



# National Institute of Standards & Technology

## Certificate of Analysis

### Standard Reference Material<sup>®</sup> 1648a

#### Urban Particulate Matter

This Standard Reference Material (SRM) is atmospheric particulate matter collected in an urban area and is intended primarily for use as a control material and in the evaluation of methods used in the inorganic analysis of atmospheric particulate matter and materials with similar matrices. All constituents for which certified, reference, and information values are provided in SRM 1648a were naturally present in the material before processing. While not represented to be typical of the area where it was collected, nor of contemporary composition of an urban aerosol, its use should typify the analytical problems of atmospheric particulate samples obtained from industrialized urban areas. A unit of SRM 1648a consists of one bottle containing 2 g of atmospheric particulate matter.

**Certified Values:** Certified values, expressed as mass fractions, for the content of 24 elements are provided in Table 1. The certified values are based on the agreement of results from two or more chemically independent analytical techniques obtained at NIST and collaborating expert laboratories [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 accounted for by NIST.

**Reference Values:** Reference values, expressed as mass fractions, are provided for the content of eight additional elements in Table 2. Reference values are non-certified values that are the best estimate of the true value. The values do not meet the 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].

**Information Values:** Information values, expressed as mass fractions, are provided in Table 3 for the content of six elements. 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 adequately the uncertainty associated with the value, or it is a value derived from a limited number of analyses [1].

**Expiration of Certification:** The certification of **SRM 1648a** is valid, within the measurement uncertainty specified, until **01 October 2027**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Handling, 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) will facilitate notification.

The coordination of the investigations and technical measurements leading to the certification of this material was under the leadership of R. Zeisler of the NIST Analytical Chemistry Division.

Consultation on the statistical design of the experimental work and evaluation of the data were 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 Measurement Services Division.

Stephen A. Wise, Chief  
Analytical Chemistry Division

Robert L. Watters, Jr., Chief  
Measurement Services Division

Gaithersburg, MD 20899  
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*Certificate Revision History is on Last Page*

Analytical measurements from the NIST Analytical Chemistry Division were performed by E.A. Mackey, A.F. Marlow, J.R. Sieber, R.O. Spatz, and R. Zeisler

Cooperating laboratories and analysts include: Desert Research Institute, Reno, NV, USA: S.D. Kohl; Federal Institute for Materials' Research and Testing (BAM), Germany: M. Hedrich and C. Segebade; National Institute of Nuclear Research (ININ) and National University of Mexico, Mexico: M. Navarrete, G. Zarazúa, P. Avila, T. Martínez, and C. Solís; Sunset Laboratory Inc., Tigard, OR: R. Cary; University of Sao Paulo, Brazil: C.S. Nomura and P.V. Oliveira

## INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

**Handling:** This material may contain constituents of unknown toxicity and is readily aerosolized. The particle size of a significant portion of the material is in the range of inhalable airborne particulate matter. Therefore, caution and care should be exercised during its handling and use.

**Storage:** SRM 1648a must be stored in its original bottle at temperatures less than 30 °C, away from sources of intense radiation, including ultraviolet lamps or sunlight.

**Use:** Prior to removal of sub-samples for analysis, the contents of the bottle should be mixed. The mass fractions of constituents in SRM 1648a are reported on a dry-mass basis. The SRM, as received, contains approximately 2.3 % moisture. The aerosol sample should be dried to a constant mass before weighing for analysis or a separate sub-sample of the SRM should be removed from the bottle at the time of analysis and dried to determine the mass fractions on a dry-mass basis. If the constituents of interest are volatile, then the moisture must be determined with a separate sub-sample. The drying procedures described below are recommended. Equivalent procedures may be used, but the temperature of 30 °C should not be exceeded.

## PREPARATION AND ANALYSIS<sup>(1)</sup>

**Sample Collection and Preparation:** The SRM was prepared from urban particulate matter collected in the St. Louis, MO area in a baghouse specially designed for this purpose. The material was collected over a period in excess of 12 months during 1976 and 1977; therefore, it is a time-integrated sample from that period. The material was removed from the filter bags, combined in a single lot, screened through a fine mesh sieve to remove extraneous materials, and thoroughly blended in a v-blender. The lot was divided; one portion was used for SRM 1648, and an 8 kg portion of the material was set aside for a later renewal. This portion was blended again and bottled as SRM 1648a. SRM 1648a is the same particulate material issued in 1978 as SRM 1648. The material has been re-blended, bottled, and reanalyzed to provide updated certified values, reference values, and information values based on a milligram size sample.

**Particle Size Distribution:** The particle size distribution of the SRM 1648a units was obtained using a commercial laser diffraction instrument manufactured by Malvern Instruments (Worcestershire, UK). The particulate matter was measured in aqueous suspension. The suspensions were prepared by a 10 minute sonication in distilled water (20 mL with approximately 0.02 mg of particulate matter with a drop of 0.1 % solution of Triton added). These suspensions were gradually introduced into the water-filled, small sample measurement cell until a 6.5 % obscuration of the laser beam was achieved. Each suspension was measured three times for 30 s with a 10 s pause between the passes. A refractive index of 1.52 and absorption index of 0.1 were selected for the measurements. Results were calculated using the General Purpose Model provided by Malvern. The results are shown in Figure 1 depicting a typical distribution for total suspended air particulate matter.

**Conversion to Dry-Mass Basis:** The results for the constituents in SRM 1648a are reported on a dry-mass basis; however, the material "as received" contains residual moisture. Drying in a desiccator over fresh  $\text{Mg}(\text{ClO}_4)_2$  for 48 h is recommended. Alternately, drying in a desiccator over  $\text{CaSO}_4$  for seven days results in similar moisture loss. Heat above 30 °C should not be used.

**Homogeneity Assessment:** The homogeneity of SRM 1648a was assessed by analyzing samples of approximately 1 mg from bottles selected by stratified random sampling. Duplicate portions of 12 bottles and duplicate portions from six randomly selected locations in one bottle were analyzed by instrumental neutron activation analysis (INAA). The results were supplemented by wavelength dispersive X-ray fluorescence spectrometry (WDXRF) analyzing samples from 12 bottles in duplicate and by solid sampling graphite furnace

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<sup>(1)</sup> 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.

atomic absorption spectrometry (SS-GFAAS) analyzing 12 test portions from one bottle. Kurfürst homogeneity factors derived from these analytical data confirmed that a smaller than 1 % relative heterogeneity component of the uncertainty in the results is encountered for most elements by selecting sample sizes of 5 mg or larger.

**Analytical Approach:** In the investigations at NIST, INAA and neutron capture prompt gamma activation analysis (PGAA) were used to directly determine mass fraction values in SRM 1648a and in the previously issued SRM 1648. WDXRF determined highly precise specific count rates for selected elements in both materials. Additional measurements with photon activation analysis (PAA), proton-induced X-ray emission spectrometry (PIXE), SS-GFAAS and WDXRF were provided by collaborating laboratories. All assays were designed to establish comparability of values between the conventionally certified in SRM 1648, representing the parent material, and the SRM 1648a measured at small sample sizes. These measurements confirmed that the composition of the material had not changed in storage and that the measured values in SRM 1648 can be utilized for confirmation of the value assignment of SRM 1648a.

**Certified Values and Uncertainties:** Each certified mass fraction value, expressed on a dry-mass basis, is an equally weighted mean of the individual sets of results provided by the individual NIST methods and individual methods of the collaborating laboratories, where used. All NIST results and some of those provided by collaborating laboratories included estimates of all recognized sources of uncertainty. Some collaborating laboratory results were provided without complete uncertainty budgets. These uncertainties were augmented using an approach that accounts for the differences among the results obtained by different methods [2]. The resulting uncertainty listed with each value is an expanded uncertainty, with coverage factor 2 (approximately 95 % confidence). The expanded uncertainties are calculated according to the method described in the ISO Guide [3].

Table 1. Certified Mass Fractions of Elements

Element	Mass Fraction	Units	Element	Mass Fraction	Units
Al <sup>(a,b)</sup>	3.43 ± 0.13	%	Mg <sup>(a,b)</sup>	0.813 ± 0.012	%
As <sup>(a,c,d,e)</sup>	115.5 ± 3.9	mg/kg	Mn <sup>(a,b,d)</sup>	790 ± 44	mg/kg
Br <sup>(a,b,d)</sup>	502 ± 10	mg/kg	Na <sup>(a,b)</sup>	4240 ± 60	mg/kg
Ca <sup>(a,b,d,e)</sup>	5.84 ± 0.19	%	Ni <sup>(b,c,d,e)</sup>	81.1 ± 6.8	mg/kg
Cd <sup>(c,f)</sup>	73.7 ± 2.3	mg/kg	Pb <sup>(b,c,d,e)</sup>	0.655 ± 0.033	%
Ce <sup>(a,e)</sup>	54.6 ± 2.2	mg/kg	Rb <sup>(a,e)</sup>	51.0 ± 1.5	mg/kg
Cl <sup>(a,b)</sup>	4543 ± 47	mg/kg	S <sup>(b,f)</sup>	5.51 ± 0.36	%
Co <sup>(a,e)</sup>	17.93 ± 0.68	mg/kg	Sb <sup>(a,e)</sup>	45.4 ± 1.4	mg/kg
Cr <sup>(a,b)</sup>	402 ± 13	mg/kg	Sr <sup>(b,d)</sup>	215 ± 17	mg/kg
Cu <sup>(a,c,d)</sup>	610 ± 70	mg/kg	Ti <sup>(a,b,d,e,f)</sup>	4021 ± 86	mg/kg
Fe <sup>(a,b,d,f)</sup>	3.92 ± 0.21	%	V <sup>(a,d)</sup>	127 ± 11	mg/kg
K <sup>(a,b,d,f)</sup>	1.056 ± 0.049	%	Zn <sup>(a,b,c,d,e)</sup>	4800 ± 270	mg/kg

- <sup>(a)</sup> INAA (NIST)
- <sup>(b)</sup> WDXRF (NIST)
- <sup>(c)</sup> SS-GFAAS
- <sup>(d)</sup> PIXE
- <sup>(e)</sup> PAA
- <sup>(f)</sup> PGAA (NIST)

**Reference Values and Uncertainties:** Reference values are based on NIST results from one method for each reported element. The results are validated by the values previously reported for SRM 1648 [4] since INAA and XRF procedures established equivalence of SRM 1648a with SRM 1648 based on previously certified values in the latter. The uncertainties of the NIST results were augmented [2] on the basis of the previously reported differences among the results obtained by different methods in SRM 1648 [4]. These results do not fulfill the criteria for certification since a full estimate of method bias for the determinations in SRM 1648a is not available. The reporting follows the ISO Guide [3].

Table 2. Reference Mass Fractions for Elements

Element	Mass Fraction	Units	Element	Mass Fraction	Units
Ag <sup>(a)</sup>	6.0 ± 0.3	mg/kg	Se <sup>(a)</sup>	28.4 ± 1.1	mg/kg
B <sup>(c)</sup>	161 ± 9	mg/kg	Si <sup>(b)</sup>	12.8 ± 0.4	%
Cs <sup>(a)</sup>	3.4 ± 0.2	mg/kg	Sm <sup>(a)</sup>	4.3 ± 0.3	mg/kg
La <sup>(a)</sup>	39 ± 3	mg/kg	W <sup>(a)</sup>	4.6 ± 0.3	mg/kg

<sup>(a)</sup> INAA (NIST)

<sup>(b)</sup> WDXRF (NIST)

<sup>(c)</sup> PGAA (NIST)

**Information Values:** Information values that may be of interest and use to the SRM user are given in Table 3. Information values are based on results that did not allow complete assessment of all sources of uncertainty, hence, only estimated means without uncertainties are given. These element values deviate from values in the previous SRM 1648. Sc and Th were found to be inhomogeneous at the 5 mg sample size.

Table 3. Information Values for the Content of Selected Elements

Element	Mass Fraction (%)	Element	Mass Fraction (mg/kg)
C <sub>total</sub> <sup>(a,b)</sup>	12.7	Hf <sup>(c)</sup>	5.2
C <sub>org</sub> <sup>(b)</sup>	10.5	Sc <sup>(c)</sup>	6 to 120
C <sub>element</sub> <sup>(b)</sup>	2.3	Th <sup>(c)</sup>	7 to 107

<sup>(a)</sup> PGAA (NIST)

<sup>(b)</sup> Thermal-optical OCEC method

<sup>(c)</sup> INAA (NIST)

Users may wish to refer to the compilation of literature data for the original SRM 1648 for further information on elements that may occur in the material and are not reported in this certificate [4].

### SUPPLEMENTAL INFORMATION

**Particle Size:** Particle size distributions in SRM 1648a determined in aqueous suspension via laser light scattering instrumentation (Malvern Mastersizer 2000) and are shown in Figure 1. Calculated 10, 50, and 90 percentile particle sizes (percent volume of particles smaller than the value) for SRM 1648a are:  $d_{0.1} = 1.35 \mu\text{m}$ ,  $d_{0.5} = 5.85 \mu\text{m}$ , and  $d_{0.9} = 30.1 \mu\text{m}$ . Uncertainties in these values are estimated at  $\pm 10\%$  relative (2s).

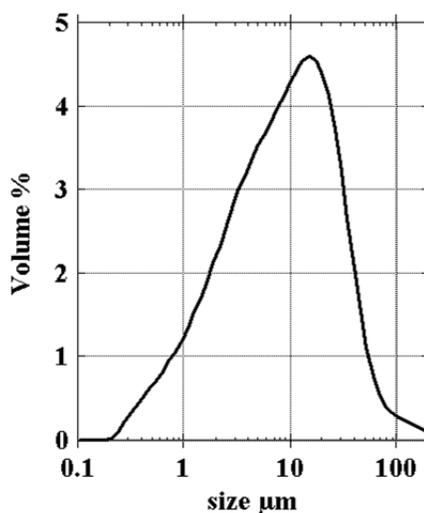


Figure 1. Particle size distributions in SRM 1648a.

**Homogeneity Assessment:** Three methods were used to investigate the homogeneity of SRM 1648a for the suggested sample size of several milligrams: small-sample INAA, SS-GFAAS, and WDXRF. Results for each of the certified elements are shown in Table 4. All results are given as the relative standard deviations. The contribution from heterogeneity  $u_{\text{HET}}$  is derived from the measured total standard deviation  $u_{\text{exp}}$  and its analytical contribution  $u_{\text{AN}}$  according to the equation below (equation 1).

$$u_{\text{exp}}^2 = u_{\text{HET}}^2 + u_{\text{AN}}^2 \quad (1)$$

Based on the models linking sample mass ( $w$ ) to the homogeneity of particulate materials [5], Kurfürst, Grobecker, and Stoepler have proposed an elemental homogeneity factor  $H_e$  that gives the relative standard deviation in percent for the element of interest if 1 mg samples were repeatedly analyzed and no analytical uncertainty were to influence the result (equation 2) [6].

$$H_e = u_{\text{HET}} \sqrt{w} \quad (2)$$

**INAA Determinations:** INAA has been shown to be applicable for the determination of heterogeneity in small samples because the small samples, which essentially form point sources, provide for great improvements in the assays [7]. In the case of this INAA procedure, the analytical variance is in many instances dominated by the uncertainty from counting statistics listed as “instrument uncertainty” in Table 4. Thirty-six test portions of SRM 1648a were analyzed and the heterogeneity components were calculated by subtracting the analytical uncertainties from the observed experimental uncertainty.

**WDXRF Determinations:** WDXRF has been used routinely for homogeneity determinations because of the excellent instrument stability. Since the X-ray intensities are attenuated in the sample, the highest contribution comes from the surface sample layers. The analyzed sample mass varies for each element and was calculated from a sample thickness that contributes to 90 % of the X-ray yield. To obtain sample mass, the calculated thickness was multiplied with the sample area exposed to the excitation beam and multiplied with the sample density. The counting statistics are listed under “instrument uncertainty” in Table 4.

**SS-GFAAS Determinations:** Solid sampling procedures were used in conjunction with GFAAS by directly weighing 20  $\mu\text{g}$  test portions into the graphite furnace. The instrument uncertainty was determined as repeatability of the determination of 20  $\mu\text{g}$  single element solution standards. Twelve measurements were done for each test.

Table 4. Homogeneity Test Results Obtained for Certified Elements

Element	Method	Sample Mass (mg)	Observed Uncertainty	Instrument Uncertainty	Other Uncertainty (estimate)	Uncertainty Due to Heterogeneity	Kurfürst Homogeneity Factor
			Relative Standard Deviation				
Al	INAA	1.15	1.1	0.24	0.5	0.91	0.98
	WDXRF	0.13	1.4	0.21	0.2	1.37	0.49
As	INAA	1.15	2.6	0.62	1.5	2.07	2.22
	SS-GFAAS	0.036	11.2	2.70	0.7	10.85	2.06
Br	INAA	1.15	1.2	0.63	0.7	0.68	0.73
Ca	INAA	1.15	1.7	1.32	0.5	1.02	1.09
	WDXRF	1.5	1.4	0.15	0.2	1.38	1.69
Cd	SS-GFAAS	0.037	11.9	2.04	0.7	11.70	2.25
Ce	INAA	1.15	3.1	1.23	1.2	2.58	2.77
Cl	INAA	1.15	1.4	1.17	0.5	0.48	0.52
	WDXRF	0.59	1.3	0.36	0.2	1.23	0.95
Co	INAA	1.15	2.5	0.91	1.2	2.00	2.14
Cr	INAA	1.15	6.4	0.51	1.2	6.27	6.72
Cu	INAA	1.15	9.6	8.34	0.5	4.73	5.07
	SS-GFAAS	0.02	19.9	2.55	0.7	19.72	2.79
Fe	INAA	1.15	2.0	0.41	1.2	1.55	1.66
	WDXRF	17	1.3	0.09	0.2	1.28	5.28
K	INAA	1.15	1.9	1.17	0.5	1.42	1.53
	WDXRF	1.1	1.5	0.32	0.2	1.45	1.52
Mg	INAA	1.15	4.2	3.92	0.7	1.38	1.48
	WDXRF	0.22	1.4	0.42	0.2	1.32	0.62
Mn	INAA	1.15	3.1	0.46	0.5	3.02	3.24
	WDXRF	7.1	2.0	0.28	0.2	1.97	5.25
Na	INAA	1.15	1.6	0.53	0.5	1.41	1.52
	WDXRF	0.13	1.4	0.99	0.2	0.97	0.35
Ni	SS-GFAAS	0.022	14.0	3.98	0.7	13.40	1.99
Pb	SS-GFAAS	0.026	11.4	3.90	0.7	10.69	1.72
Rb	INAA	1.15	10.2	9.13	1.2	4.39	4.70
S	WDXRF	0.59	1.5	0.13	0.2	1.48	1.14
Sb	INAA	1.15	2.8	0.60	1.2	2.46	2.64
Sr	WDXRF	36	1.7	0.25	0.2	1.67	10.02
Ti	INAA	1.15	5.9	4.00	0.7	4.24	4.55
	WDXRF	2.6	1.8	0.40	0.2	1.74	2.81
V	INAA	1.15	1.1	0.51	0.5	0.80	0.85
Zn	INAA	1.15	1.9	0.25	1.2	1.45	1.56
	SS-GFAAS	0.028	14.6	2.38	0.7	14.39	2.41

The results are to some degree dependent on the method used, but in general, follow the predictions of the sampling models. Best estimates for heterogeneity may be obtained by analyses at the desired sample size (e.g., 1 mg) with a method that has smaller than 1 % uncertainties. Nevertheless, WDXRF and particularly GFAAS results, from much smaller sample sizes, fall into the same range as the INAA results obtained with 1.15 mg samples. The results reveal that most of the certified elements may exhibit 1 % or less relative uncertainty due to heterogeneity when the recommended sample size of 5 mg is used. A small group of metals, Co, Cr, Fe, Mn, and Ti seem to be affected by about 2 %, and Sr by nearly 5 %. However, these uncertainties are included in the expanded uncertainties of the certified values. The values in Table 4 nevertheless can give some guidance to analysts using significantly smaller sample sizes.

## REFERENCES

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<b>Certificate Revision History:</b> 05 January 2012 (Correction of values for organic carbon and elemental carbon in Table 3; editorial changes); 08 April 2008 (Original certificate date).
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*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) 926-4751; e-mail [srminfo@nist.gov](mailto:srminfo@nist.gov); or via the Internet at <http://www.nist.gov/srm>.*