National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2429

Flue Gas Desulfurization Gypsum

This Standard Reference Material (SRM) is intended for use in the evaluation of chemical methods of analysis for mercury and other contaminants in gypsum materials. A unit of SRM 2429 consists of 200 g of gypsum derived from flue gas desulfurization (FGD) technologies, further processed to pass a 74 µm (200 mesh) sieve, homogenized, and packaged in an amber glass bottle.

Certified Mass Fraction Values: A certified value for mercury, expressed as a mass fraction [1] on a dry-mass basis, is provided in Table 1. 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 [1]. The measurand is the amount of mercury listed in Table 1. Metrological traceability is to the SI derived units for mass fraction (expressed as mg/kg).

Reference Mass Fraction Values: Reference mass fraction values on a dry-mass basis for major constituents, trace elements, arsenic, barium, chromium, lead, selenium and strontium are provided in Table 2. 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 reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods [1]. The measurands are the mass fractions of the elements or element oxides reported in Table 2 as determined by the methods indicated in Table 4. Metrological traceability is to the SI derived units for mass fraction (expressed as mg/kg and percent).

Information Mass Fraction Values: Information values for constituents and properties are provided in Table 3. An information value is considered to be a value that will be of interest and use to the SRM user, but for which insufficient information is available to assess adequately the uncertainty associated with the value, or only a limited number of analyses were performed [1]. Information values cannot be used to establish metrological traceability.

Expiration of Certification: The certification of **SRM 2429** is valid, within the measurement uncertainty specified, until **01 July 2020**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Storage and 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 the technical measurements leading to the certification of SRM 2429 was provided by S.E. Long of the NIST Chemical Sciences Division.

Analytical measurements leading to certification were made by D. Cleveland, S.E. Long, J.L. Mann, A.F. Marlow, J.R. Sieber, and L.L. Yu of the NIST Chemical Sciences Division.

Statistical consultation was provided by Z.Q.J. Lu of the NIST Statistical Engineering Division.

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

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Certificate Issue Date: 07 October 2015

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Additional collaborative laboratory measurements were performed by A. Brown and B. Lynch of Santee Cooper (Moncks Corner, SC), and by D. Broton and R. Kelly of CTL Group (Skokie, IL).

NOTICE AND WARNINGS TO USERS

Caution and care should be exercised when handling this material. This material has been processed to maintain homogeneity and is composed of a particle size distribution that is readily respirable. Precautions should be taken to avoid inhalation of dust during sampling. See Safety Data Sheet for health and safety information.

INSTRUCTIONS FOR STORAGE AND USE

Storage: SRM 2429 must be stored in its original bottle tightly capped at temperatures less than 30 ºC.

Use: A minimum sample mass of 100 mg should be used for analytical determinations to be related to the certified values in this certificate. Prior to use, the contents of the bottle should be thoroughly mixed by gently rotating the bottle by hand and inverting several times. The mass fractions of constituents in SRM 2429 are reported on a dry-mass basis.

Moisture Correction Factor Determination: A separate sub-sample of not less than one gram should be removed from the bottle at the time of analysis and dried to determine a moisture correction factor. The moisture content at the time of bottling was determined to be <0.1 % mass fraction, however, the moisture content may change over time depending on laboratory and storage conditions [2]. Samples should be dried for 2 h at 45 °C in a laboratory convection oven to obtain a correction factor for moisture. Correction for moisture is to be made to the data before comparison with the certified values.

PREPARATION AND ANALYSIS ANALYSIS[(1)]

Preparation of Material: The source material for SRM 2429 was a commercial synthetic gypsum material derived from an electric utility flue gas desulfurization process. The bulk material was blended and bottled at NIST. Bulk material was spread into trays to a depth of approximately 25 mm and dried for 18 d in a continuous airflow oven at 39.4 °C. The dried material was placed in batches into a Robot Coupe chopper, fitted with titanium blades, and processed for 45 s. The resulting material was then sieved using a No. 200 sieve, blended using a large V blender, and dispensed into 8 oz amber borosilicate glass bottles.

Homogeneity: The homogeneity of SRM 2429 was assessed at NIST by analyzing duplicate samples from 22 bottles selected by stratified random sampling. Homogeneity testing was performed using X-ray fluorescence spectrometry (XRF). For most constituents, material heterogeneity was low and fit for its intended use in the elemental analysis of gypsum and associated products.

Certified Mass Fraction Value: The certified value for mercury is based on a single NIST primary method consisting of cold-vapor isotope dilution inductively coupled plasma mass spectrometry (CV-ID-ICP-MS) [3,4]. The uncertainty of the certified value is given as an expanded uncertainty about the mean to cover the measurand with approximately 95 % confidence. The expanded uncertainty is calculated as $U = ku_c$ where u_c is the combined uncertainty consistent with the ISO/JCGM Guide [5], and k is a coverage factor ($k = 2$) corresponding to approximately 95 % confidence.

Table 1. Certified Mass Fraction Value (Dry-Mass Basis) for SRM 2429

	Mass Fraction (mg/kg)
Mercury (Hg)	0.778 ± 0.024

[(1)] Certain commercial instruments, materials, or processes are identified in this report to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the instruments, materials, or processes identified are necessarily the best available for the purpose.

Reference Mass Fraction Values: The reference mass fraction values are the means of results from a single method. The uncertainty provided is an expanded uncertainty about the mean to cover the measurand with approximately 95 % confidence, consistent with the ISO/JCGM Guide [5]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is the combined uncertainty that incorporates within-method uncertainty and uncertainty components related to the analysis, and k is the coverage factor corresponding to approximately 95 % confidence for each measurand.

Table 2. Reference Mass Fraction Values (Dry-Mass Basis) for SRM 2429

Elements[a]	Mass Fraction (%)			k	Element	Mass Fraction (mg/kg)			k
Al_2O_3	0.221 0	±	0.005 7	2	As	2.53	±	0.14	2.20
CaO	31.93	±	0.36	2	Ba	49.6	±	1.4	2.36
Fe_2O_3	0.235 7	±	0.009 3	2	Cr	2.74	±	0.59	2.23
K_2O	0.045 87	±	0.000 91	2	Pb	0.763	±	0.046	2.20
MgO	0.043 1	±	0.001 3	2	Se	5.27	±	0.25	2.45
P_2O_5	0.015 60	±	0.000 41	2	Sr	328.9	±	2.0	2.11
SiO_2	0.810	±	0.012	2					
SO_3	43.42	±	0.66	2					
TiO_2	0.020	±	0.002	2					
LoF[b]	21.24	±	0.16	2					

[a] Elements are reported as the oxides consistent with ASTM STP 861 [6].
[b] LoF – Loss of mass during borate fusion at 975 °C.

Information Values: Information values are single method results provided by collaborating laboratories.

Table 3. Information Values (As-Received Basis) for Selected Constituents and Properties in SRM 2429[a]

Constituent/Property	Mass Fraction (%)	Constituent/Property	Mass Fraction (mg/kg)
Gypsum purity	97.4	Total Organic Carbon (TOC)	463.7
SO_3 combined as gypsum	45.3	Cl	23.5
Excess SO_3	0.35	Soluble K	9.6
Anhydrite, $CaSO_4$	0.60	Soluble Mg	12.1
CaO combined as gypsum	31.7	Soluble Na	11.6
CaO combined as anhydrite	0.25		
Excess CaO	0.44		
$CaCO_3$	0.79		
$MgCO_3$	0.03		
LOI (ambient to 45 °C)	0.02		
LOI (45 °C to 220 °C)	20.4		
LOI (220 °C to 550 °C)	0.25		
LOI (550 °C to 950 °C)	0.19		

[a] Compounds calculated per ASTM C471M-14 [7].

Analytical Methods: The analytical methods used for the analysis of SRM 2429 are listed in Table 4.

Table 4. Analytical Methods Used for Value Assignment in SRM 2429

Element	Methods
Hg	CV-ID-ICP-MS following microwave digestion [3,4]
Al, Ca, Fe, K, Mg, P, Si, S, Ti	WD-XRF following borate fusion preparation
As, Ba, Cr, Pb, Se, Sr	ICP-MS following acid digestion

REFERENCES

[1] 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 (2000); available at http://www.nist.gov/srm/upload/SP260-136.PDF (accessed Oct 2015).

[2] Mann, J.L.; Kelly, W.R.; MacDonald, B.S.; *Observations of Anomalous Mass-Loss Behavior in SRM Coals and Cokes on Drying*; Anal. Chem., Vol. 74, pp. 3585–3591 (2002).

[3] Christopher, S.J.; Long, S.E.; Rearick, M.S.; Fassett, J.D.; *Development of Isotope Dilution Cold Vapor Inductively Coupled Plasma Mass Spectrometry and Its Application to the Certification of Mercury in NIST Standard Reference Materials*; Anal. Chem., Vol. 73, pp. 2190–2199 (2001).

[4] Long, S.E.; Kelly, W.R.; *Determination of Mercury in Coal by Isotope Dilution Cold-Vapor Generation Inductively Coupled Plasma Mass Spectrometry*; Anal. Chem., Vol. 74, pp. 1477–1483 (2002).

[5] 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 (JCGM) (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Oct 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/index.cfm (accessed Oct 2015).

[6] Kocman, V.; *Rapid Multielement Analysis of Gypsum and Gypsum Products by X-Ray Fluorescence Spectroscopy,* in *The Chemistry and Technology of Gypsum*; ASTM STP 861, R.A. Kuntze, Ed., Am. Soc. Test. Mater., pp. 72–83 (1984).

[7] ASTM C 471M-14; *Standard Test Methods for Chemical Analysis of Gypsum and Gypsum Products (Metric)*; ASTM International, West Conshohocken, PA, 2014.

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.