

Standard Reference Material[®] 1573a

Tomato Leaves

CERTIFICATE OF ANALYSIS

Purpose: This Standard Reference Material (SRM) is intended primarily for use in validating analytical methods for the determination of major, minor, and trace elements in botanical materials, agricultural food products, and similar materials. This SRM can be used for quality assurance when assigning values to in-house control materials.

Description: A unit of SRM 1573a consists of 50 grams of dried tomato leaves.

Certified Mass Fraction Values: Certified mass fraction values are 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 taken into account [1].

Table 1. Certified Mass Fraction Values for Elements in SRM 1573a

The measurand is the total mass fraction for each element on a dry-mass basis and metrological traceability is to the International System of Units (SI) derived unit for mass fraction expressed as milligrams per kilogram [2].

	Mass Fraction (mg/kg) ^(a)			Mass Fraction (mg/kg) ^(a)		
Aluminum (Al)	598.4	±	7.1	Mercury (Hg)	0.0341	± 0.0015
Antimony (Sb)	0.0619	±	0.0032	Nitrogen (N) (Total)	30200	± 2300
Arsenic (As)	0.1126	±	0.0024	Nickel (Ni)	1.582	± 0.041
Boron (B)	33.13	±	0.42	Phosphorus (P)	2161	± 28
Cadmium (Cd)	1.517	±	0.027	Potassium (K)	26760	± 480
Calcium (Ca)	50450	±	550	Rubidium (Rb)	14.83	± 0.31
Chromium (Cr)	1.988	±	0.034	Selenium (Se)	0.0543	± 0.0020
Cobalt (Co)	0.5773	±	0.0071	Sodium (Na)	136.1	± 3.7
Copper (Cu)	4.70	±	0.14	Vanadium (V)	0.835	± 0.034
Iron (Fe)	367.5	±	4.3	Zinc (Zn)	30.94	± 0.55
Manganese (Mn)	246.3	±	7.1			

^(a) Values are expressed as $x \pm U_{95\%}(x)$, where x is the certified value and $U_{95\%}(x)$ is the expanded uncertainty of the certified value. The true value of the analyte is believed to lie within the interval $x \pm U_{95\%}(x)$ with 95 % confidence. To propagate this uncertainty, treat the certified value as a normally distributed random variable with mean x and standard deviation $U_{95\%}(x)/2$. NIST methods used for certification can be found in Table A1.

Expiration of Certification: The certification of **SRM 1573a** is valid, within the measurement uncertainty specified, until **01 August 2027**, 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.

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Non-Certified Values: Table 2 provides estimated values for additional measurands that do not meet the NIST criteria for certification and are provided as additional information on the composition of the material. 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, and therefore no uncertainty is provided [1].

Table 2. Information Mass Fraction Values for Elements in SRM 1573a

Values are reported on a dry-mass basis in mass fraction units [2]. Information values cannot be used to establish metrological traceability.

	Mass Fraction (mg/kg)		Mass Fraction (mg/kg)
Barium (Ba)	63	Magnesium (Mg)	12000
Bromine (Br)	1300	Molybdenum (Mo)	0.46
Cerium (Ce)	2	Nitrogen (N) ^(a)	29200
Cesium (Cs)	0.053	Samarium (Sm)	0.19
Chlorine (Cl)	6600	Scandium (Sc)	0.1
Gadolinium (Gd)	0.17	Silver (Ag)	0.017
Hafnium (Hf)	0.14	Strontium (Sr)	85
Hydrogen (H)	52000	Sulfur (S)	9600
Iodine (I)	0.85	Thorium (Th)	0.12
Lanthanum (La)	2.3	Uranium (U)	0.035

^(a) NIST Kjeldahl (KJEL). Although total nitrogen is certified, nitrogen determined by the Kjeldahl procedure is not.

Storage and Handling: The SRM should be stored in the dark, at controlled room temperature (20 °C to 25 °C), in its original unopened bottle, until required for use. The SRM should not be exposed to intense sources of radiation. The bottle can be resealed and test portions removed and analyzed until the material reaches its expiration date.

Use: The contents of the bottle should be thoroughly mixed by rotating and/or rolling the bottle before each use. Allow the contents to settle for one minute prior to opening to minimize the loss of fine particles. To relate analytical determinations to the certified values in this certificate, the test portion mass indicated in the description of the NIST analyses for each group of analytes (see “Source, Preparation, and Analysis” below) should be used. Test portions should be taken by gently tapping material needed from the SRM bottle. Results in this certificate are reported on a dry-mass basis; sample(s) need to be dried using one of the recommended techniques (see “Determination of Moisture”) to compare results to certified values found in this certificate. Results obtained in analyses should include their own estimates of uncertainty and can be compared to the certified values using procedures described in reference [3].

Determination of Moisture: Moisture content of SRM 1573a was determined at NIST by (1) drying over fresh anhydrous magnesium perchlorate in a desiccator at room temperature for 120 h (the sample depth should not exceed 1 cm) and (2) freeze drying for 24 h at a pressure of 13.3 Pa or lower and a shelf temperature of –5 °C or lower after having frozen the sample (not to exceed 1 cm in depth) at –40 °C or lower for at least 1 h. At the end of the 24-h period, samples were placed immediately in a desiccator with fresh anhydrous magnesium perchlorate. Samples were weighed after allowing a minimum of 4 h to establish temperature equilibrium. It is preferable to analyze volatile elements such as mercury from the bottle without drying, determine the moisture content on a separate sample from the same bottle, and correct the analytical results to a dry-mass basis.

Vacuum drying at room temperature and oven drying at elevated temperatures have resulted in excessive mass losses and therefore are **NOT** recommended.

Safety: SRM 1573a is intended for research use; not for human consumption.

Source: The material for this SRM is leaves selected from “Count II” tomato plants grown in three lime and fertilizer experiments covering about three acres at the Horticultural Research Farm (Rock Springs, PA). Mature leaves were collected and prepared (Plant Analysis Laboratory, The Pennsylvania State University (University Park, PA)). The leaves were selected from guard plants which had not received any treatment in order to obtain as uniform a material as possible. Twenty-four batches, or three tons, of leaves were collected. Fungicide sprays were avoided to prevent contamination of the leaves. After each collection, the leaves were transported to the Plant Analysis Laboratory, washed, dipped in a detergent solution, rinsed with tap water, then triple rinsed with distilled water. The leaves were SRM 1573a

drained and placed in pasteboard trays for oven drying at a temperature of 60 °C to 70 °C. The leaves were passed through a 40-mesh screen in a Wiley Mill. Representative samples were taken from each batch for analysis before mixing batches together. At NIST, the ground leaves were jet milled and air classified to a particle size of approximately 75 µm (200 mesh). Prior to bottling, the material was irradiated by ⁶⁰Co to an estimated minimum absorbed dose of 25 kGy for microbial control.

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; U.S. Government Printing Office: Washington, DC (2000); available at <https://www.nist.gov/srm/publications-sp260s> (accessed Aug 2018).
- [2] 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 (2008); available at <https://www.nist.gov/pml/pubs/sp811/index.cfm> (accessed Aug 2018).
- [3] Sharpless, K.E.; Lippa, K.A.; Duewer, D.L.; Rukhin, A.L.; *The ABCs of Using Standard Reference Materials in the Analysis of Foods and Dietary Supplements: A Practical Guide*; NIST Special Publication 260-181; U.S. Government Printing Office: Washington, DC (2014); available at <https://www.nist.gov/sites/default/files/documents/srm/SP260-181.pdf> (accessed Aug 2018).
- [4] DerSimonian, R.; Laird, N.; *Meta-Analysis in Clinical Trials*; *Controlled Clin. Trials*, Vol. 7, pp. 177–188 (1986).
- [5] Rukhin, A.L.; *Weighted Means Statistics in Interlaboratory Studies*; *Metrologia*, Vol. 46, pp 323-331 (2009).
- [6] Possolo, A.; *Random Effects-Functions R, Working File of R Source Code for Fitting Gaussian Random Effects Models*; Personal communication, (2011).
- [7] 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 https://www.bipm.org/utis/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Aug 2018); 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 <https://www.nist.gov/pml/nist-technical-note-1297> (accessed Aug 2018).
- [8] JCGM 101:2008; *Evaluation of Measurement Data – Supplement 1 to the “Guide to the Expression of Uncertainty in Measurement” - Propagation of Distributions using a Monte Carlo Method*; JCGM (2008); available at https://www.bipm.org/utis/common/documents/jcgm/JCGM_101_2008_E.pdf (accessed Aug 2018).
- [9] US EPA; *Methods for Chemical Analysis of Water and Wastes*; U.S. Environmental Protection Agency, 625/6-74-003 pp. 252-254.

Certificate Revision History: 22 August 2018 (Certified values brought into compliance with the NIST uncertainty policy; updated instructions for use; Change of expiration date; Editorial revisions); 22 November 1995 (Revision of certificate); 19 October 1993 (Original certificate date).

Certain commercial equipment, instruments or materials may be identified in this Certificate of Analysis 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 materials or equipment identified are necessarily the best available for the purpose.

NIST will monitor this SRM until its certification expires. If substantive technical changes occur that affect the certified values before this certificate expires, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. Contact the Office of Reference Materials 100 Bureau Drive, Stop 2300, Gaithersburg, Maryland 20899-2300; telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or the internet at <https://www.nist.gov/srm>.

Appendix A

RESPONSIBILITIES

Coordination: D.A. Becker, NIST Inorganic Analytical Research Division; L.J. Wood, (certificate revision) NIST Chemical Sciences Division.

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Statistical Analysis: W.F. Guthrie and S.B. Schiller, NIST Statistical Engineering Division.

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Table A1. NIST Methods Used for Certified Elemental Determinations

Element	Method
P	Colorimetry
Hg	Cold-vapor atomic absorption spectrometry (CVAAS)
Na	Flame atomic emission spectrometry (FAES)
As, Se	Flow injection-hydride generation atomic absorption spectrometry (HAAS)
Al, Cu, Fe, P, Zn	Inductively coupled plasma optical emission spectrometry (ICP-OES)
B, Cd, Ni	Isotope dilution inductively coupled plasma mass spectrometry (ID ICP-MS)
Ca, K, Rb, V	Isotope dilution thermal ionization mass spectrometry (ID TIMS)
Al, Ca, Co, Cr, Fe, K, Mn, Na, Rb, Sb, Se, V, Zn	Instrumental neutron activation analysis (INAA)
N	Kjeldhal nitrogen determination (KJEL)
Mn	Laser-excited atomic fluorescence spectrometry (LEAFS)
B, Cd, K, N	Prompt gamma activation analysis (PGAA)
As, Cd, Cu, Sb, Se	Radiochemical nuclear neutron activation analysis (RNAA)

Appendix B

Homogeneity Assessment: Samples from fifteen randomly selected bottles of SRM 1573a were tested for homogeneity by INAA. No evidence of statistically significant inhomogeneity was observed.

Value Assignment: Calculation of assigned values are based on results from a single definitive method or on weighted means of multiple assessments of the mass fraction of each element made using different chemical methods or in different laboratories. Weighted means were calculated using the DerSimonian-Laird procedure [4-6], which weights the results from each method in proportion to the inverse of the square of its uncertainty. The weights include uncertainty contributions from both between- and within-method dispersion of values. The associated uncertainties are expressed at an approximately 95 % level of confidence [7-8].

Analytical Approach for Determination of Elements: Value assignment of the mass fractions of elements in SRM 1573a was based on measurements provided by NIST and collaborating laboratories, where appropriate. NIST provided measurements by using colorimetry, cold-vapor atomic absorption spectrometry (CVAAS), flame atomic emission spectrometry (FAES); hydride generation atomic absorption spectrometry (HAAS), inductively coupled plasma optical emission spectrometry (ICP-OES), isotope dilution inductively coupled plasma mass spectrometry (ID ICP-MS), isotope dilution thermal ionization mass spectrometry (ID TIMS), instrumental neutron activation analysis (INAA), Kjeldahl nitrogen determination (KJEL), laser-excited atomic fluorescence spectrometry (LEAFS), neutron-capture prompt gamma-ray activation analysis (PGAA), and radiochemical neutron activation analysis (RNAA). Quantification was based on the SRM 3100 series single element standard solutions.

NIST Analyses for P by Colorimetry: Duplicate, nominal 0.15 g test portions were taken from six bottles of SRM 1573a. Samples were placed in Teflon beakers using a $\text{HNO}_3/\text{HF}/\text{HClO}_4$ acid mixture. Solutions were heated to near dryness and transferred to 100 mL volumetric flasks with dilute HCl. A colorimetric reagent (2.5 molar H_2SO_4 /antimony potassium tartrate/ammonium molybdate/0.1 molar ascorbic acid) was added to each sample dilution. The absorbance of each solution was read on a Cary spectrophotometer at 650 nm in a 1-cm cell with a slit width of 0.2 mm. Quantification was based on the method of standard additions.

NIST Analyses for Hg by CVAAS: Duplicate, nominal 2 g test portions were taken from three bottles of SRM 1573a. Samples were digested under reflux conditions using $\text{HNO}_3/\text{HClO}_4/\text{H}_2\text{SO}_4$. Samples were analyzed using a FIAS-200 flow injection system and a Perkin Elmer 2380 or 5000 AAS. Quantification for the above analyses was based on a five-point calibration curve.

NIST Analyses for Na by FAES: Duplicate, nominal 1 g test portions were taken from six bottles of SRM 1573a. Samples were digested overnight under reflux conditions using a $\text{HNO}_3/\text{HF}/\text{HClO}_4$ acid mixture. Solutions were heated to near dryness and transferred to 100 mL volumetric flasks with 1% HNO_3 . Quantification was based on the method of standard additions.

NIST Analyses for As and Se by HAAS: Duplicate, nominal 1 g test portions were taken from three bottles of SRM 1573a. Samples were digested under reflux conditions using a $\text{HNO}_3/\text{HClO}_4/\text{H}_2\text{SO}_4$ acid mixture until fumes of H_2SO_4 appeared. Samples were cooled and 2 mL of HCl were added, solutions were heated for 15 min at near boiling then transferred to 100 mL volumetric flasks. For determination of As, a solution of 10 % KI and 5 % ascorbic acid was added to each sample and allowed to stand for 1 h to reduce As. For determination of Se, a solution of 10 % HCl and 0.5 % sodium borohydride was used as a reducing agent.

NIST Analyses for Al, Cu, Fe, P, and Zn by ICP-OES: Duplicate, nominal 1 g test portions were taken from six bottles of SRM 1573a. Samples were placed in Teflon beakers and wet ashed with a $\text{HNO}_3/\text{HF}/\text{HClO}_4$ acid mixture. When dissolved, samples were evaporated and diluted to 100 mL in 1.5 % HNO_3 . Quantification was based on the method of standard additions.

NIST Analyses for B, Cd, and Ni, by ID ICP-MS: Duplicate, nominal 1.0 g test portions were taken from each of six bottles of SRM 1573a. For cadmium and nickel samples were spiked with isotopically enriched ^{111}Cd , ^{62}Ni , then wet ashed with a $\text{HNO}_3/\text{HF}/\text{HClO}_4$ acid mixture in Teflon beakers. The digests were re-dissolved in $\text{NH}_4\text{COOCH}_3$ and placed on either an anion or cation exchange column to selectively remove the elements of interest. For boron, samples were spiked with isotopically enriched ^{10}B and then dissolved in quartz flasks with reflux condensers using a $\text{HNO}_3/\text{H}_2\text{O}_2$ mixture. The digests were evaporated to approximately 5 mL and neutralized with NH_4OH to a final concentration of 2% NH_4OH . The isotopic ratios were measured by ICP-MS using standard operating conditions. The ^{10}B spike, SRM 952 Enriched Boric Acid Standard, SRM 951 Boric Acid Isotopic Standard, and metals of known purity were used for calibration.

NIST Analyses for Ca, K, Rb, and V by ID TIMS: Single, nominal 0.5 or 1.0 g test portions were taken from each of six bottles of SRM 1573a. Samples were spiked with isotopically enriched ^{42}Ca , ^{41}K , ^{87}Rb and ^{50}V then wet ashed with a $\text{HNO}_3/\text{HF}/\text{HClO}_4$ acid mixture in Teflon beakers. The digests were placed on either an anion or cation exchange column to selectively remove the elements of interest. Thermal ionization was performed using a triple filament procedure and internal normalization of measured ratios.

NIST Analyses for Al, Ba, Ca, Co, Cr, Fe, K, Mn, Na, Rb, Sb, Se, V and Zn by INAA: Duplicate, nominal 0.15 g test portions were taken from each of six bottles of SRM 1573a. All samples, controls and standards were pressed into cylindrical pellets and packaged individually in clean polyethylene bags. For determination of antimony, chromium, cobalt, iron, rubidium, selenium, and zinc, samples were irradiated for 8 h and radioactive decay was counted for up to 24 h after a decay of 20 d. For determination of aluminum, barium, calcium, manganese, potassium, sodium, and vanadium, samples were irradiated for 40 s. For barium, manganese, potassium and sodium, radioactive decay was counted for 60 min after a decay of 40 min. For calcium, radioactive decay was counted for 10 min after a decay of 10 min. For aluminum and vanadium, radioactive decay was counted for 6 min after a decay of 2 min.

NIST Analyses for N by KJEL: Single, nominal 2 g test portions were taken from fifteen bottles of SRM 1573a. Sample preparation was based on the AOAC method 2.057, Improved method for Nitrate-Free Samples, 14th edition.

NIST Analyses for Mn by LEAFS: Duplicate, nominal 1 g test portions were taken from six bottles of SRM 1573a. Samples were ashed with a $\text{HNO}_3/\text{HF}/\text{HClO}_4$ acid mixture in Teflon beakers, refluxed overnight, then evaporated to near dryness. Samples were diluted to 400 mL with 1 % HNO_3 . Resonance fluorescence measurements were made with both excitation and fluorescence wavelengths at the 279.482 nm wavelength. Quantification was by the method of standard additions.

NIST Analyses for B, Cd, K, and N by PGAA: Single 1 g test portions were taken from each of six bottles of SRM 1573a. Each sample was pressed into a cylindrical pellet and irradiated for 13 h. Standards used were ACS grade borax, a standard solution of boric acid, a set of pure nitrogen compounds, and a standardized set of solutions of the metals. Spectral peaks were integrated by two analysts and corrections were made for flux, dead time, pulse pileup, background, and interference peaks.

NIST Analyses for As, Cd, Cu, Sb, and Se by RNAA: Duplicate, nominal 0.25 g test portions were taken from each of six bottles of SRM 1573a. Disks were formed from each aliquot, encapsulated into polyethylene bags, and irradiated for 3 h at 15 MW. After several days, samples were placed in Teflon beakers with a $\text{HNO}_3/\text{HF}/\text{HClO}_4$ acid mixture. Samples were heated, the acid reduced and samples brought up to volume in 1 M HNO_3 and samples were passed through a column before counting.