National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1632e

Trace Elements in Coal

(Bituminous)

This Standard Reference Material (SRM) is intended primarily for use in the evaluation of techniques used in the analysis of coals and materials of a similar matrix. A unit of SRM 1632e consists of 50 g of bituminous coal that was ground to pass a 250 µm (60 mesh) sieve, homogenized, bottled under an argon atmosphere, and sealed in an aluminized bag.

Certified Mass Fraction Values: Certified mass fraction [1] values for elements, expressed on a dry-mass basis, are provided in Table 1. A 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 accounted for by NIST [2]. The certified value for mercury is based on analyses by a single NIST primary method. The certified values for all other elements are based on analyses by two or more critically evaluated independent methods.

Reference Mass Fraction Values: Reference mass fraction values for elements, expressed on a dry-mass basis, are provided in Table 2. A reference value is a non-certified value that is the best estimate of the true value; however, the value does not meet NIST criteria for certification and is provided with an associated uncertainty that may reflect only measurement precision and may not include all sources of uncertainty [2]. The reference value for chlorine is based on two NIST analytical methods. The reference values for other constituents are from a single NIST analytical method.

Information Values: Information mass fraction values for elements are provided in Table 3 for information purposes only. An information value is considered to be a value that will be of interest and use to the SRM user, but insufficient information is available to assess the uncertainty associated with the value [2].

Expiration of Certification: The certification of **SRM 1632e** is valid, within the measurement uncertainty specified, until **01 May 2036**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Storage and Use"). This 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 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 certification of SRM 1632e was provided by T.W. Vetter of the NIST Chemical Sciences Division.

Analytical measurements leading to certification were made by H. Cho, S.J. Christopher, B.R. Lang, S.E. Long, A.F. Marlow, J.L. Molloy, J.M. Ness, R. Oflaz, R.L. Paul, N.E. Sharp, J.R. Sieber, and T.W. Vetter of the NIST Chemical Sciences Division.

Statistical consultation for this SRM was provided by A.L. Pintar of the NIST Statistical Engineering Division.

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

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Gaithersburg, MD 20899
Certificate Issue Date: 25 April 2018

Steven J. Choquette, Director
Office of Reference Materials

INSTRUCTIONS FOR STORAGE AND USE

Storage: The SRM should be stored in its original bottle, tightly sealed and away from sunlight and intense sources of radiation, under normal laboratory conditions.

Use: Before it is sampled, the unit should be thoroughly mixed by carefully inverting and rotating the tightly sealed bottle. A minimum test portion mass of 30 mg for aluminum, calcium, chlorine, chromium, copper, iron, magnesium, manganese, potassium, silicon, sodium, strontium, sulfur, titanium, vanadium, and zinc; 100 mg for barium and scandium; 200 mg for antimony, arsenic, boron, bromine, cerium, cesium, cobalt, europium, rubidium, selenium, and uranium; 250 mg for mercury; 400 mg for nickel; and 750 mg for hydrogen should be used for analytical determinations.

Drying Instructions: To relate measurements directly to the certified and reference values, which are expressed on a dry-mass basis, users should determine a drying correction at the time of the analysis. The correction is determined by oven-drying a separate 1 g sample in a nitrogen atmosphere at 107 °C ± 3 °C to a constant mass [3] or equivalent technique. Attainment of constant mass is defined according to the ASTM thermogravimetric (TG) method as either a mass loss of ≤ 0.05 %, relative, over a nine-minute period or the mass loss after one hour of heating [3]. At NIST, the mass losses determined in both manners, and in both nitrogen and air, were similar.

The mass loss determined in both a nitrogen and air atmosphere, which is reported ***for information purposes only***, was nominally 2 %. The mass loss determined by the user may be different, depending on ambient conditions when the bottle is sampled.

NOTICE TO USERS

NIST strives to maintain the SRM inventory supply, but NIST cannot guarantee the continued or continuous supply of any specific SRM. Accordingly, NIST encourages the use of this SRM as a primary benchmark for the quality and accuracy of the user's in-house reference materials and working standards. As such, the SRM should be used to validate the more routinely used reference materials in a laboratory. Comparisons between the SRM and in-house reference materials or working measurement standards should take place at intervals appropriate to the conservation of the SRM and the stability of relevant in-house materials. For further guidance on how this approach can be implemented, contact NIST by email at srms@nist.gov.

SOURCE, PREPARATION, AND HOMOGENEITY ASSESSMENT[1]

Source and Preparation of Material: The coal for this SRM was obtained from the Bailey Mine of CONSOL Energy Inc. in southwestern Green County, PA. This mine produces bituminous coal obtained from the Pittsburgh seam. The collection of the approximately 450 kg of coal was performed under the direction of D. Wilson. The coal was air-dried and subsequently pulverized to pass a 250 µm (60 mesh) sieve by a company under contract to NIST. The entire lot was divided into two portions using the spinning riffler technique. One portion of the lot was sealed in Mylar® bags filled under an argon atmosphere for long-term storage. The other portion was further divided by the spinning riffler technique, bottled under an argon atmosphere, and sealed in Mylar® bags to prepare SRM 1632e.

Heterogeneity Assessment: Heterogeneity was assessed for selected elements in the bottled material using wavelength dispersive X-ray fluorescence spectrometry (WDXRF), instrumental neutron activation analysis (INAA), prompt gamma-ray activation analysis (PGAA), and isotope dilution cold vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS).

VALUE ASSIGNMENT

Measurements were modeled using linear mixed effects statistical models, the parameters of which were estimated using the Bayesian inference paradigm [4]. The Monte Carlo method [5] was used to propagate all components of uncertainty. Certified and reference values are each given with an expanded uncertainty, U, which can be expressed in a manner that is consistent with the ISO/JCGM Guide [6] as $U = ku_c$. The quantity, k, is the effective coverage factor used to obtain an expanded uncertainty that provides a symmetric, approximately 95 % coverage interval. An effective value of k was calculated as the ratio U/u_c, which resulted in a value of $k < 1.96$ for two elements, manganese and vanadium. A value of $k < 1.96$ can occur when the distribution of Monte Carlo samples deviates substantially from a Gaussian distribution. For all elements, except bromine, hydrogen, nickel, and rubidium, the quantity u_c

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[1]Certain commercial equipment, instruments, or materials are identified in this certificate 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.

represents, at the level of one standard deviation, the estimated uncertainty in the mass fraction for the mean of all bottles of SRM 1632e, because the underlying mass fraction is assumed to be the same for each bottle. For bromine, hydrogen, nickel, and rubidium, the quantity u_c represents, at the level of one standard deviation, the estimated uncertainty for the mean of a single randomly chosen bottle of SRM 1632e, which accounts for possible material heterogeneity. The analytical techniques used for each element are listed in Table 4.

Metrological Traceability: The measurands for the certified values in Table 1 are the total mass fractions for the elements on a dry-mass basis. The measurands for the reference values in Table 2 are the mass fractions for the elements on a dry-mass basis as determined by the methods indicated in Table 4. Metrological traceability is to the SI derived unit for mass fraction, expressed as milligrams per kilogram for all elements except aluminum, calcium, hydrogen, iron, potassium, silicon, and sulfur, which are expressed as percentages [1].

Certified Mass Fraction Values: The certified values and the corresponding expanded uncertainty values are given in Table 1. The uncertainty listed with each certified value is an expanded uncertainty with a coverage factor, k, providing approximately 95 % coverage. The certified value and expanded uncertainty for sulfur were calculated by combining two sets of results using the approach in reference 7.

Table 1. Certified Mass Fraction Values for Elements (Dry-Mass Basis) in SRM 1632e

Major Constituents

Element	Mass Fraction (%)		k	Element	Mass Fraction (%)		k
Iron (Fe)	1.42	± 0.13	2.20	Aluminum (Al)	0.960	± 0.049	2.15
Silicon (Si)	1.81	± 0.13	2.13	Calcium (Ca)	0.1714	± 0.0084	2.08
Sulfur (S)	2.738	± 0.057	2	Potassium (K)	0.1248	± 0.0052	2.20

Minor Constituents (header appears above right columns)

Trace Elements

	Mass Fraction (mg/kg)		k		Mass Fraction (mg/kg)		k
Mercury (Hg)	0.1351	± 0.0035	2	Strontium (Sr)	84.1	± 5.3	2.32
Rubidium (Rb)	8.49	± 0.87	2.13	Titanium (Ti)	519	± 19	2.05
Sodium (Na)	374	± 16	2.10	Zinc (Zn)	13.0	± 1.3	2.17

Reference Mass Fraction Values: The reference values and the corresponding expanded uncertainty values are given in Table 2. The uncertainty listed with the reference values is an expanded uncertainty with a coverage factor, k, providing approximately 95 % coverage.

Table 2. Reference Mass Fraction Values for Elements (Dry-Mass Basis) in SRM 1632e

Major Constituent

Element	Mass Fraction (%)		k
Hydrogen (H)	4.97	± 0.16	2

Trace Elements

Element	Mass Fraction (mg/kg)		k	Element	Mass Fraction (mg/kg)		k
Antimony (Sb)	0.428	± 0.040	2.05	Copper (Cu)	5.70	± 0.14	2
Arsenic (As)	8.55	± 0.49	2	Europium (Eu)	0.2457	± 0.0063	2
Barium (Ba)	62.8	± 3.5	2	Magnesium (Mg)	391	± 32	2
Boron (B)	75.7	± 4.1	2.05	Manganese (Mn)	18.4	± 1.1	1.81
Bromine (Br)	11.9	± 1.0	2.11	Nickel (Ni)	11.08	± 0.35	2
Cerium (Ce)	12.24	± 0.27	2	Scandium (Sc)	3.583	± 0.088	2
Cesium (Cs)	0.648	± 0.021	2	Selenium (Se)	1.525	± 0.078	2
Chlorine (Cl)	963	± 23	2.09	Uranium (U)	0.636	± 0.032	2.06
Chromium (Cr)	16.57	± 0.34	2	Vanadium (V)	29.2	± 1.5	1.72
Cobalt (Co)	3.622	± 0.090	2				

Information Values: Particle size measurements were made using a laser-based light scattering system. Approximately 0.5 g of material (refractive index: 1.746, absorption index: 1.0) was measured using water as the dispersant, (refractive index: 1.33) and 0.01 % Triton X-100 as a pre-wetting surfactant. Calculated 10th percentile ($d_{0.1}$), 50th percentile ($d_{0.5}$), and 90th percentile ($d_{0.9}$) particle sizes (percent volume of particles smaller than the value) are $d_{0.1} = 10.4$ µm, $d_{0.5} = 67.7$ µm, and $d_{0.9} = 179$ µm. The fraction of material smaller than 10 µm in diameter is 10 %. The particle size distribution is shown in Figure 1.
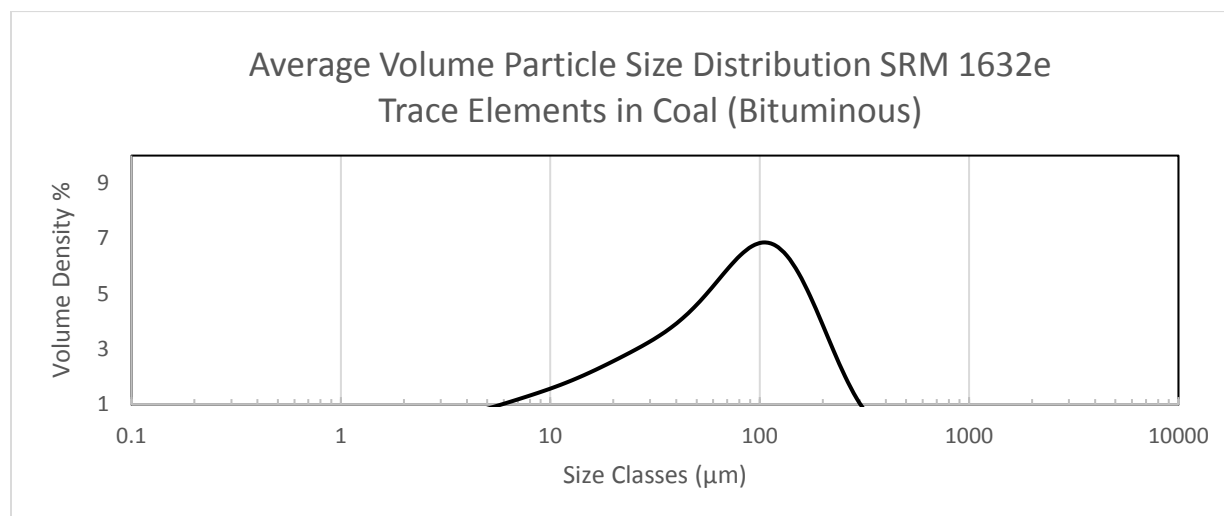

Figure 1. Average Volume Particle Size Distribution for SRM 1632e as measured by a laser-based light scattering system.

The information mass fraction values given in Table 3 are provided without uncertainty estimates and are given as additional information on the matrix. Information values cannot be used to establish metrological traceability.

Table 3. Information Mass Fraction Values (Dry-Mass Basis) for Elements in SRM 1632e

Major Constituents

Element	Mass Fraction (%)	Element	Mass Fraction (%)
Carbon (C)	76	Oxygen (O)	7
Nitrogen (N)	1.4		

Trace Elements

Element	Mass Fraction (mg/kg)	Element	Mass Fraction (mg/kg)
Silver (Ag)	0.02	Neodymium (Nd)	6
Beryllium (Be)	1	Niobium (Nb)	2
Bismuth (Bi)	<1	Osmium (Os)	<1
Cadmium (Cd)	0.1	Palladium (Pd)	<1
Dysprosium (Dy)	1	Phosphorus (P)	150
Erbium (Er)	0.7	Platinum (Pt)	<1
Fluorine (F)	60	Praseodymium (Pr)	1.5
Gadolinium (Gd)	1	Rhenium (Re)	<10
Gallium (Ga)	5	Rhodium (Rh)	<1
Germanium (Ge)	3	Ruthenium (Ru)	<1
Gold (Au)	<1	Samarium (Sm)	1
Hafnium (Hf)	0.6	Tantalum (Ta)	0.1
Holmium (Ho)	0.2	Tellurium (Te)	<1
Indium (In)	0.01	Terbium (Tb)	0.2
Iodine (I)	1	Thallium (Tl)	0.4
Iridium (Ir)	<1	Thorium (Th)	1
Lanthanum (La)	7	Thulium (Tm)	0.1
Lead (Pb)	5	Tin (Sn)	0.8
Lithium (Li)	8	Tungsten (W)	<10
Lutetium (Lu)	0.1	Ytterbium (Yb)	0.6
Molybdenum (Mo)	1	Yttrium (Y)	6
		Zirconium (Zr)	20

Table 4. Methods of Analysis

Methods	Element
CANSPEX Interlaboratory Study	S
ID-CV-ICP-MS at NIST	Hg
Isotope dilution sector field inductively coupled plasma mass spectrometry (ID-SF-ICP-MS) at NIST	S
INAA at NIST	Al, As, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Cu, Eu, Fe, Mg, Mn, Na, Rb, Sb, Sc, Se, Sr, Ti, U, V, Zn
PGAA at NIST	Al, B, Cl, Fe, H, K, Si, Ti
WDXRF at NIST	Al, Ca, Fe, K, Na, Ni, Rb, Si, Sr, Ti, Zn

SUPPLEMENTAL INFORMATION

Summary statistics reported by Quality Assurance International, Ltd. for the Coal and Ash Sample Proficiency Exchange (CANSPEX) 2015-3 interlaboratory test using SRM 1632e as an unknown coal sample are provided in Appendix A of this certificate to demonstrate user experience with this material using conventional methods and to better characterize the matrix. The CANSPEX Round Robin results should **NOT** be used as substitutes for NIST values.

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 (2008); available at https://www.nist.gov/pml/pubs/ (accessed Apr 2018).

[2]   May, W.E.; Gills, T.E.; Parris, R.; Beck, II, C.M.; Fassett, J.D.; Gettings, R.J.; Greenberg, R.D.; Guenther, F.R.; Kramer, G.; MacDonald, B.S.; Wise, S.A.; *Definitions 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.cfm (accessed Apr 2018).

[3]   ASTM D7582-15; *Standard Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis*; Annu. Book ASTM Stand., Vol 05.06, pp. 914-922 (2016).

[4]   Gelman, A.; Carlin, J.B.; Stern, H.S.; Rubin, D.B.; *Bayesian Data Analysis*; Chapman & Hall (2004).

[5]   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 http://www.bipm.org/en/publications/guides/gum.html (accessed Apr 2018).

[6]   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/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Apr 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 Apr 2018).

[7]   Stone, M.; *The Opinion Pool*; Ann. Math. Stat., Vol. 32, pp. 1339–1342 (1961).

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 https://www.nist.gov/srm.

APPENDIX A

Portions of SRM 1632e were analyzed as unknown samples in the round robin study CANSPEX 2015-3, conducted by Quality Associates International, Ltd. Summary results shown in Table A1 were provided by Quality Associates International, Ltd. These results are included as an Appendix to the Certificate of Analysis for SRM 1632e to demonstrate user experience with this material using conventional methods and to better characterized the matrix. Results from this study should **NOT** be used as substitutes for the NIST values.

Table A1. SRM 1632e CANSPEX Interlaboratory Study Results						
Parameter	Most Likely Value [a]	Unit	95 % Coverage Interval of Most Likely Value	Pooled Within Lab Standard Deviation (s_w)	Pooled Between Lab Standard Deviation (s_B)	Total Number of Labs
Moisture	1.664	%	0.033	0.033	0.158	127
Ash	8.488	%	0.013	0.034	0.053	125
Volatile	38.19	%	0.19	0.12	0.81	101
Btu	13 678	per lb	10	16	46	116
Carbon	75.85	%	0.19	0.13	0.66	66
Hydrogen	5.130	%	0.037	0.032	0.119	61
Nitrogen	1.444	%	0.014	0.018	0.039	58
Total Sulfur	2.761	%	0.023	0.021	0.106	121
Pyritic Sulfur	1.291	%	0.049	0.023	0.080	19
Sulfate Sulfur	0.049	%	0.009	0.004	0.015	20
Chlorine	942	µg/g	25	18	73	52
Fluorine	65	µg/g	5	2	14	39
Mercury	135	ng/g	3	4	8	46
Selenium	1.40	µg/g	0.24	0.10	0.33	13
FSI[b]	8.0		0.2	0.3	0.4	58

[a] Values are expressed on a dry-mass basis for all parameters except moisture. The moisture value is expressed on an "as received" basis.
[b] Free Swelling Index

Table A2. Derived Standard Deviations (in %) of Repeatability (s_r) and Reproducibility (s_R), and Tally of Published Methods Used in CANSPEX Interlaboratory Study[a]

Parameter[b]	Total Number of Labs	AS	s_r	s_R	No.	ASTM	s_r	s_R	No.	BSI	s_r	s_R	No.	DIN	s_r	s_R	No.	GB	s_r	s_R	No.	ISO	s_r	s_R	No.	NF	s_r	s_R	No.	SABS	s_r	s_R	No.	In-house No.
Moisture %	127	1038.3	0.04	-	2	D2013	0.04	0.09	0	1016	0.04	-	1	51718	0.07	-	2	212	0.07	-	1	589	0.11	-	1	3-037	-	-		925	-	-	0	18
						D3173	0.04	0.09	56													11722	0.04	-	12									
						D3302	0.04	0.09	0													5068	0.07	-	1									
						D5142	0.08	0.11	11																									
						D7582	0.09	0.28	22																									
Ash % dry basis	127	1038.3	0.04	0.05	2	D3174	0.08	0.11	53	1016	0.05	0.11	1	51719	0.07	0.11	3	212	0.07	0.11	1	1171	0.07	0.11	16	3-003	-	-			-	-		16
						D5142	0.09	0.12	12																									
						D7582	0.07	0.11	23																									
Volatile % dry basis	101	1038.3	0.07	0.35	2	D3175	0.18	0.35	40	1016	0.11	0.35	1	51720	0.41	0.54	2	212	0.18	0.35	1	562	0.41	0.54	19									13
						D5142	0.29	0.86	15																									
						D7582	0.13	0.47	8																									
Btu/lb dry basis	116	1038.5	20	46	1	D1989	23	39	2	1016	18	43	0	51900	18	46	4	213	18	46	1	1928	43	106	19									11
						D2015	24	38	0																									
						D3286	18	35	3																									
						D5865	24	38	75																									
Carbon % dry basis	66	1038.6.4	0.11	0.21	3	D3178	0.11	-	0					51732	-	-	2	476	0.18	0.35	1	609	0.09	0.18	2									8
						D5373	0.16	0.35	44													29541	0.18	0.46	6									
Hydrogen % dry basis	61	1038.6.4	0.04	0.07	3	D3178	0.02	-	0					51732	-	-	2	476	0.05	0.09	1	609	0.04	0.09	2									5
						D5373	0.04	0.09	42													29541	0.04	0.14	6									
Nitrogen % dry basis	58	1038.6.4	0.01	0.03	3	D3179	0.07	0.12	0					51732	-	-	2	476	0.03	0.05	1	333	0.02	0.04	1									8
						D5373	0.02	0.05	39													29541	0.01	0.05	4									
Total Sulfur % dry basis	121	1038.6.3.3	0.02	0.08	2	D3177	0.02	0.04	1	1016	0.02	0.04	1	51724-3	0.01	0.02	2	214	0.04	0.09	1	351	0.02	0.04	3	3-038	-	-	0		-	-		17
						D4239	0.04	0.10	83													19579	0.04	0.10	7									
						D5016	0.08	0.27	4																								
Pyritic Sulfur % dry basis	19	1038.11	0.02	0.05	1	D2492	0.07	0.18	15									215	0.02	0.04	1													2
Sulfate Sulfur % dry basis	20	1038.11	0.007	0.011	1	D2492	0.007	0.014	16									215	0.01	0.04	1													2
Chlorine µg/g dry basis	52	1038.8.2	35	71	1	D2361	106	213	1	1016	177	177	1	51727	71	106	1	3558	35	71	1	587	-	-	0	3-009	-	-	1		-	-		21
						D4208	61	148	19																									
						D6721	21	26	8																									
Fluorine µg/g dry basis	39					D3761	5	5	16					51723	8	14	0	4663	6	7	1	11724	4	7	2	03-009	-	-						18
						D5987	4	7	2																									
Mercury ng/g dry basis	46					D6414	10	13	2					22022	-	-																		7
						D6722	3	9	37																									
Selenium µg/g dry basis	12					D4606	0.210	0.18	2	5.000																								10
FSI	58	1038.17	0.18	0.35	1	D720	0.35	0.71	40	1016	-	-	0	51741	-	-	0	5448	0.35	0.53	1	501	0.35	0.18	9									7

[a] The above precision standard deviations are derived from the division of each method's published precision values by an estimate of the coverage factor used.

[b] Method is designated "In-house" if lab reports method as In-house; lab reports methods as modified; or does not report a method. CANSPEX does not provide repeatability or reproducibility information for In-house methods.

[c] "-" indicates documentation confirming the repeatability or reproducibility is not available.

The above referenced methods are available through the following websites:

AS	https://www.standards.org.au (accessed Apr 2018)	GB	https://www.standardsportal.org.cn/zmen/English/Resources/ (accessed Apr 2018)
ASTM	https://www.astm.org/ (accessed Apr 2018)	ISO	https://www.iso.org/standards.html (accessed Apr 2018)
BSI	https://www.bsigroup.com/ (accessed Apr 2018)	NF	https://www.afnor.org/en/ (accessed Apr 2018)
DIN	https://www.din.de/en (accessed Apr 2018)	SABS	https://www.sabs.co.za/ (accessed Apr 2018)