for Hg) for which a complete evaluation of all sources of uncertainty has been performed. The uncertainty for each certified value represents an expanded uncertainty with a coverage factor of 2, with uncertainty components combined following the ISO/JCGM Guide [4]. The measurand is the mass fraction for each element listed in Table 1. Metrological traceability is to the SI derived unit for mass fraction (expressed as milligrams per kilogram).

Table 2. Reference Values (Dry-Mass Basis) for Selected Elements in SRM 695

Major and Minor Constituent Elements ^(a)	
Element	Mass Fraction (%)
Aluminum	0.61 ± 0.03
Boron	0.111 ± 0.002
Nitrogen	13.9 ± 0.4
Phosphorous	7.2 ± 0.1
Trace Elements ^(a)	
Elements	Mass Fraction (mg/kg)
Selenium	2.1 ± 0.1

^(a) Reference values for all elements except aluminum are based on results of one analytical method at NIST and the uncertainty values represent the expanded uncertainties which include the combined Type A and Type B with a coverage factor of 2, following the ISO/JCGM Guide [4]. The certified value for aluminum is the unweighted mean of results from two analytical methods and the uncertainty listed is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance with a pooled, within method variance [3] following the ISO/JCGM Guide [4]. The measurand is the mass fraction for each element listed in Table 2 as determined by the method indicated. Metrological traceability is to the SI derived unit for mass fraction (expressed as a percent or milligrams per kilogram).

Table 3. Information Values (Dry-Mass Basis) for Selected Elements in SRM 695^(a)

Element	Mass Fraction
Chlorine	4.6 %
Titanium	310 mg/kg

^(a) Information values are based on results of one analytical method at NIST.

Table 4. Methods of Analysis for SRM 695

Element	Method(s)	Element	Method(s)
Al	INAA, XRF	Mg	INAA, XRF
As	INAA	Mn	PGAA, XRF, INAA
B	PGAA	Mo	ICP-OES, XRF
Ca	XRF, INAA	N	PGAA
Cd	ID-ICP-MS, PGAA	Na	INAA, XRF
Cl	INAA	Ni	ICP-OES, XRF
Co	INAA, XRF	P	XRF
Cr	INAA, XRF	Pb	ICP-OES, XRF
Cu	ID-ICP-MS, ICP-OES, XRF	Se	INAA
Fe	INAA, PGAA, XRF	Ti	XRF
Hg	CV ID-ICP-MS	V	INAA, XRF
K	PGAA, XRF	Zn	INAA, XRF

Methods:

CV ID-ICP-MS	Cold Vapor, Isotope Dilution, Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ID-ICP-MS	Isotope Dilution Inductively Coupled Plasma Mass Spectrometry
INAA	Instrumental Neutron Activation Analysis
HG-AAS	Hydride Generation Atomic Absorption Spectrometry
PGAA	Prompt Gamma-ray Activation Analysis
XRF	X-ray Fluorescence Spectrometry

REFERENCES

- [1] Thompson, A.; Taylor, B.N.; *Guide for the Use of the International System of Units (SI)*; NIST Special Publication 811; U.S. Government Printing Office: Washington, DC (1995); available at <http://physics.nist.gov/cuu/pdf/sp811.pdf> (accessed Dec 2015).
- [2] May, W.; Parris, R.; Beck II, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definition of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136; U.S. Government Printing Office: Washington, DC (2000); available at <http://www.nist.gov/srm/publications.cfm> (accessed Dec 2015).
- [3] Levenson, M.S.; Banks, D.L.; Eberhardt, K.R.; Gill, L.M.; Guthrie, W.F.; Liu, H.-k.; Vangel, M.G.; Yen, J.H.; Zhang, N.F.; *An Approach to Combining Results from Multiple Methods Motivated by the ISO GUM*; J. Res. Natl. Inst. Stand. Technol., Vol. 105, pp. 571–579 (2000).
- [4] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement* (GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (2008); available at http://www.bipm.org/utis/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Dec 2015); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at <http://www.nist.gov/pml/pubs/tn1297/index.cfm> (accessed Dec 2015).

Certificate Revision History: 28 December 2015 (Change of expiration date; editorial changes); 26 June 2006 (Original certificate date).

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at <http://www.nist.gov/srm>.

ADDENDUM

Results from Test Method for Determination of Analysis of As, Cd, Co, Cr, Mo, Ni, Pb, and Se in Fertilizers by Microwave Digestion in Nitric Acid and ICP-OES Detection

The certified, reference and information values presented in the Certificate of Analysis for SRM 695 represent the total element content per unit mass of material. These values are obtained either from methods that are non-destructive such as instrumental neutron activation analysis or methods that involve a complete dissolution of the material prior to performing measurements. For more routine analysis of metals in fertilizer materials, a method was developed and tested by members of the Association of American Plant Food Control Officials (AAPFCO). William Hall initiated the development of this method and Peter Kane coordinated and led this study in which ten laboratories participated. This test method involves microwave digestion with concentrated nitric acid followed by ICP-OES detection and is described in detail elsewhere [1].

Note that this digestion method does not completely dissolve this fertilizer material. Results indicate that some elements are completely extracted but that others are not. The results obtained using this method are shown in Table 1, together with the total element content as determined at NIST for certification of this material, and the percent recovery defined as the ratio of the values obtained from the test method to total element content determined for certification of SRM 695. Collaborating laboratories and analysts are listed in Table 2.

Table 1. Results from Test Method for Determination of As Cd, Co, Cr, Mo, Ni, Pb, and Se in Fertilizers^(a)

Element	Test Method Results Average Mass Fraction (1s); Range (mg/kg) ^(b)	% Recovery Average; Range	Total Element Content Mass Fraction (mg/kg) ^(b)
As	193 (19); 171 – 235	96 %; 85 % – 117 %	200 (5)
Cd	16.1 (2.9); 12.4 – 23.2	95 %; 74 % – 137 %	16.9 (0.2)
Co	47.5 (12.3); 27.4 – 65.7	73 %; 42 % – 101 %	65.3 (2.4)
Cr	174 (19); 136 – 192	71 %; 56 % – 79 %	244 (6)
Mo	14.0 (2.0); 10.2 – 16.8	70 %; 51 % – 84 %	20.0 (0.3)
Ni	112 (15); 85 – 131	83 %; 63 % – 97 %	135 (2)
Pb	257 (15); 231 – 281	94 %; 85 % – 103 %	273 (17)

^(a) Selenium values are not included because the mass fraction of Se in SRM 695 is below the method detection limit.

^(b) The values shown here are the certified total element mass fraction values from Table 1 of the Certificate of Analysis.

Table 2. Collaborating Laboratories and Analysts

James Bartos	Division of Regulatory Services, University of Kentucky
Rhonda Boles	Experiment Station, University of Missouri
M. Dupuis	Ottawa Lab (Carling) Canadian Food Inspection Agency
Elaine Hasty	CEM Corporation
William Hall, Charles Kinsey and Kwasi Sakyi-Amfo	The Mosaic Company
Peter Kane, Sally Mullins and Natalie Newlon	Office of the Indiana State Chemist
Judy Purkiss	Michigan Department of Agriculture
Christine Rivera	Varian Inc.
Wayne Robarge	North Carolina State University
Craig Seeley	Teledyne Leeman Labs
Sanford Seigel	CF Industries
Marcus Svec	Montana Department of Agriculture
Terri Van Erem	South Dakota State University
Argentina Vindiola	Office of the Texas State Chemist

REFERENCE

- [1] Kane, P.F.; Hall, W.L., Jr.; *Analysis of Arsenic, Cadmium, Cobalt, Chromium, Lead, Molybdenum, Nickel, and Selenium by Microwave Digestion and ICP-OES Detection: Collaborative Study*; Paper 2006-17920 of the Office of Indiana State Chemist, Purdue University Agricultural Experiment Station, W. Lafayette, IN (2006).