NIST Special Publication 260-166

Certification of SRM 114q: Part II
(Particle size distribution)

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[1] At Boulder, CO 80303

[2] Some elements at Boulder, CO

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Abstract

The standard reference material (SRM) for fineness of cement, SRM 114, is an integral part of the calibration material routinely used in the cement industry to qualify cements. Being a powder, the important physical properties of cement, prior to hydration, are its surface area and particle size distribution (PSD). Since 1934, NIST has provided SRM 114 for cement fineness and it will continue to do so as long as the industry requires it. Different lots of SRM 114 are designated by a unique letter suffix to the SRM number, e.g., 114a, 114b, …, 114q. A certificate that gives the values obtained using ASTM C204 (Blaine), C115 (Wagner) and C430 (45 µm sieve residue) is included with each lot of the material. For the SRM 114p an addendum was developed in 2003 providing the PSD curve. The supply of SRM 114p was released in 1994 and depleted in 2004.

Therefore, a new batch of SRM 114 needed to be developed. This process included selection of the cement, packaging the cement in small vials, and determining the values for the relevant ASTM tests. In “Certification of SRM 114q: Part I” (SP26-161), the development of the values for the ASTM C204 (Blaine), C115 (Wagner) and C430 (45 µm sieve residue) tests were discussed. In this report, the PSD for SRM 114q is presented.

The measurement of the PSD in this report was based on light scattering technology, or as it is commonly referred to, laser diffraction (LD). Other methods could be used to develop the PSD of cement but after two round robins and a survey, data obtained from other methods were insufficient to allow a statistically valid calculation of the mean PSD.

The purpose of this report is to complement the description of the process to certify SRM 114q described in Part I. All measurements used for the development of the PSD reference curve are provided along with statistical analyses.

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The authors would like to thank all participants of the round-robin (listed below in alphabetical order by institution) for providing time and staff to perform the particle size distribution (PSD) tests used for certification of this material.

Also, we would like to thank the staff of the Cement and Concrete Reference Laboratory (CCRL), who were instrumental in providing the samples to the round-robin participants.

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Round-Robin Participants for the PSD (Alphabetical)

Buzzi Unicem USA, New Orleans Slag Facility, New Orleans, LA: Ronald J. Rajki
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Construction Technology Laboratories, Skokie, IL: Ella Shkolnik
F.L. Smidth A/S, LaboratoryCopenhagen: Bjarne Osbaeck
Holcim Group Support Ltd., Holderbank: Werner Flueckiger
Lafarge North America Sugar Creek Plant, Sugar Creek, MO: Nick Ewing
Lehigh Cement Company Union Bridge, Union Bridge, MD: Jeff Hook
Mitsubishi Cement Corp., Lucerne Valley, CA: Tom Gepford
RMC Pacific Materials Inc.,Davenport, CA: Chow Yip
St. Lawrence Cement, Inc., Mississauga, Ontario: John Falletta
St. Marys Cement, Detroit, MI: Linda Harris
Texas DOT, Austin, TX: Lisa Lukefahr

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1 Introduction

A standard reference material (SRM) is a material that has been extensively characterized with regard to its chemical composition, physical properties, or both. The National Institute of Standards and Technology (NIST) provides over 1300 different SRMs to industry and academia. These certified materials are used in quality assurance programs, for calibration, and to verify the accuracy of experimental procedures. Every NIST SRM is provided with a certificate of analysis that gives the official characterization of the material's properties. In addition, supplementary documentation, such as this report, describing the development, analysis, and use of SRMs, is also often published by NIST to provide the context necessary for effective use of these materials.

There are several SRMs related to cement (http://ts.nist.gov/ts/htdocs/230/232/232.htm). SRM 114 is related to the fineness of cement, as measured by various indirect methods giving its surface area and by passing the material through a fine sieve. This SRM is an integral part of the calibration materials routinely used in the cement industry to qualify a cement. Being a powder, the main physical properties of cement are its surface area and particle size distribution (PSD). Since 1934, NIST has provided SRM 114 for cement fineness and it will continue to do so as long as the industry requires it. Different lots of SRM 114 are designated by a unique letter suffixed to the SRM number. A certificate that gives the values obtained using ASTM C 204 (Blaine) [1], C 115 (Wagner) [2], C 430 (45 µm residue) [3] and measures of the cement particle size distribution (PSD) by laser diffraction are included with each lot of the material.

In 1934, only the results of the Wagner test and the 45 µm residue test were listed. In 1944, the Blaine test measurement was added to the SRM 114 certificate. In 2003, the PSD measured by laser diffraction was added as an information value, i.e., not certified. The PSD was obtained under the sponsorship of ASTM Task Group C01.25.01 [4, 5, 6].

The SRM 114p was released in 1994, and depleted in 2004. Therefore, a new batch of SRM 114 had to be developed. The development process included the selection of a cement, packaging of the cement in small vials, and determination of the values for the ASTM tests reported. In ref [7], the development of the values for the ASTM C204 (Blaine), C115 (Wagner) and C430 (45 µm sieve residue) tests were discussed. In this report, the establishment of the PSD for SRM 114q is presented.

The values given in this report were obtained through a round-robin by volunteer participants from companies participating in the Cement and Concrete Reference Laboratory (CCRL) certification program. The development of the PSD in this report was based on the light scattering technology, or as it is commonly referred to, laser diffraction (LD). Other methods could be used to measure the PSD of cement but after two round robins and a survey [4, 5, 6], there were insufficient data by other methods to allow a statistically valid calculation of the mean PSD.

The purpose of this report is to provide the description of the development of the PSD curve. A brief description of the methodology to measure PSD, and all measurements used for the PSD determination, are provided along with the statistical analysis.

2 Description of particle size distribution methods

2.1 Introduction

Based on the results of two round-robins conducted under ASTM sponsorship [4, 5, 6], and a survey conducted through CCRL during the development of this SRM, the most commonly used techniques for characterization of the particle size distribution (PSD) in cement are as follows:

1. Laser Diffraction (LD)
    a. with the specimen dispersed in liquid (suspension-based) (LD-W)
    b. with the specimen dispersed in air (aerosol-based) (LD-D)
2. Electrical Zone Sensing (Coulter Principle) (EZS)
3. Sedimentation
4. Sieving
5. Scanning Electron Microscopy (SEM)

The laser diffraction method is used by over 90 % of the cement industry for measuring PSD. The other methods could be classified from the most used to the least used in the following order: Electrical zone sensing (Coulter Principle or EZS), sedimentation and sieving. The SEM method is not yet used by the cement industry as a quality control method.

Laser diffraction measurements can be performed with the powder either dispersed in air or in a liquid. The industry is almost evenly divided between the two techniques and some have the capability to use both.

A full description of each method can be found elsewhere [4, 8]. In this section, we present a very brief description of laser diffraction methods. We discuss the principles of operation, the range of application, the key parameters, and the requirements for sample preparation and their potential impact on the measurement results.

2.2 Laser diffraction [4]

The laser diffraction (LD) method involves the detection and analysis of the angular distribution of light produced by a laser beam passing through a dilute dispersion of particles. Typically, a He-Ne laser (wavelength λ = 632.8 nm) in the 5 mW to 10 mW range is employed as the coherent light source, but more recently solid-state diode lasers have come into use and provide a range of available wavelengths in the visible and UV spectrum. Since the focal volume of the beam senses many particles simultaneously, and thus provides an average value, it is referred to as an *ensemble* technique. With the exception of single particle optical scattering (SPOS), all scattering methods are ensemble techniques, and only ensemble methods will be considered here. There are a number of different diffraction and scattering phenomena that can be utilized for particle sizing. Likewise, there are a number of different ways to define and classify these methods, depending on the underlying principle or its application. We have chosen to classify all time-averaged scattering and diffraction phenomena involving laser optics, under the general heading of laser diffraction; however, it should be noted that "laser diffraction" is often used in a more narrow way to refer to techniques that utilize only low-angle scattering. See ref [8] for a list of equivalent or related methods.

One can differentiate between light waves that are *scattered*, *diffracted* or *absorbed* by the dispersed particles. The scattered light consists of reflected and refracted waves, and depends on the form, size, and composition of the particles. The diffracted light arises from edge phenomena, and is dependent only on the geometric shadow created by each particle in the light beam path: diffraction is therefore independent of the composition of the particles. In the case of absorption, light waves are removed from the incident beam and converted to heat or electrical energy by interaction with the particles; absorption depends on both size and composition.

The influence of composition is controlled by the complex refractive index, $m = n - ik$, where $i = \sqrt{-1}$. For non-absorbing (i.e., transparent) particles, $k = 0$, where k, the imaginary component of the refractive index, is related to the absorption coefficient of the material. Both the real part of the refractive index, n, and the imaginary part, k, are wavelength-dependent. Scattering arises due to differences in the refractive index of the particle and the surrounding medium (or internal variations in heterogeneous particles). Therefore, to use a scattering model to calculate the PSD that produced a specific scattering pattern, one must first know the complex refractive index of both the particles and the medium (typically, a medium is selected that has an imaginary component value of k=0). Values of n have been published for many bulk materials [9], but in the case of cement, n is routinely estimated based on a mass average of the refractive indices for the individual material components [10] and its value was fixed at 1.7 for all round-robins [4, 5] and in this report. The imaginary refractive component is more difficult to determine and/or find in the published literature [11,12], and this often represents a significant challenge to the use of scattering methods for fine particle size measurements [13].

As a general rule of thumb, the darker or more colored a specimen appears, the higher the imaginary component. For white powders, such as high-purity alumina, k=0. Cement, on the other hand, is generally gray to off-white in color, and therefore one can anticipate a finite, but relatively low value for the imaginary component. k = 1 was fixed for cement in this round-robin, although this value is unverified and will likely vary for different formulations. In the literature, the value of k=0.1 is also often used for cement. Further studies are needed to determine the correct value.

Mie theory, which describes scattering by homogeneous spheres of arbitrary size, is the most rigorous scattering model available, and is used in many commercial instruments. For non-spherical particles like cement, Mie theory provides a volume-weighted equivalent spherical diameter. Mie theory has been applied with mixed success to the analysis of fine powders with diameters from several 100s of micrometers down to several tenths of micrometers. An accurate representation of the "true" size distribution by Mie scattering is dependent on a knowledge of the complex refractive index, and will be impacted by the degree of asymmetry present in the particles and the dispersion procedure used to prepare the test sample. The Mie approach does not work well for extremely fine particulates with sizes below 100 nm, possibly because of increased sensitivity to uncertainties in the refractive index that occur with these materials. Hackley et al. [18] determined the range of value of the refractive indices for cement.

For very large particles (relative to the wavelength of the light used [18]), the diffraction effect can be exploited without reference to Mie theory or the complex index of refraction. Diffracted light is concentrated in the forward direction, forming the so-called Fraunhofer diffraction rings. The intensity and distribution of diffracted light around the central beam can be related to particle size, again assuming spherical geometry. The validity for this method is limited, on the low end, to particle diameters a few times greater than the wavelength of the incident light for particles that are opaque or have a large refractive index contrast with the medium [14]. For near transparent particles, or particle with a moderate refraction contrast, the lower limit is increased to about 40 times the wavelength of light. For a He-Ne laser, this corresponds to about 25 μm. The benefit of using Fraunhofer diffraction is that the interpretation is not dependent on the absorptive or refractive properties of the material. A totally absorbing black powder, a translucent glass powder, and a highly reflective white powder, having the same particle size and shape, will produce identical Fraunhofer patterns within the valid size range. On the other hand, inappropriate use of the Fraunhofer approximation outside of the valid range can lead to large systematic errors in the calculated PSD [10,15]. These errors are especially prevalent in the size range below one micrometer, where errors exceeding 100 % are possible. Partial transparency can lead to the appearance of "ghost" particles, generally in the size range below one micrometer, produced as an artifact of the refractive dispersion of light within the transparent particles. The refracted light is registered at large scattering angles as anomalous diffraction, and is therefore interpreted by the Fraunhofer analysis as being produced by very small particles.

In general, the LD method requires that the particles be dispersed, either in liquid (suspension) or in air (aerosol). The former is commonly referred to as the "wet" method (LD-W) while the latter is termed the "dry" method (LD-D). In Fraunhofer diffraction, the pattern does not depend on the refractive index, so there is no theoretical difference between using a liquid or a gas as a dispersing medium as long as the particles are equally well dispersed. For Mie scattering, the higher refractive index contrast in air, compared with most liquids, may impact the scattering pattern, without altering the results.

Differences between LD-D and LD-W methods arise primarily from the different ways in which the particles are dispersed in each case. In liquid, it is possible to modify solution conditions, e.g., by changing pH or adding chemical dispersing agents, or to break up aggregates using mechanical or ultrasonic energy. Thus, in general, a better state of dispersion can be achieved in a properly selected liquid medium, i.e., a liquid not chemically reactive with the powder and with a different refractive index than the powder. For silicates and most metal oxides, water is an excellent dispersing medium. However, due to the reactive nature of cement in water, alcohols, such as isopropanol, methanol, and ethanol, are commonly used instead. In the LD-D method, a stream of compressed air (or a vacuum) is used to both disperse the particles and to transport them to the sensing zone. This method of dispersion works well for large, non-colloidal-phase spheroids, where the interfacial contact area is small and the physical bonds holding the individual particles together are relatively weak. For the particles smaller than one micrometer and highly asymmetric, the higher surface-to-volume ratio results in more intimate and numerous contact points and, as a consequence, a greater driving force is needed to separate aggregated particles.

3 Materials

3.1 Characteristics of the cement

Based on the properties of past lots of SRM 114, CCRL and NIST identified a plant with a suitable cement for SRM 114q. The selected plant was Lehigh Cement Company[1], Union Bridge, Maryland, which donated 1300 kg of cement. The material selected was Type I according to the ASTM C 150 Standard Classification as was SRM 114p. Material was collected directly from the finish mill process stream into bags for shipment to NIST.

The approximate chemical composition has been determined by ASTM Standard Test Method C 114-02 to provide additional information on this cement. The analyses of this cement (CCRL Portland Cement Proficiency Sample No. 150) were performed by 170 laboratories. The chemical composition, which is not certified but is provided for information only, is shown in Table 1.

Calculation of the mass fraction of cement compounds, according to ASTM C 150-02, are shown in Table 2. These values are not part of the certified values that will be published in the certificate.

The density of the cement was also measured using a modified ASTM C 188 method. The modification was to use isopropanol (IPA) as the medium instead of kerosene, with a calibrated Le Chatelier flask as described in the ASTM test. Two density measurements were done with the results of: 3255 kg/m^3 and 3248 kg/m^3 (3.255 g/cm^3 and 3.248 g/cm^3). This leads to an average of 3251 kg/m^3 ± 0.5 kg/m^3 (3.25 g/cm^3 ± 0.005 g/cm^3).

Table 1: Chemical composition

	CaO	SiO_2	$A1_2O_3$	Fe_2O_3	SO_3	K_2O	TiO_2	P_2O_5	Na_2O	MgO	loss on ignition
Percent by mass fraction	64	20.7	4.7	3.2	2.4	0.7	0.3	0.12	0.07	2.2	1.67

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[1] Commercial equipment, instruments, and materials mentioned in this report are identified to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology (NIST), nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 2: Potential cement compounds according to ASTM C150

Compound	Mass Fraction
C_3S (tricalcium silicate)	60 %
C_2S (dicalcium silicate)	14 %
C_3A (tricalcium aluminate)	7 %
C_4AF (tetracalcium alumino-ferrite)	10 %

3.2 Packaging

Upon arrival at NIST, the cement was blended in a V-blender (1.7 m^3 or 60 ft^3) and then transferred to 0.2 m^3 (55 gal) drums lined with 0.15 mm (6 mil) polyethylene liners to minimize hydration of the cement in storage prior to preparation and packaging. Over the next two days, the cement from each drum was sealed in foil bags, each containing about 16 kg of cement. The foil bags were stored, and subsequently packaged as described below into vials, in a climate-controlled area.

Each foil bag was packaged into vials, which were then capped and boxed. Each box contained approximately 500 sealed vials and the boxes were sequentially labeled from 1 to 118. Usually about five boxes were filled per day. The more than 59 000 glass vials produced, each containing approximately 5 g of cement, were subsequently sealed into smaller individual foil bags. The vials were randomly selected (see section 4) and shipped to the participating laboratories for measurements. After the analysis of the results was completed, the vials were packaged in boxes containing 20 vials each.

3.3 Homogeneity determination

It is paramount that all the vials contain essentially similar material; therefore efforts were made to determine that the material properties of the powder within the vials could be considered identical. Loss of ignition (LOI) measurements were performed and are described in ref. [7].

PSDs were also measured to determine the best technique to obtain a representative and homogeneous specimen from each vial. It was determined that the methodology described in the certificate was correct and should be used prior to any PSD measurements. The recommendations in the certificate are:

“Allow the sealed foil bag to equilibrate to testing temperature before opening. Hold the pouch at one end and cut off the end of the pouch with scissors. Fluff the cement in accordance with ASTM standard C204, Section 3.4 and allow the cement to settle for 2 min, then measure without delay.”

4 Experimental design and data analysis

4.1 Experimental Design

To determine the box-to-box, lab-to-lab, and vial-to-vial inhomogeneity, each round-robin participant received 4 vials: one of SRM 114p and three of SRM 114q. The vials were randomly selected from boxes that were also randomly selected (from the 118 boxes with approximately 500 vials each). For LD-D, the selected boxes were: 2, 6, 13, 24, 45, 100 and 118. For LD-W, the selected boxes were 19, 29, 33, 88, 92, 94, 101, and 120. Participants were asked to perform three replicate measurements using the single SRM 114p vial and three replicates for each of the three vials of SRM 114q. They were asked to report what box number was used for SRM 114q.

4.2 Parameters used

In this round-robin, the participants were free to use either method (LD-W or LD-D), but they had to respond to a questionnaire (Appendix A) and some parameters were fixed.

The fixed parameters were:
Refractive index: 1.7
Imaginary index: 1
In LD-W: Isopropanol was requested and the refractive index of isopropanol was set to be 1.39

The responses to the questionnaire are summarized in Table 3 and Table 4. It can be noticed that some participants did not return the questionnaire and some elected not to use the refractive indices requested or were not aware of them.

It should be noted that a value of the imaginary index of 0.1 is often selected for cements but the value imposed on the participants was 1. In Ref. [18], it has been shown that the selection of an imaginary index larger than 0.1 does not affect the results for cement. Therefore, the same results should be obtained for imaginary index values of 0.1 to 1.

Table 3: Parameters reported by participants for LD-W

Lab #	Refractive index			Normal Medium[a]	Concentration of cement in the medium[b]	Dilution from stock	Ultra sound			LD Measurement Duration [sec]	Model (M/F/B)[d]
	Real	Imag.	Medium				Y/N	Duration[c]	Where		
84	1.7	1	1.39	IPA	0.000256 g/mL	No	Y	10 % for 30 s	Inside	10	M
92	1.7	1	1.39	IPA		No	N			10	M
175	1.7	1	1.39	IPA			N				N/A
209	1.7	1	1.39	Ethanol	20 %	No	N			8	B
284	1.7	1	1.39	IPA	0.001 g/mL	No	N			60	N/A
557	1.7	1	1.39	No		N/A	Y	5 min	Prior to device (bath-concentrate)	10	B
605	1.7	1	1.39	IPA	Unknown	No	Y	40 W for 60 s	Inside	30	B
690	1.7	1	1.39	No (25/75 propylene)		No	N			60	M
736	1.7	1	1.39	No (Ethanol)		No	Y	100 % for 60 s	Inside	25	M
932	1.7	1	1.39	No (Ethanol)	Unknown	No	N				M
1251	1.7	1	1.39	IPA	0.0003 g/mL	No	Y	60 s	Inside	30	M
1916				N/A		N/A	N/A				N/A
1940	1.7	1	1.39	IPA	Unknown	No	Y	60 s	Inside	145	B
2116	1.7	1	1.39	IPA			Y	38 kHz for 60 s	Inside	60	F

Notes:

[a]: The participants were requested to use IPA but they were also asked if this was the alcohol that they normally use. If not they were asked to indicate what alcohol they used normally. Therefore, this column gives the name of the alcohol that they normally use.

[b]: The concentration of cement is reported here as given by the participants. The units are as given by the participant. They are given here for information only.

[c]: The intensity of the ultrasound is reported here as given by the participants. The units are as given by the device and they are device/manufacturer dependent. Therefore, they cannot be converted to fundamental units. They are given here for information only.

[d] : The participants were asked to state the model that they used to interpret the data: M= Mie; F= Fraunhofer; B=both

Table 4: Parameters reported by participants for LD-D

Lab #	Refractive Index		Air pressure [bar]	Measurement duration [sec]	Model (M/F/B)[#]	Comments[+]
	Real	Imag.				
73	1.7	1	3.3	12	N/A	
105	1.7	1	6	15	N/A	The LD needs at least 5 g for analysis (the whole vial)
124	1.7	1	3.05	3.1	F	
148	1.68	N/A	3.4	10	F	
151	1.7	1	2	30	F	
255	Not used	Not used	1	7-12	F	
303			N/A	N/A	N/A	
354	1.7	1	4	10	M	Material was placed in a 2 oz jar and the jar shaken for 10 s before transfer to the PSD device
619			N/A	N/A	N/A	
736	1.7	1	3	5	M	feed rate 37 %; obscuration 1 % to 3 %
1251	1.7	1	5.7-6.1	30	M	

Note:
: The participants were asked to state the model that they used to interpret their data: M= Mie; F= Fraunhofer; B=both
+: The comments are as reported by the participants. They refer on how the cement to be tested was treated before the measurement.

4.3 Analysis of the Particle Size Distribution Data

4.3.1 Introduction

Each participating lab provided three replicates from one pouch[2] with SRM 114p and three replicates from three different vials for SRM 114q. The data were transmitted in a standard spreadsheet. To simplify the data interpretation the cumulative particle size distribution were reduced to the following sizes: (1, 1.5, 2, 3, 4, 6, 8, 12, 16, 24, 32, 48, 64, 96, 128) µm. All data are shown in Appendix B.

Each participant laboratory is identified by their CCRL number in this report

There were 11 participants who provided data with LD-D (44 %) and 14 with LD-W (54 %). These participants represent 38 % of the laboratories that participated in the round-robin for the Blaine [3, 4], ASTM C 204 [1]. The lower participation is probably due to the lack of a standard test method available for PSD. Nevertheless, the participation was sufficient for statistical analysis.

The statistical analysis of the results allowed the calculation of mean particle size distribution for the two cements (SRM 114p and SRM 114q). The heterogeneity between the vials was also examined and was incorporated in these results.

A bootstrap statistical analysis (Appendix C and Ref [4, 5]) was used to calculate the mean PSD given in this report. One major conceptual difference from the analysis of the results in Ref [4, 5] and those given here is the identification and handling of the outliers. The bootstrap procedure used to identify outliers in Ref [4, 5] was probably too aggressive because it was based on a percentage of points that fell outside a confidence interval for the mean PSD. The alternative chosen for the analysis of the data described in this report was to identify curves that significantly differed from the bulk of the data by visual inspection.

The PSD results for SRM 114p and SRM 114q are presented in below, followed by a discussion of the results in section 4.4 and 4.5. As discussed in Section 4.5, no significant difference was found between the two methods, LD-D and LD-W, therefore a single particle size distribution based on the combined results from both methods was computed and will be used in the certificate of the SRM 114q.

4.3.2 Data for SRM 114p by LD-D

All the curves obtained are shown in Figure 1. Lab 1251 was visually identified as an outlier and thus was excluded from subsequent analyses.

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[2] The SRM 114p was packaged in pouches directly while the SRM 114q was placed in a vial that was then sealed in a pouch.

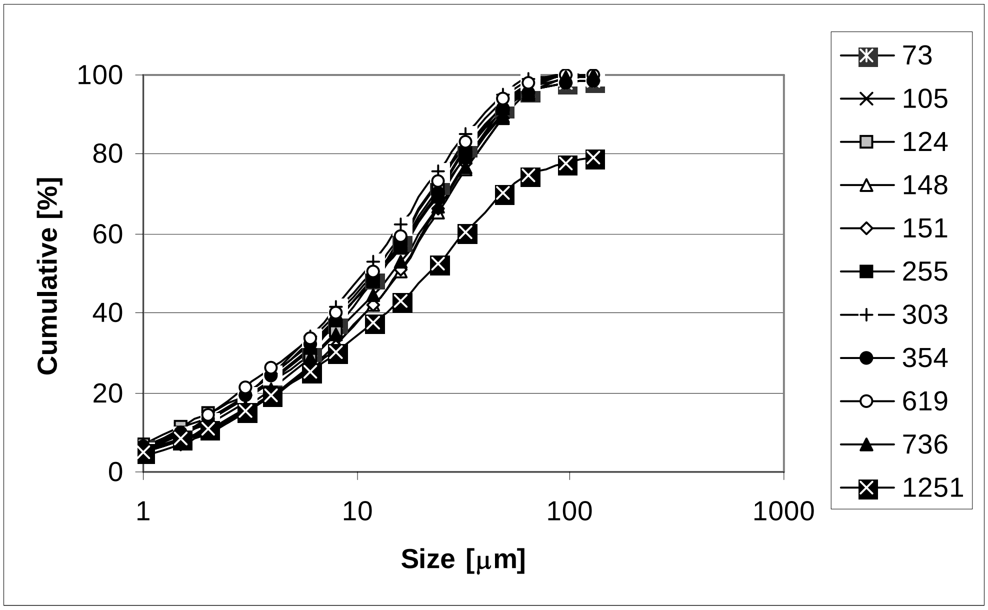

Figure 1: LD-D for SRM 114p for each laboratory identified by the CCRL number. Each curve is the average of 3 replicates.

4.3.3 Data for SRM 114p by LD-W

All the curves obtained are shown in Figure 2. Based on visual inspection, no outliers were identified.

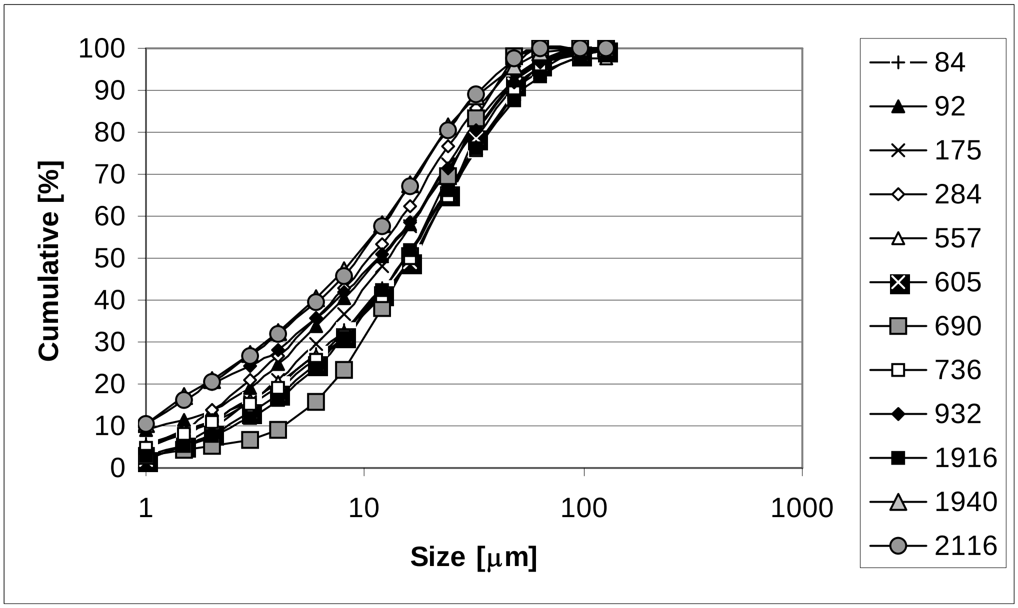

Figure 2: LD-W for SRM 114p for each laboratory identified by the CCRL number. Each curve is the average of 3 replicates.

4.3.4 Data for SRM 114q by LD-D

All the curves obtained are shown in

Figure 3. No outliers were identified. However, lab 619 was not used in the analyses because data for only a single replicate was reported.

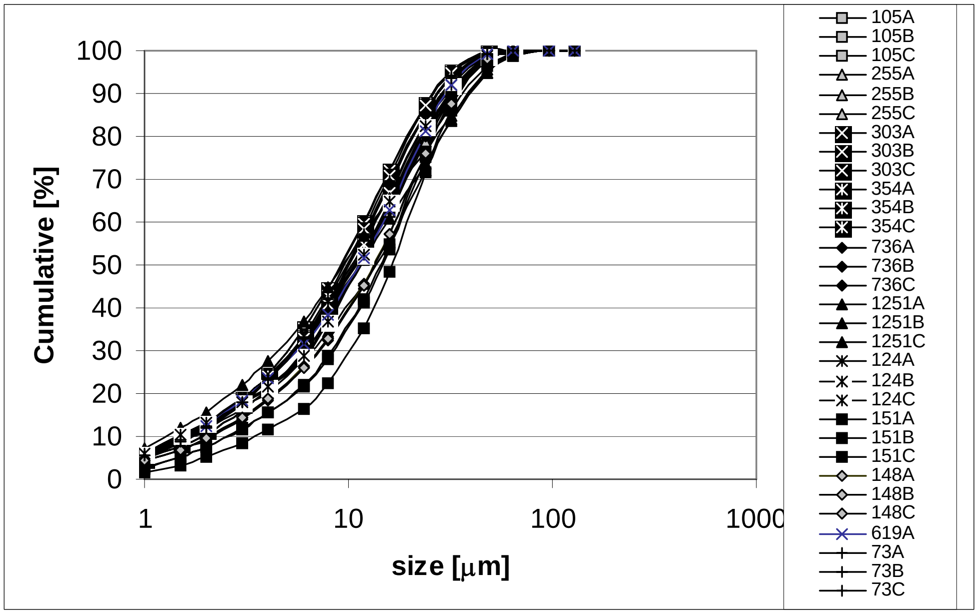

Figure 3: LD-D for SRM 114q for each laboratory identified by the CCRL number. Each curve is the average of 3 replicates. The letters ABC stand for each of the 3 vials used by each laboratory.

4.3.5 Data for SRM 114q by LD-W

All the curves obtained are shown in Figure 4. No outliers were identified.

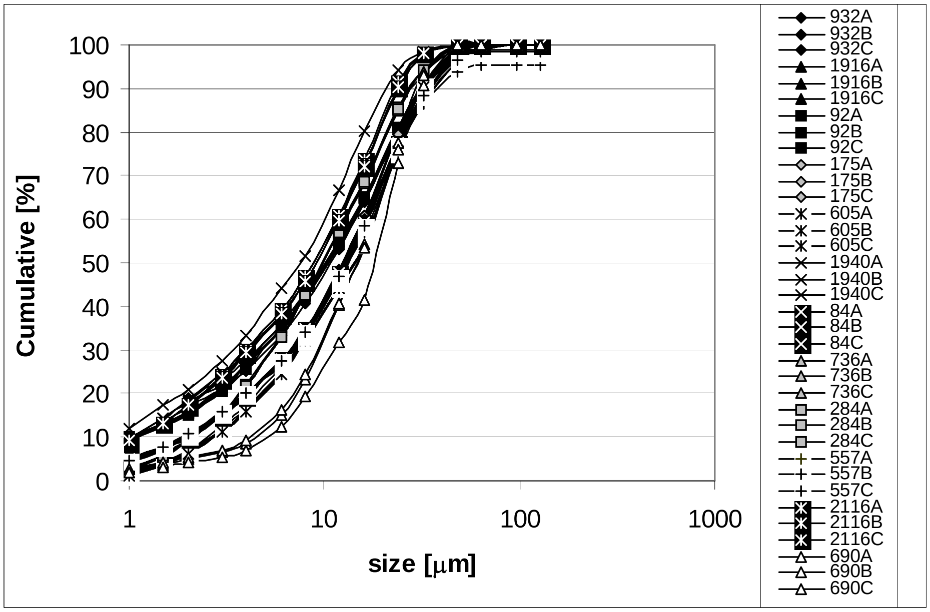

Figure 4: LD-W for SRM 114q for each laboratory identified by the CCRL number. Each curve is the average of 3 replicates. The letters ABC stand for each of the 3 vials used by each laboratory.

4.4 Homogeneity

Several sources of uncertainty may have affected the results observed for SRM 114q in additional to the random measurement error that affects each measurement. Some of the sources that may affect these results include heterogeneity of material between vials or boxes. Therefore, a statistical analysis was conducted to determine whether the results from this round robin show significant box-to-box, lab-to-lab or vial-to-vial scatter. This was achieved using the results collected for SRM 114q, since that is the material of primary interest for this report and data on multiple vials were measured by each lab. The results for SRM 114p were treated analogously, however, when using it as a control to confirm that the measurement results obtained in this study were consistent with past results.

To assess the effects of box-to-box and lab-to-lab variation, a nested, random-effects, analysis of variance (ANOVA) model [16] was fit to the data for each particle size selected (see section 4.3.1). To aid in the interpretation of the results, however, a subset of data that provided a balanced design was used to fit the model. The subsetting of the data was required because the balance of the original design required all laboratories to make measurements using each method (LD-D and LD-W) but not all of the labs returned results for each method.

For the LD-D measurements, data from boxes 2, 6, 13, and 100 collected by laboratories 105, 124, 148, 151, 255, 303, 354, and 736, were used, since at least two laboratories returned results for vials from each of those four boxes. The data from labs 1251 (box 45), and 73 (box 118) were not used since those boxes were measured only by one laboratory.

For the LD-W measurements, data from boxes 19, 33, 92, and 129 collected by laboratories 92, 175, 284, 557, 605, 932, 1916, and 1940, were used. The data from labs 2116 (box 29), 209 (box 66 and box 113), 736 (box 88), 84 (box 94), and 690 (box 101) were not used since those boxes were measured only by one laboratory.

Residual plots indicated that the model fit the data well for central particle sizes where variation in the measurements was observed. Typical output from the analysis of variance for one particle size is shown in Table 5. The low p value (<0.05) corresponding to the F test for the significance of lab-to-lab variability provides strong evidence that there is significant lab-to-lab variation. The high p value for the F test for box-to-box variability (0.1187) indicates that there is not strong evidence of significant box-to-box heterogeneity in this data.

Table 5: ANOVA output from the fit of a nested, random-effects model with factors box and lab to the PSD data (LD-D, particle size=32 µm).

Source	**Degrees of Freedom**	**Sums of Squares**	**Mean Squares**	**F Statistic**	**p value**
Box-to-Box	3	92.1946	30.7315	3.7132	0.1187166
Lab-to-Lab (in Box)	4	33.1050	8.2763	21.1534	0.0000032
Residuals	16	6.2600	0.3913		

To assess vial-to-vial variation or heterogeneity, a one-factor nested ANOVA model for the factor vial was fit to the individual data reported by each laboratory for each particle size. Then, to control for the increased probability of false positive results that would arise from carrying out multiple tests, significance was determined using a simple binomial multiple comparisons procedure [19].

The multiple comparisons procedure, carried out for each particle size, was implemented by interpreting the results of each ANOVA in which vial-to-vial variation was significant as the outcome of a Bernoulli trial with probability of success $p = 0.05$. Then, because the data from each laboratory are considered independent of one another, the probabilities of different numbers of successes that could be observed by chance when measuring homogeneous cement can be computed to determine how many significant results must be observed to conclude with 95 % confidence that the observed vial-to-vial variation is significant.

Using this procedure, it was found that for both the LD-W and LD-D determinations in this study, observing two or more significant vial-to-vial results for different labs for each particle size would happen less than 5 % of the time if the cement were homogeneous. For small particle sizes (below about 10 µm) up to five significant results were observed, however, and for larger particle sizes two significant results were observed, indicating that this material is not likely to be homogeneous. To account for the heterogeneity observed for most particle sizes in the uncertainty of certified PSDs, prediction intervals were used at each particle size to account for the vial-to-vial variation in the material for distribution to customers. The vial-to-vial standard uncertainty was computed by pooling the standard deviations of the mean results for each of the three vials measured within each laboratory. This results in a slightly conservative estimate of the standard uncertainty due to heterogeneity. The between vial variation was also assumed to follow a normal or Gaussian distribution.

Because there was also significant lab-to-lab variation, replicate measurements within labs were averaged so that the certified values would be computed using individual, independent values from each laboratory.

After averaging the replicated determinations made within each lab, the mean particle size distributions for wet and dry LD were computed using bootstrap prediction intervals. General background on the bootstrap procedure is given in Appendix C. Bootstrap intervals were used because for some of the largest particle sizes many laboratories observed identical results for each of the three vials they measured, which is inconsistent with the typical assumption of normally-distributed data required for uncertainty intervals computed using the procedures outlined in the ISO Guide to the Expression of Uncertainty in Measurement [20] or the NIST Uncertainty Policy [21]. The bootstrap results for the more central particle sizes should give results that are essentially the same as the standard results based on Ref [20, 21], however.

Figure 5 and Table 6 show the results obtained in this study for SRM 114p using both the LD-W and LD-D methods for determining the particle size distribution. Results are also given for the combined data from the two methods under the assumption that the methods do not give significantly different results. The fact that the intervals for the wet, dry, and combined show good agreement for all particle sizes indicates that the difference between methods is not statistically significant, so only the combined result will ultimately be used. Figure 6 and Table 7 show the analogous results for SRM 114q. The particle size distribution based on the combined wet and dry methods will be used on the certificate of the SRM 114q since the two methods were not statistically distinguishable.

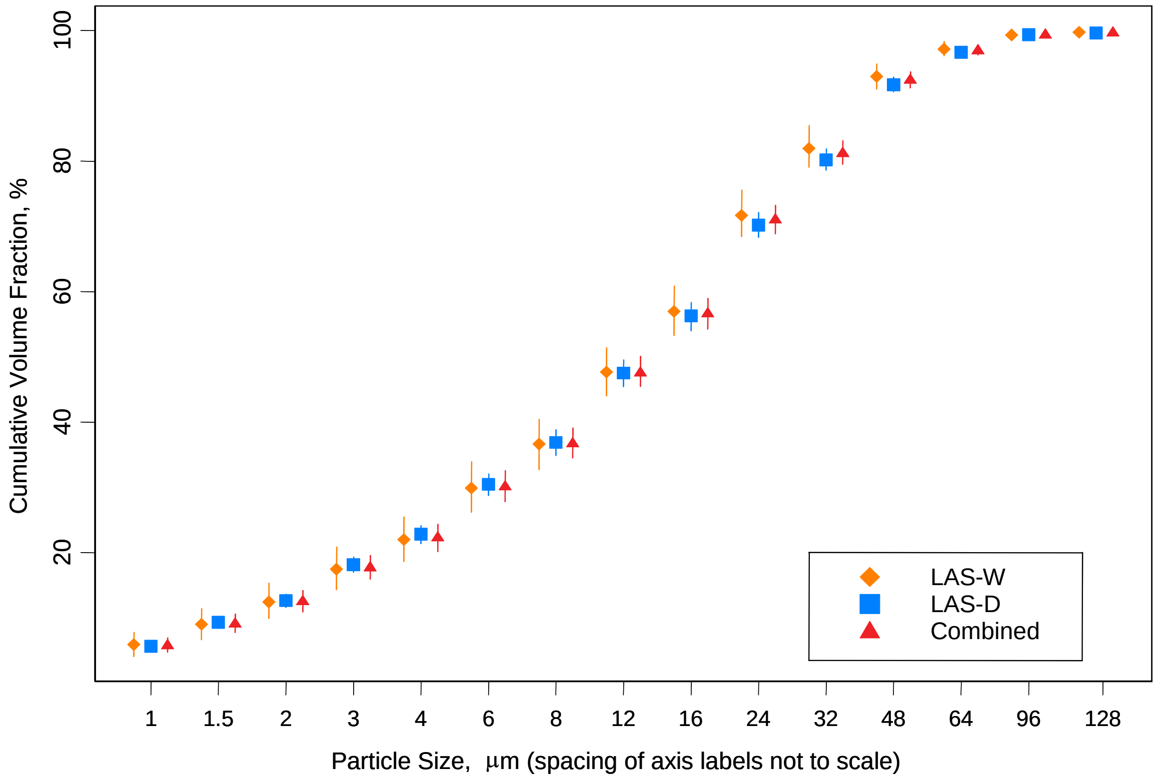

Figure 5: Comparison of particle size distributions using wet, dry, and combined LD for SRM 114p. The x-axis is designed to emphasize the points by spacing them at equal distance.

Table 6: Comparison of particle size distribution results for SRM 114p using different methods.

Particle Size [µm]	Wet [%]			Dry [%]			Combined [%]		
	Lower Bound	Mean	Upper Bound	Lower Bound	Mean	Upper Bound	Lower Bound	Mean	Upper Bound
1.0	4.1	5.9	7.7	5.0	5.6	6.1	4.7	5.8	6.9
1.5	6.6	9.0	11.4	8.4	9.3	10.2	7.7	9.1	10.6
2.0	9.9	12.4	15.3	11.6	12.6	13.6	10.9	12.5	14.2
3.0	14.3	17.4	20.8	17.0	18.2	19.3	15.9	17.7	19.5
4.0	18.6	22.0	25.4	21.4	22.8	24.1	20.1	22.3	24.3
6.0	26.2	29.9	33.9	28.7	30.5	32.0	27.8	30.1	32.5
8.0	32.7	36.6	40.4	34.9	36.9	38.8	34.5	36.7	39.1
12.0	44.0	47.7	51.4	45.4	47.5	49.5	45.4	47.6	50.1
16.0	53.3	56.9	60.9	54.0	56.3	58.3	54.3	56.7	58.9
24.0	68.4	71.7	75.5	68.3	70.2	72.1	68.8	71.0	73.2
32.0	79.1	81.9	85.4	78.6	80.2	81.8	79.5	81.2	83.1
48.0	91.0	93.0	94.9	90.6	91.7	92.8	91.2	92.4	93.7
64.0	96.1	97.2	98.3	96.0	96.7	97.5	96.3	97.0	97.7
96.0	98.9	99.3	99.7	98.9	99.4	99.8	99.0	99.3	99.6
128.0	99.4	99.7	99.9	99.3	99.7	100.0	99.4	99.7	99.9

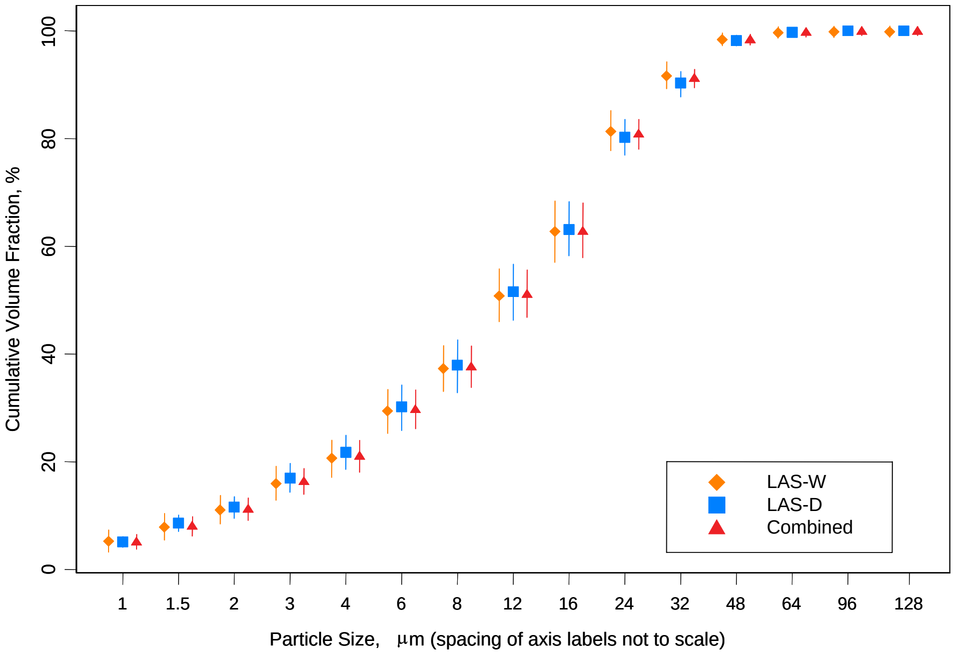

Figure 6: Comparison of particle size distributions using wet, dry, and combined LD for SRM 114q. The x-axis is designed to emphasize the points by spacing them at equal distance.

Table 7: Comparison of particle size distribution results for SRM 114q using different methods[3].

Particle Size [µm]	Wet [%]			Dry [%]			Combined [%]		
	Lower Bound	Mean	Upper Bound	Lower Bound	Mean	Upper Bound	Lower Bound	Mean	Upper Bound
1.0	3.2	5.2	7.3	4.1	5.1	6.1	3.8	5.1	6.5
1.5	5.5	7.9	10.4	7.0	8.6	10.1	6.2	8.0	9.8
2.0	8.5	11.1	13.8	9.5	11.6	13.5	9.1	11.2	13.3
3.0	12.9	15.9	19.1	14.4	17.0	19.7	13.9	16.3	18.8
4.0	17.1	20.7	24.0	18.6	21.7	24.9	18.1	21.0	24.0
6.0	25.3	29.5	33.4	25.8	30.2	34.2	26.1	29.6	33.3
8.0	33.1	37.3	41.5	32.8	37.9	42.6	33.8	37.6	41.5
12.0	46.0	50.8	55.8	46.3	51.6	56.7	46.8	51.0	55.6
16.0	57.0	62.7	68.4	58.3	63.1	68.3	57.9	62.8	68.0
24.0	77.7	81.3	85.2	76.9	80.2	83.6	78.0	80.8	83.6
32.0	89.2	91.6	94.2	87.8	90.3	92.5	89.4	91.2	92.9
48.0	97.3	98.4	99.6	97.2	98.2	99.2	97.4	98.4	99.4
64.0	98.6	99.7	100.0	99.3	99.8	100.0	98.9	99.7	100.0
96.0	98.8	99.8	100.0	100.0	100.0	100.0	99.1	99.9	100.0
128.0	98.8	99.8	100.0	100.0	100.0	100.0	99.1	99.9	100.0

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[3] This table has been changed from the original version of the report by replacing the values of the upper bound on the cumulative particle size distribution that had been reported to be slightly over 100 % by 100 %. This correction was done to better reflect the physical meaning of the boundary, which for this quantity cannot be over 100 %.

4.5 Discussion of results

4.5.1 Comparison of SRM 114p with certified values

From Figure 7, it can be seen that the results obtained for SRM 114p measured as a control for this study are consistent with the values that were given in the SRM 114p certificate [1], as indicated by the overlap of the expanded uncertainty intervals. Note that these intervals agree within the stated levels of uncertainty despite the fact that they were obtained using different values for the imaginary refractive index. A imaginary refractive index of 1.0 was used in this round robin and a value of 0.1 was to obtain the results shown on the SRM 114p certificate, further confirming the results found in Ref. [18] that there is no PSD dependence on the imaginary refractive index for values above 0.1.

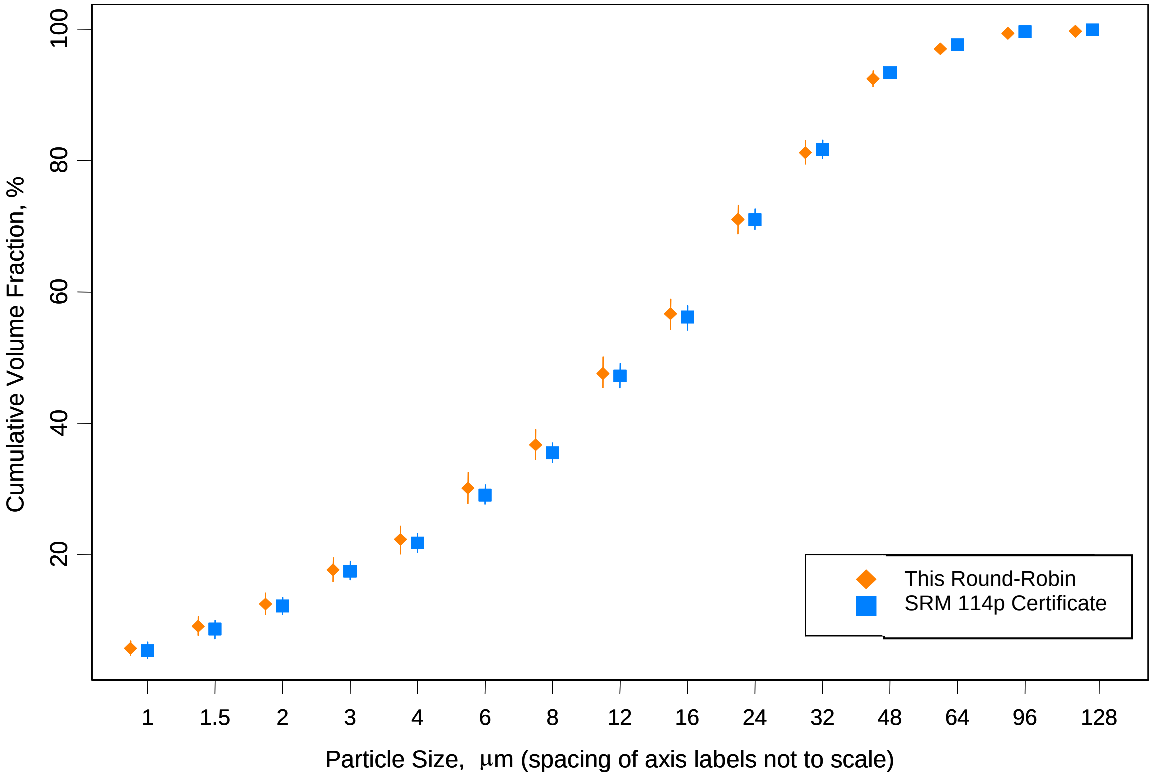

Figure 7: Comparison of PSD results for SRM 114p (leftmost interval in each pair) with values from the SRM 114p certificate (rightmost interval in each pair) showing the agreement of the current results with the certified values.

4.5.2 Comparison of SRM's 114p and 114q

Figure 8 shows the particle size distributions for SRM 114p and SRM 114q. The SRM 114q is finer than the SRM 114p. This is not surprising as the certified value for the 45 µm sieve residue ASTM C430 [3] for SRM 114q is 0.79 % ± 0.19 % while for SRM 114p the value is 8.24 % ± 0.37 % [16].

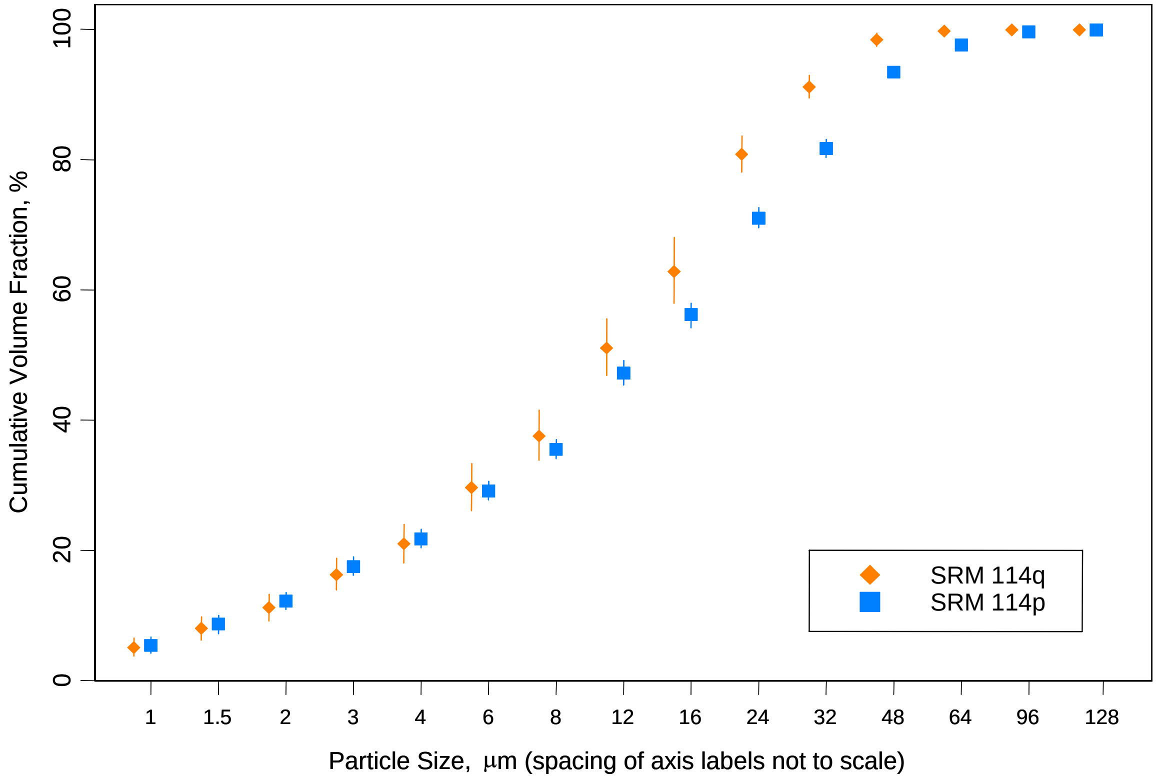

Figure 8: Comparison of particle size distributions for SRM's 114q and 114p.

5 Summary

5.1 The PSD for SRM 114q

The SRM 114q particle size distribution (PSD) was determined using laser diffraction (LD) techniques in a round-robin evaluation. The values were measured by volunteer participants from companies participating in the CCRL proficiency program. Two LD methods were included in the tests: LD-D, in which the powder was measured in a dry dispersed state as an aerosol (dry) and LD-W, in which the powder was dispersed in a non-aqueous liquid medium (wet) . The parameters used to develop the PSD were:

- The real part of the complex refractive index was 1.7 and the imaginary part was 1.0 for both methods
- For LD-W: IPA was used as the medium and the refractive index used for IPA was 1.39 (imaginary = 0).

The differences between the results from these two methods was not found to be statistically significant, so that data from both methods was combined and used to calculate the mean particle size distribution, shown graphically in Figure 9 and in tabulated in Table 8. This particle size distribution could be used as a reference to validate methodology and instrument operation as described in Section 5.3 below. It should be made clear that the uncertainty values shown in Table 8 are intended to represent how well the SRM 114q size distribution is known at this time. Therefore, it is not expected that all the participant laboratories data would fall within these boundaries. In theory, if there were many more laboratories the uncertainty could be even smaller. The uncertainty between laboratories and within laboratories is discussed in Section 5.2.

In summary, the data obtained in this report could be used in the following manner:

- Table 8 and Figure 9: SRM 114 q values that are on the certificate (how well SRM 114q is known)

Table 9 and Figure 10 and section 5.2: Precision statement that could be used for developing a standard test method. Column 2 of

Table 9 gives the uncertainty for measurements in one laboratory and column 4 of

- Table 9 gives the uncertainty between laboratories.
- Table 10 and section 5.3.2: Criteria to determine whether a PSD measurement conforms with the measured SRM 114q PSD.

A draft method to measure the PSD by LD using SRM 114 is given in Appendix D (section 7.4).

5.2 Precision statement based on SRM 114q

The data from this interlaboratory study was used to obtain typical uncertainties within and between laboratories. The results of these determinations are given in

Table 9 and illustrated in Figure 10.

To obtain the standard deviation of PSD determinations within a laboratory for a given material, the square root of the median of the variances of the three measurements made on different vials of SRM 114q by each lab at each particle size was used. These values are given in the second column of Table 9. The standard deviations for the different particle sizes are indexed by the cumulative volume fractions observed for this material, given in the first column of Table 9, since the variation depends on the cumulative volume fraction. The particle sizes for SRM 114q are not used to index these values because for other materials with different particle size distributions the particle sizes associated with each cumulative volume fraction will not be the same.

To reduce the amount of computation that is required to compare two PSD values for a particular particle size within a laboratory, the expanded uncertainty of the difference of two cumulative volume fractions is given in the third column of Table 9. This value gives the acceptable range of two measurements that is likely to be caused by random variation.

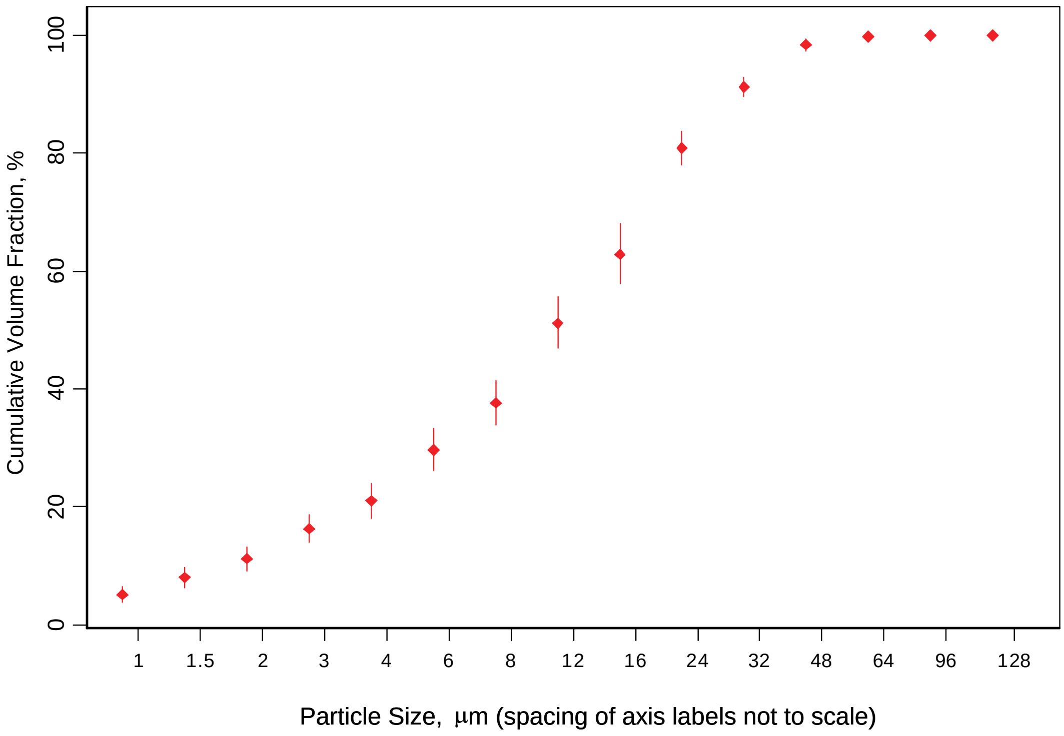

Figure 9: Particle size distribution for SRM 114q using LD (combined wet and dry).

Table 8: Particle size distribution for SRM 114q using LD (combined wet and dry)[4].

Particle Size, µm	1.0	1.5	2.0	3.0	4.0	6.0	8.0	12.0	16.0	24.0	32.0	48.0	64.0	96.0	128.0
Mean Cumulative Volume Fraction, [%]	5.1	8	11.2	16.3	21	29.6	37.6	51	62.8	80.8	91.2	98.4	99.7	99.9	99.9
95 % Lower Expanded Uncertainty Bound [%]	3.8	6.2	9.1	13.9	18.1	26.1	33.8	46.8	57.9	78	89.4	97.4	98.9	99.1	99.1
95 % Upper Expanded Uncertainty Bound [%]	6.5	9.8	13.3	18.8	24	33.3	41.5	55.6	68	83.6	92.9	99.4	100.0	100.0	100.0

Table 9: Standard uncertainties and expanded uncertainties for the difference of two cumulative volume fractions within- and between-labs.

Cumulative Volume Fraction (CVF), %	Standard Uncertainty of CVF's Obtained from a Typical Lab[*], %	Expanded Uncertainty for the Difference of Two CVF's Obtained from a Typical Lab[*], %	Standard Uncertainty of CVF's Obtained from Different Labs, %	Expanded Uncertainty for the Difference of Two CVF's Obtained from Different Labs, %
5.075	0.175	0.496	2.511	7.103
8.033	0.281	0.794	3.233	9.144
11.195	0.342	0.969	3.889	10.999
16.286	0.450	1.274	4.526	12.801
21.005	0.530	1.500	5.138	14.532
29.636	0.565	1.598	5.948	16.823
37.573	0.600	1.696	6.191	17.509
51.045	0.603	1.706	6.352	17.967
62.795	0.552	1.561	6.385	18.058
80.823	0.501	1.417	4.982	14.092
91.150	0.384	1.085	3.453	9.766
98.359	0.217	0.614	1.326	3.750
99.695	0.049	0.139	0.565	1.597
99.886	0.003	0.009	0.458	1.295
99.895	0.000	0.000	0.460	1.300

[*] **Note**: Different laboratories have significantly different within-lab standard deviations, some labs will find that smaller differences are statistically significant while others will find that larger differences are not significant.

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[4] This table has been changed from the original version of the report by replacing the values of the upper bound on the cumulative particle size distribution that had been reported to be slightly over 100 % by 100 %. This correction was done to better reflect the physical meaning of the boundary, which for this quantity cannot be over 100 %.

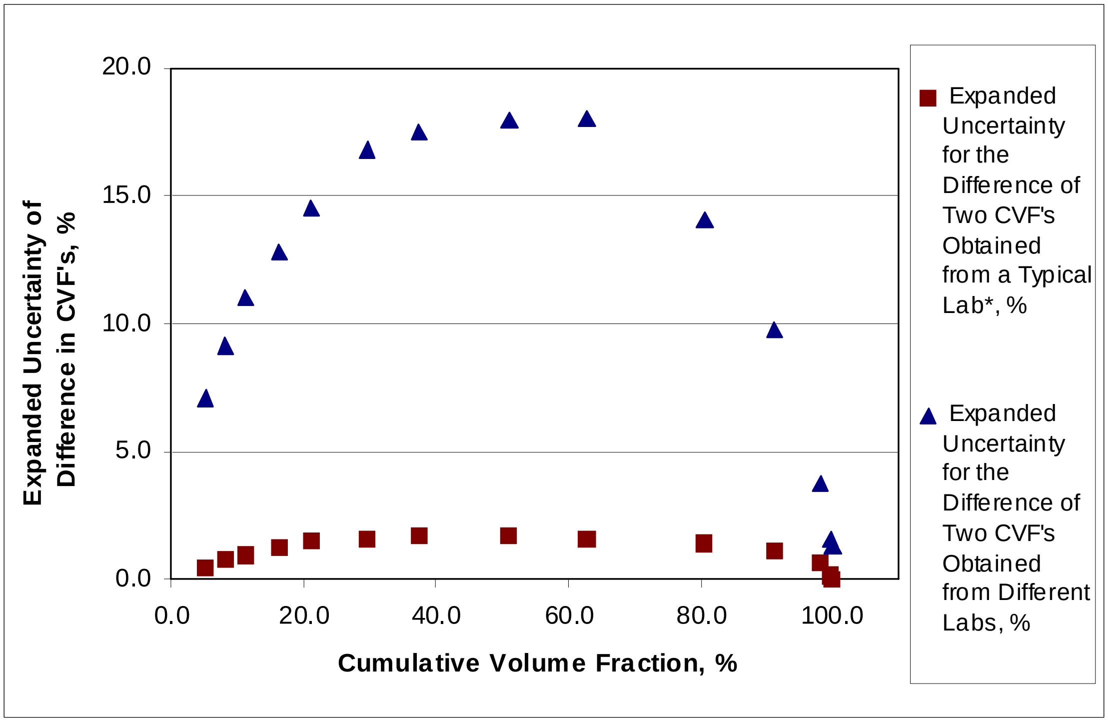

Figure 10: Plot illustrating the expanded uncertainties of the differences between two PSD determinations within- and between-laboratories. CVF = Cumulative volume fraction. *Note: Different laboratories have significantly different within-lab standard deviations, so some labs will find that smaller differences are statistically significant while others will find that larger differences are not significant.

Differences larger than the

Table 9 value for a particular cumulative volume fraction are likely to be caused by additional significant sources of variation that should be identified and addressed appropriately. The expanded uncertainties were obtained by multiplying the standard uncertainties associated with each cumulative volume fraction by the factor $2\sqrt{2}$. The $\sqrt{2}$ accounts for the fact that we are computing the uncertainty of the difference of two independent measurements while the 2 is the coverage factor used to convert the uncertainty from a standard uncertainty to an expanded uncertainty.

Because the different labs taking part in this study had significantly different levels of random variability in their measurements, the within-lab standard uncertainties and the uncertainties of the differences between two measurements within a lab represent the uncertainties that a typical lab might expect to have. However, the uncertainties within some labs could be smaller while the uncertainties within other labs could be larger.

Uncertainties analogous to those given within a typical laboratory are given for results obtained between laboratories in the last two columns of

Table 9. The standard uncertainties were obtained by taking the standard deviation of the mean PSD values for each laboratory at each particle size. The expanded uncertainties of the differences between two measurements were obtained from the standard uncertainties by multiplying each standard uncertainty by the factor $2\sqrt{2}$, as was done for the within-lab values.

5.3 How to use these values

5.3.1 Introduction

The purpose of a reference PSD based on an easily accessible reference material is to allow the operator to verify the performance of an instrument and the measurement procedure being used. If the results are found to be statistically different from the SRM certified values, the operator should check the performance of the device, the parameters used (such as the refractive indices) or the procedure used (dispersion, ultrasound, duration of measurement, et cetera). A proposed procedure to compare the results obtained with the SRM 114q is illustrated below. Nevertheless, this procedure is considered valid only if the measurements are done using a LD method. From previous work [4, 5], it was found that the PSD of a powder is strongly dependent on the measurement methodology. The LD distributions might not match a curve obtained using SEM, EZS or sedimentation. This is due to the fact that each of these methods is based on different assumptions and theories to calculate a particle size from the measurements. For instance, LD assumes that the particles are spherical and that the refractive indices of the powder are known. The other methods make other assumptions to calculate the PSD from the raw data.

5.3.2 Conformity determination

The operator should start by measuring at least 3 replicate measurements of the SRM 114q using the LD procedure and instrument. These results can then be used to determine conformity at the following levels:

- General agreement of the results with other laboratories that participated in this round-robin: Because there is no standard test method, a relatively large amount of between-lab variation is allowed in this situation
- Agreement to within-laboratory reproducibility: This level of agreement indicates that the user's results will not differ from the certified value of SRM 114q by more than expected based on the within-lab reproducibility of a typical laboratory.

As stated above, these expanded uncertainty intervals allow for two levels of conformance assessment. The first level indicates agreement with the results typically obtained by laboratories that participated in the interlaboratory study used for certification of the particle size distribution of SRM 114q. Because there is no currently agreed upon standard test method for obtaining particles size distributions using laser diffraction, however, a relatively large amount of between-lab variation is allowed for in these uncertainties, given in column 4 of Table 10.

For laboratories that would like to assure tighter agreement with SRM 114q, the uncertainties in column 3 of Table 10 can be used instead. This level of agreement indicates that the user's results will not typically differ from the certified value of SRM 114q by more than the within-lab reproducibility of a typical laboratory.

Table 10: Simultaneous Expanded Uncertainties for Conformance Assessment with SRM 114q

Particle Size, µm	Cumulative Volume Fraction (CVF) of SRM 114q, %	Simultaneous 95% Expanded Uncertainties for the Difference Between a Typical Lab and the Certified Value of SRM 114q, %	Simultaneous 95% Expanded Uncertainties for the Difference Between a Typical Lab and the Certified Value of SRM 114q Including Between Lab Variation, %
1	5.1	2.0	7.6
1.5	8.0	2.8	9.9
2	11.2	3.2	11.8
3	16.3	3.8	13.8
4	21.0	4.6	15.7
6	29.6	5.5	18.2
8	37.6	5.9	19.0
12	51.0	6.7	19.7
16	62.8	7.6	20.2
24	80.8	4.4	15.2
32	91.2	2.8	10.5
48	98.4	1.6	4.2
64	99.7	1.2	2.0
96	99.9	1.2	1.8
128	99.9	1.2	1.8

To use these uncertainties to assess agreement with other laboratories, the user should compute the absolute difference in cumulative volume fraction between his or her results and the certified values for SRM 114q for each particle size. These differences should then be compared to the appropriate expanded uncertainties in columns 3 or 4 of Table 10 to determine conformance. If the observed absolute difference between the user's results and the certified values for SRM 114q is always less than the corresponding expanded uncertainty, then the user can conclude that his or her results are in agreement with other laboratories with a confidence level of approximately 95 %. If one or more of the observed absolute differences is larger than the corresponding expanded uncertainty, on the other hand, this is evidence that the user's results are not in agreement with the results of other laboratories and that changes to the measurement procedures are needed.

The expanded uncertainty intervals given in Table 10 are computed using the formula

$$U_{\text{Conformance}} = k\sqrt{u^2_{\text{Typical Lab}} + u^2_{\text{SRM 114q}}}$$

where $u_{\text{Typical Lab}}$ is the appropriate standard uncertainty obtained from columns 2 or 4 of

Table 9 and $u_{\text{SRM 114q}}$ is obtained by converting the expanded uncertainty intervals given for the certified value of SRM 114q in Table 8 using the formula

$$u_{\text{SRM 114q}} = \frac{\text{Upper Uncertainty Bound} - \text{Lower Uncertainty Bound}}{4}.$$

The coverage factor, k, which is used to control the confidence level of the expanded uncertainty intervals, is computed so that the confidence level applies simultaneously to the 15 comparisons for each particle size certified for the SRM. This is done using the Bonferonni inequality [19] and a normal distribution cut-off for 95 % confidence and results in a value of $k = 2.935$.

6 References

1. "Standard Test Method for Fineness of Hydraulic Cement by Air Permeability Apparatus", ASTM C204-00 Volume: 04.01
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7 Appendix

7.1 Appendix A: Questionnaire for participants

Note: Underlined and in bold the values that were assigned by NIST

SECTION A: Laser Diffraction (wet): specimen dispersed in a liquid

Device brand and model: ______________________________

____

____

Parameters to use (mandatory)

- Medium: **Isopropanol (IPA)**

  Is this the medium that you normally use (circle one): Yes No

  If no, please specify what you normally use: ______________________________

  ____

- Complex refractive index used for powder: Real: **1.7** Imaginary: **1.0**
- Refractive index (real) used for medium: **1.39**
- Do not use a surfactant

Some information on your method

- Concentration of the dispersion: [g/mL] ______________ (if known)

  Diluted from more concentrated stock? YES NO

  If yes, give stock concentration [g/L]: ___________

  - Note: use particle density of 3.2 g/mL for calculation of solids concentration. Also indicate density used for medium [g/mL]: ________________

- Ultrasonication of sample suspension (circle one): Yes No

  If yes, please specify intensity and duration: ______________________________

____

- Was ultrasonic treatment performed (circle one):

  (a) inside PSD device; (b) prior to introduction into device; (c) both

  - If (b) or (c), please identify type of external ultrasonicator used (circle one)

    bath submersible horn

- If (b) or (c), was the external ultrasonication performed on a (circle one)

  concentrate or dilute dispersion*

  *refers to a suspension at or near the solids concentration used in the actual measurement

<u>Test and results</u>:

- Duration of the measurement in the PSD device [sec]: ____________________________
- Model used to interpret the results: (circle one): Mie Fraunhofer Both

<u>Notes</u>: (add any information that could be useful to better describe the procedure used):

SECTION B: Laser Diffraction (Dry): specimen dispersed in air

Device brand and model: ____

____

____

<u>Parameters to use (mandatory)</u>

- Complex refractive index used for powder: Real: **<u>1.7</u>** Imaginary: **<u>1.0</u>**

<u>Particle dispersion</u>:

- Dispersion procedure: (circle one) compressed air vacuum

  If compressed air, pressure setting used [bar] ____________________________

<u>Test and results</u>:

- Duration of the measurement in the PSD device [s]: ____________________________
- Model used to interpret the results: (circle one): Mie Fraunhofer Both

<u>Notes</u>: (add any information that could be useful to better describe the procedure used):

7.2 Appendix B: Data received from the Round-robin

SRM 114 p by LD-D

Size [µm]	Cumulative Particle size distribution by Laboratory (CCRL Code) [%]										
	1251	255	736	105	354	303	124	151	148	619	73
1	5.1	5.6	5.00	6.04	6.6	5.6	6.7	3.8	5.1		6.0
1.5	8.3	10.0	8.00	10.70	10.1	9.5	11.4	7.1	7.7		9.3
2	11.0	13.4	10.88	14.05	13.4	13.0	14.7	10.0	10.2	14.26	12.4
3	15.5	18.8	16.26	19.50	19.3	19.3	19.3	14.9	15.0	21.14	18.0
4	19.3	23.2	20.96	24.38	24.3	24.8	22.8	18.9	19.4	26.19	22.8
6	25.4	31.2	28.61	32.66	32.0	34.0	29.1	25.7	26.5	33.86	30.9
8	30.3	38.1	34.71	39.23	38.1	41.4	35.8	31.6	32.3	39.96	37.6
12	37.6	48.5	44.68	49.29	48.2	52.9	48.0	42.0	42.1	50.65	48.8
16	43.1	56.2	53.09	57.22	56.9	62.1	57.6	51.2	50.7	59.56	58.2
24	52.3	69.3	66.79	69.86	70.5	76.0	71.4	66.6	65.2	73.50	72.5
32	60.2	79.2	76.87	79.43	80.7	85.3	81.0	77.8	76.1	83.35	82.1
48	70.2	91.4	89.09	90.81	91.4	95.1	92.7	90.8	89.4	94.16	92.1
64	74.9	97.0	95.16	95.71	95.8	99.1	97.7	96.3	95.9	98.11	96.0
96	77.9	100.0	99.57	98.84	98.1	100.0	100.0	99.2	99.8	99.86	98.2
128	79.2	100.0	100.00	99.67	98.5	100.0	100.0	99.7	100.0	100.00	98.7

SRM 114 p by LD-W

Size [µm]	Cumulative Particle size distribution by Laboratory (CCRL Code) [%]													
	932	1916	92	175	605	1940	84	736	284	557	2116	209	1251	690
1		2.6	9.2		2.0	10.7	5.6	5.0	4.9	5.4	10.5	2.0	10.0	2.7
1.5		5.2	11.7	5.5	5.1	17.1	8.6	8.2	8.9	8.8	16.3	3.5	13.7	4.2
2	20.0	7.6	14.0	9.4	8.1	21.1	11.4	10.8	13.8	11.6	20.3	5.2	15.6	5.1
3	24.2	12.1	19.2	15.9	13.4	27.4	16.1	15.4	21.0	16.3	26.5	9.4	20.1	6.9
4	28.3	16.3	24.6	21.1	17.7	32.6	20.2	19.2	26.9	20.3	31.7	13.7	26.0	9.2
6	35.7	24.0	33.7	29.4	24.9	40.7	26.9	25.7	35.6	26.8	39.6	21.9	37.6	15.7
8	41.7	30.9	40.5	36.6	31.5	47.2	32.7	31.2	42.9	32.4	45.9	29.1	46.5	23.4
12	50.9	42.4	50.5	48.1	41.3	58.3	42.8	41.0	53.6	42.4	57.6	40.8	59.2	38.2
16	58.8	52.0	58.3	57.6	49.2	67.7	51.6	49.8	62.6	51.2	67.2	50.4	70.1	50.5
24	71.2	66.1	71.1	72.6	65.3	81.2	66.1	64.6	76.8	65.7	80.6	65.5	86.8	69.5
32	80.6	76.1	80.9	82.6	78.6	88.8	76.7	75.8	85.7	76.4	88.9	76.8	95.5	83.4
48	91.8	87.7	92.4	92.7	91.7	96.0	89.5	89.3	95.5	89.0	97.6	90.3	99.7	98.1
64	96.8	93.6	97.3	96.5	96.2	99.0	95.4	95.6	99.9	94.4	99.9	95.9	99.9	100.0
96	99.7	98.2	99.9	98.9	98.8	100.0	99.1	99.5	100.0	97.4	100.0	99.0	100.0	100.0
128	100.0	99.5	100.0	99.6	99.7	100.0	99.8	99.8	100.0	97.9	100.0	99.6	100.0	100.0

SRM 114 q by LD-D

Size [µm]	Cumulative Particle size distribution by Laboratory (CCRL Code) [%]											
	1251			255			736			105		
Box	45	45	45	2	2	2	13	13	13	100?	100?	100?
1	6.1	7.3	5.4	5.2	5.4	5.2	4.8	4.8	4.8	5.6	5.7	5.7
1.5	10.0	11.8	8.7	9.4	9.8	9.4	7.7	7.6	7.7	10.0	10.1	10.0
2	13.2	15.7	11.6	12.8	13.2	12.8	10.5	10.4	10.6	13.2	13.3	13.1
3	18.7	22.2	16.4	18.6	19.0	18.6	15.9	15.9	16.0	18.5	18.5	18.3
4	23.5	27.7	20.5	23.6	23.9	23.5	20.8	20.8	21.0	23.5	23.4	23.2
6	31.8	37.0	27.8	32.6	32.9	32.6	29.5	29.5	29.8	32.4	32.3	32.0
8	39.1	44.7	34.3	40.4	40.8	40.5	37.2	37.2	37.6	40.2	40.0	39.7
12	51.3	56.7	45.5	52.7	53.1	52.8	51.1	51.0	51.3	53.2	53.0	52.6
16	60.8	65.6	55.2	62.4	62.9	62.5	63.0	62.8	63.0	64.0	63.8	63.4
24	73.5	76.5	72.2	78.8	79.6	78.9	80.3	80.1	80.1	80.4	80.4	79.9
32	83.5	84.7	84.2	89.4	90.2	89.5	90.3	90.2	90.1	90.4	90.4	90.1
48	94.8	94.9	95.5	97.5	98.1	97.7	98.5	98.5	98.5	98.6	98.6	98.3
64	98.6	98.9	99.0	99.5	99.7	99.6	100.0	100.0	100.0	100.0	100.0	99.9
96	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
128	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

SRM 114 q by LD-D (continued 1)

Size [µm]	Cumulative Particle size distribution by Laboratory (CCRL Code) [%]											
	354			303			124			151		
Box	6	6	6	6	6	6	2	2	2	13	13	13
1	6.1	5.9	5.9	4.9	5.0	5.0	5.9	6.0	6.0	1.5	2.6	2.6
1.5	9.4	9.2	9.2	8.5	8.5	8.4	10.0	10.3	10.2	3.3	5.1	5.2
2	12.7	12.5	12.4	11.8	11.8	11.5	13.1	13.3	13.3	5.1	7.5	7.6
3	18.7	18.5	18.5	18.2	18.2	17.6	17.6	17.9	17.9	8.5	11.8	12.0
4	24.0	23.9	23.8	24.3	24.2	23.3	21.2	21.6	21.6	11.4	15.4	15.7
6	33.0	33.0	32.9	35.1	35.1	33.7	28.4	28.9	28.9	16.5	21.8	22.2
8	40.8	40.9	40.8	44.5	44.5	42.8	36.3	36.9	36.9	22.4	28.2	28.8
12	54.7	54.8	54.8	59.9	59.8	58.2	51.7	52.3	52.3	35.3	41.2	42.1
16	66.5	66.7	66.7	72.1	72.0	70.8	64.3	64.8	64.9	48.4	53.8	55.0
24	82.8	83.0	83.0	87.8	87.7	87.1	81.8	82.3	82.4	71.7	75.2	76.4
32	92.5	92.7	92.6	95.2	95.1	94.9	91.3	91.9	92.0	86.0	88.3	89.2
48	99.0	99.1	99.0	99.8	99.8	99.8	98.4	98.7	98.7	96.5	97.7	98.2
64	100.0	100.0	100.0	100.0	100.0	100.0	99.8	99.8	99.8	98.8	99.5	99.7
96	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.9
128	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.9

SRM 114 q by LD-D (continued 2)

Size [μm]	Cumulative Particle size distribution by Laboratory (CCRL Code) [%]								
	148			619			73		
Box	100	100	100	24?			118	118	118
1	4.4	4.4	4.4				5.7	5.7	5.7
1.5	7.0	6.9	7.0				9.0	9.0	9.1
2	9.5	9.4	9.5	12.3			12.1	12.1	12.2
3	14.4	14.1	14.3	18.5			17.9	18.1	18.1
4	18.8	18.5	18.6	23.4			23.2	23.5	23.3
6	26.3	25.9	26.0	31.5			32.6	33.1	32.7
8	32.9	32.6	32.6	38.5			41.2	41.8	41.2
12	45.5	45.2	45.3	51.5			56.5	57.1	56.5
16	57.3	57.0	57.1	62.9			68.9	69.4	68.9
24	75.9	75.8	75.8	81.0			85.4	85.6	85.4
32	87.8	87.8	87.8	92.0			93.7	93.8	93.8
48	97.9	97.9	97.9	99.3			99.3	99.3	99.3
64	100.0	100.0	100.0	100.0			100.0	100.0	100.0
96	100.0	100.0	100.0	100.0			100.0	100.0	100.0
128	100.0	100.0	100.0	100.0			100.0	100.0	100.0

SRM 114 q by LD-W

Size [µm]	Cumulative Particle size distribution by Laboratory (CCRL Code) [%]											
	932			1916			92			175		
Box	19	19	19	92?	92?	92?	120	120	120	33	33	33
1				2.1	2.2	2.1	10.1	9.2	9.8			
1.5				4.3	4.4	4.3	13.2	12.3	13.0	3.8	4.1	3.7
2	17.4	18.9	18.1	6.6	6.7	6.6	16.0	15.0	15.7	6.6	7.1	6.4
3	21.1	23.3	22.3	11.3	11.4	11.1	21.4	20.4	21.0	11.9	12.6	11.5
4	25.2	27.6	26.6	15.9	16.1	15.8	26.7	25.7	26.2	16.6	17.5	16.3
6	33.2	35.5	34.8	24.9	25.1	24.7	35.9	34.8	35.3	25.3	26.3	25.0
8	40.5	42.4	41.9	33.3	33.5	33.2	43.1	42.1	42.6	33.6	34.4	33.4
12	53.0	54.0	53.7	47.8	48.0	47.8	55.0	54.2	54.5	48.1	48.5	47.7
16	64.0	64.4	64.1	59.9	60.1	60.1	65.0	64.6	64.7	60.7	61.0	60.2
24	81.1	80.4	80.0	76.7	76.8	77.0	80.8	81.1	80.7	79.6	80.0	79.4
32	91.2	90.1	89.8	87.0	87.0	87.3	90.5	91.0	90.6	90.0	90.5	90.3
48	99.0	98.2	98.3	96.1	96.0	96.2	98.5	98.7	98.6	97.5	97.8	97.7
64	100.0	100.0	100.0	98.8	98.8	98.9	100.0	100.0	100.0	99.2	99.4	99.3
96	100.0	100.0	100.0	99.9	99.9	99.9	100.0	100.0	100.0	99.9	99.9	99.9
128	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

SRM 114 q by LD-W (continued 1)

Size [µm]	Cumulative Particle size distribution by Laboratory (CCRL Code) [%]											
	605			1940			84			736		
Box	120	120	120	92	92	92	94	94	94	88	88	88
1	1.2	1.1	1.1	9.6	12.0	9.5	4.7	4.9	4.9	4.3	4.4	4.1
1.5	3.7	3.6	3.5	14.2	17.4	14.5	7.3	7.7	7.6	7.4	7.6	7.1
2	6.4	6.1	6.0	18.2	20.9	18.4	9.8	10.4	10.3	10.2	10.4	9.9
3	11.5	11.3	11.1	24.6	27.4	24.9	14.8	15.4	15.4	15.2	15.4	15.1
4	16.0	15.9	15.7	30.2	33.3	30.3	19.3	19.9	19.9	19.5	19.7	19.5
6	24.5	24.4	24.2	39.3	44.3	39.3	27.2	27.7	27.8	27.0	27.1	27.2
8	32.7	32.5	32.3	47.0	51.5	46.9	34.3	34.7	34.8	33.9	33.8	34.0
12	44.2	44.3	44.1	60.6	66.6	60.7	47.4	47.6	47.7	46.9	46.7	46.8
16	54.6	54.7	54.5	72.5	80.3	72.5	59.1	59.3	59.4	58.6	58.3	58.5
24	76.8	77.0	76.7	89.9	94.1	89.7	77.2	77.3	77.3	76.6	76.4	76.6
32	90.4	90.6	90.2	97.7	98.6	97.6	88.4	88.5	88.3	87.8	87.8	87.8
48	97.8	97.9	97.6	100.0	100.0	100.0	98.0	98.0	97.8	97.6	97.7	97.7
64	99.4	99.5	99.3	100.0	100.0	100.0	100.0	100.0	99.9	99.9	100.0	100.0
96	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
128	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

SRM 114 q by LD-W (continued 2)

Size [µm]	Cumulative Particle size distribution by Laboratory (CCRL Code) [%]											
	284			557			2116			690		
Box	33	33	33	19	19	19	29	29	29	101	101	101
1	3.1	2.8	2.9	4.5	4.5	4.6	9.1	9.0	9.2	2.6	2.6	1.9
1.5	6.0	5.6	5.7	7.7	7.7	7.9	13.3	13.0	13.3	4.0	4.2	3.2
2	9.8	9.4	9.5	10.6	10.5	10.7	17.3	17.0	17.3	5.0	5.3	4.2
3	15.7	15.3	15.5	15.6	15.4	15.8	24.0	23.4	23.8	6.5	6.9	5.5
4	22.0	21.5	21.6	20.0	19.7	20.1	29.8	29.0	29.3	8.5	9.2	7.0
6	33.2	32.9	32.8	27.3	26.9	27.5	39.2	38.1	38.3	15.0	16.1	12.4
8	42.7	42.8	42.6	34.0	33.4	34.2	46.8	45.8	45.8	23.4	24.6	19.4
12	56.9	57.3	56.9	46.6	45.7	46.7	60.7	59.8	59.6	40.2	40.6	31.6
16	68.3	69.1	68.5	58.3	57.0	58.4	73.5	72.4	71.9	54.1	53.6	41.5
24	84.8	85.7	85.4	77.1	75.2	76.9	91.5	90.5	90.2	77.5	76.1	73.0
32	93.4	94.1	94.2	88.6	86.3	88.2	98.2	98.1	98.1	94.0	90.7	92.8
48	99.1	99.5	99.5	97.1	94.0	96.7	99.9	100.0	100.0	100.0	100.0	100.0
64	100.0	99.9	100.0	98.9	95.5	98.6	100.0	100.0	100.0	100.0	100.0	100.0
96	100.0	99.9	100.0	98.9	95.5	98.6	100.0	100.0	100.0	100.0	100.0	100.0
128	100.0	100.0	100.0	98.9	95.5	98.6	100.0	100.0	100.0	100.0	100.0	100.0

SRM 114 q LD-W (continued 3)

Size [µm]	Cumulative Particle size distribution by Laboratory (CCRL Code) [%]					
	209			1251		
Box	66	66	113	57	57	57
1	1.7	2.0	1.9	9.8	9.7	9.7
1.5	3.3	3.3	3.4	13.5	13.3	13.5
2	5.2	4.9	5.2	15.3	15.1	15.3
3	9.5	8.9	9.4	19.2	19.0	19.2
4	14.1	13.4	13.8	24.5	24.4	24.7
6	23.0	22.3	22.7	36.0	36.0	36.5
8	31.2	30.8	31.0	45.3	45.3	46.2
12	45.7	45.6	45.7	59.6	59.7	60.2
16	57.9	58.0	58.1	73.9	74.0	75.6
24	76.6	76.6	77.0	93.7	93.6	95.4
32	88.3	88.1	88.6	99.5	99.3	99.7
48	98.0	97.9	98.3	100.0	100.0	100.0
64	99.9	99.9	100.0	100.0	100.0	100.0
96	100.0	100.0	100.0	100.0	100.0	100.0
128	100.0	100.0	100.0	100.0	100.0	100.0

7.3 Appendix C: Bootstrap method

Suppose a random sample $\mathbf{x} = (x_1, x_2, \ldots x_n)$ from an unknown probability distribution F has been observed and we wish to estimate a parameter of interest $\theta = t(F)$ on the basis of **x**. For this purpose, we calculate an estimate $\hat{\theta} = s(\mathbf{x})$ from **x**. How accurate is $\hat{\theta}$? The bootstrap was introduced in 1979 as a computer-based method for estimating the standard error of $\hat{\theta}$.

The bootstrap is a data-based simulation method for statistical inference. It allows scientists to explore data and draw valid statistical inferences without worrying about mathematical formulas and derivations. The bootstrap parameter estimate is available no matter how mathematically complicated the estimator $\hat{\theta} = s(\mathbf{x})$ may be. In its non-parametric form, the bootstrap provides standard errors and confidence intervals without the usual normal-theory assumptions.

The bootstrap method draws repeated samples (with replacement) from the observed sample itself to generate the sampling distribution of a statistic (a data set of size n has 2^{n-1} nonempty subsets).

Bootstrapping of a statistic $\hat{\theta} = s(\mathbf{x})$ consists of the following steps:

1. B samples are drawn with replacement from the original data set **x**, with each sample the same size as the original data set. Call these bootstrap samples $\mathbf{x}^{*1}, \mathbf{x}^{*2}, \ldots \mathbf{x}^{*B}$.
2. The statistic of interest $\hat{\theta}$ is computed for each bootstrap sample, that is $\hat{\theta}(b) = s(\mathbf{x}^{*b})$ for $b = 1,2,\ldots B$. The mean, standard deviation, and percentiles of these B values form the basis for the bootstrap approach to inference.

Implementation of these steps in a computer language is not difficult. A necessary ingredient for any bootstrap program is a high quality uniform number generator. It is important to keep in mind that the bootstrap (and associated methods) are not tools that are used in isolation but rather are applied to other statistical techniques. For this reason, they are most effectively used in an integrated environment for data analysis. In such an environment, a bootstrap procedure has the ability to call other procedures with different sets of inputs (data) and then collect them together and analyze the results. The S, S-PLUS, Gauss and Matlab packages are examples of integrated environment. In this report, we use the S-PLUS function *summary.bootstrap()*. For each data-column, 1000 samples of the data (with replacement) or replicates were generated and the mean of these samples was calculated. The 2.5 % and 97.5 % empirical percentiles for the replicates of the parameter estimate (sample mean) are lower and upper bounds of the data set, respectively.

7.4 Appendix D: DRAFT Test Method for Particle Size Analysis of Hydraulic Cement and Related Materials by Light Scattering.

DRAFT – NOT APPROVED BY ASTM

1. Scope
   - 1.1. This test method covers the determination of the particle size distribution of hydraulic cement and related compounds by means of the laser diffraction technique, reported as volume percent of particulate materials.[5]
   - 1.2. This test method applies to analyses with both non-aqueous dispersions and in gaseous dispersion.
   - 1.3. This test method is applicable to the measurement of particulate materials in the size range of 0.4 μm to 2000 μm.
   - *1.4.* The values stated in SI units are to be regarded as the standard.
   - *1.5. This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Reference documents

2.1. ASTM standards

B 822 Test Method for Particle Size Distribution of Metal Powders and Related Compounds by Light Scattering[6]

C 219 Terminology Relating to Hydraulic Cement

C 115 Test Method for Fineness of Portland Cement by the Turbidimeter[7]

C430 Standard Test Method for Fineness of Hydraulic Cement by the 45-μm (No. 325) Sieve

C 204 Test Method for Fineness of Hydraulic Cement by Air Permeability Apparatus[7]

E 1458 Test Method for Calibration Verification of Laser Diffraction Particle Sizing Instruments using Photomask Reticles[8]

E 1617 Practice for Reporting Particle Size Characterization Data[8]

2.2. ISO standards

ISO 13320-1 (E), Particle Size Analysis — Laser Diffraction Methods — Part 1: General Principles.

ISO 14887:2000, Sample Preparation -- Dispersing Procedures for Powders in Liquids.

3. Terminology

3.1. *Definitions:*

For definitions of terms used in this test method, refer to Terminology C219

3.2. Definition of Terms Specific to this Standard:

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[5] This test method is a modification of Test Method B 822, so that it can be used for hydraulic cement.

[6] *Annual Book of ASTM Standards*, Vol. 02.05

[7] *Annual Book of ASTM Standards*, Vol. 04.01

[8] *Annual Book of ASTM Standards*, Vol. 14.02

3.2.1. *laser diffraction, n* – a method for determining the particle size distribution based on the detection and analysis of the angular distribution of scattered light, produced by a laser, passing through a dilute dispersion of particles.

3.2.2. *Background, n* – extraneous scattering of light by elements other than the particles to be measured; includes scattering by contamination in the measurement path.

3.2.3. *Mie theory, n* - the electromagnetic theory that describes the scattering of light by spherical particles.

3.2.4. *Fraunhofer diffraction, n* - the optical theory that describes the low-angle scattering of light by particles that are large compared with the wavelength of the incident light.

3.2.5. *multiple scattering, n* – The rescattering of light by a particle in the path of light scattered by another particle. This typically occurs in dispersions with high particle concentrations.

3.2.6. *wet method, n* - The particles are dispersed in isopropyl alcohol, then recirculated through the path of the light beam.

3.2.7. *dry method, n* - The particles are dispersed in air, then passed through the path of the light beam.

3.2.8. d_{10}, d_{50} *and* d_{90} –particle size values corresponding to a cumulative distribution at 10 %, 50 % and 90 % respectively.

3.2.9. *span* – The width of the differential particle size distribution, calculated using the following formula:

$$span = \frac{(d_{90} - d_{10})}{d_{50}}$$

4. Summary of the Test Method

4.1 *The wet method involves a sample of cement powder dispersed* in isopropyl alcohol (IPA) and recirculated through the path of the light beam. A dry sample can be pushed under air pressure or pulled under vacuum so that it flows through the light beam. The particles pass through the beam and scatter light. Photodetector arrays collect the scattered light, which is then converted to electrical signals and analyzed by a computer. The signals are converted to a particle size distribution (PSD) using an optical model based on Fraunhofer diffraction or Mie scattering. Scattering information is analyzed assuming spherical particles. Calculated particle sizes are therefore presented as equivalent spherical diameters. Additional information pertaining to the general principles of PSD analysis by light scattering can be found in ISO Standard 13320-1 or in the publications by Ferraris et al.[9, 10][11]

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[9] Ferraris, C.F, Hackley V.A., Aviles A.I., Buchanan C.E., "Analysis of the ASTM Round-Robin Test on Particle Size Distribution of Portland Cement: Phase I" NISTIR 6883, Nat. Inst. Of Stds. And Tech., May 2002 (http://ciks.cbt.nist.gov/~garbocz/nist6883/nistir6883.htm)

[10] Ferraris, C.F, Hackley V.A., Aviles A.I., Buchanan C.E., "Analysis of the ASTM Round-Robin Test on Particle Size Distribution of Portland Cement: Phase II" NISTIR 6931, December 2002

5. Significance and use

5.1. Accurate measurement of the PSD of cement powder is *a beneficial tool* for process monitoring in the cement industry. In addition, the PSD is a key factor in on-going computational efforts to simulate microstructure development and predict the performance of cement-based materials.

5.2. The only other relevant standard method is Test Method C 115, a sedimentation method. Designed primarily to determine fineness of cement in terms of surface area per unit mass, this sedimentation method also provides a non-mandatory procedure to determine the PSD down to a particle size of 7.5 µm. This lower limit is not acceptable for proper description of the PSD of hydraulic cement.

5.3. The Blaine procedure for fineness of cement, given in Test Method C 204, does not provide the PSD, but provides the specific surface area based on the air permeability of a compacted specimen of cement.

5.4. The fineness of cement is also measured using Test Method C 430. This method is limited to the measurement of the percentage of particles less than 45 µm, and therefore does not provide the full PSD.

5.5. The laser diffraction method is capable of measuring powders with a size distribution ranging from 0.4 µm to 2000 µm, covering the full size range in hydraulic cement. The interpretation of the measurements is related to the type of light scattering model used, either Fraunhofer or Mie. The limitation of this test method is that it is not a direct measurement of particle size. In order to calculate the PSD, some assumptions must be made: (1) the particles are spherical; (2) the refractive indices of the particles and of the medium are known (needed for the Mie model only). Also, to correctly measure the particles, the powder must be dispersed so that individual particles, and not agglomerates of particles, will scatter light independently.

5.5.1 Diffracted light is concentrated in the forward direction, forming the so-called Fraunhofer diffraction rings. The intensity and distribution of diffracted light around the central beam can be related to particle size, assuming a circular cross-section geometry for the diffracting entities. The range of validity for this test method is limited on the low end to particle diameters a few times greater than the wavelength of the incident light for particles that are opaque or have a large refractive index contrast with the medium. In Fraunhofer diffraction, the pattern does not depend on the refractive index, so in theory there is no difference between using a liquid or a gas as a dispersing medium.

5.5.2 For non-spherical particles like cement, Mie theory provides a volume-weighted equivalent spherical diameter. An accurate representation of the "true" size distribution by Mie scattering depends on knowledge of the complex refractive index, and will be affected by the degree of particle non-sphericity and the dispersion procedure used to prepare the test specimen. For Mie scattering, the higher refractive index contrast in air,

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[11] Ferraris C.F., Hackley V.A., Avilés A.I., "Measurement of Particle Size Distribution in Portland Cement Powder: Analysis of ASTM Round-Robin Studies", Cement, Concrete and Aggregate Journal, Dec. 2004, vol. 26 #2, p71-81.

compared with most liquids, may somewhat affect the scattering pattern, but should not alter the PSD results significantly.

5.5.3 It is important to recognize that the results obtained by this test method may disagree with the results obtained from other methods for particle size determination using different physical principles. The results are influenced strongly by the physical principles employed by each method of particle size analysis. The results of any indirect particle sizing method should not be regarded as absolute when comparing with results obtained by other methods.

5.5.4 A key aspect of the procedure is to ensure dispersion of the cement particles. To verify the adequacy of the procedure that is used, the PSD of a sample of SRM 114[12] is measured, and the resulting PSD is compared with the reference PSD. Lack of agreement means that the procedure for dispersing the cement sample needs to be modified or that the instrument is not functioning properly.

6. Interferences

6.1. Air bubbles entrained in the circulating fluid will scatter light and be reported as particles. Circulating fluids may require degassing, and shall be bubble-free upon visual inspection. The presence of air bubbles can also be detected by the presence of two peaks in the particle size distribution, with the second peak being at about 1500 µm or higher.

6.2. In most devices using a fluid, there is the option of dispersing the particles by applying an ultrasound vibration to the suspension. This method is highly effective in dispersing the particles but it could also increase the temperature of the medium. Therefore, after satisfactory dispersion is achieved, the suspension should be allowed to regain an equilibrium temperature. Typically a wait of about 10-15 min is enough.

6.3. Contaminants, such as particles or foreign substances dispersed in IPA, scatter light, and thus are reported as part of the PSD.

6.4. The presence of oil, water, or foreign substances in air will cause clogging or agglomeration in dry dispersal that will bias the particle size results. The air supplied shall be free of such substances.

6.5. Agglomeration or settling of particles during analysis will cause erroneous results. Dispersions shall be prepared in accordance with the instrument manufacturer's instructions, and a stable dispersion shall be maintained throughout the analysis. A sufficient flow rate for wet dispersions shall be maintained during the analysis in order to prevent settling of large particles.

6.6. A low concentration of particles in the dispersion may result in poor data repeatability. A high concentration of particles in the dispersion may cause excessive light attenuation and multiple scattering, resulting in an erroneous PSD. Follow the instrument manufacturer's instructions in determining the correct light attenuation level.

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[12] SRM 114 can be obtained from NIST. To order go to the URL: www.nist.gov and select "Standard Reference Materials" under the heading "NIST Products and Services".

7. Apparatus
   7.1. *Particle Size Analyzer,* based on Fraunhofer diffraction or Mie scattering, or a combination of both models. Use care to ensure that the analyzer system or its subsystems are appropriate for the size range of hydraulic cement or related compounds.
   7.2. *Liquid or air sample handling system* – to transport the dispersed test specimen across the light beam.

8. Reagents and materials
   8.1. *IPA* – isopropyl alcohol, reagent grade, to be used with the wet method
   8.2. *Dry, clean air for air dispersion* – follow suggestions of manufacturer for providing acceptable air supply or vacuum.
   8.3. *Fine Sand* – as recommended by the manufacturer to clean the instrument after a measurement using the dry method.
   8.4. *SRM 114* – current reference cement available from NIST[12]. A letter indicating the lot numbers follows the number 114. This material is provided with a certificate including a reference PSD. This reference PSD is obtained by statistical analysis of test results from an ASTM sponsored round-robin[9, 10] for SRM 114P and from NIST sponsored round-robins for subsequent reference materials.

9. Sampling and Sample Size
   9.1. Obtain a representative specimen of hydraulic cement. The amount needed for the wet method is less than 1 g and for the dry method is about 3 g to 4 g. The exact amount depends on the loading method adopted.

   Note 1– The operator needs to ensure that fines are not lost. It is suggested that samples should be homogenized in closed vessels, and settled layers should be gently recombined before extracting the final samples.

   9.2. For the wet method, disperse the specimen either in the device or external to the device. Follow the manufacturer's recommendations to determine the most appropriate method.
   9.3. For the dry method, load the specimen directly on the device feeder.

10. Calibration and Standardization
   10.1. Verify proper operation of the instrument using Test Method E 1458 or the manufacturer's calibration procedure.
   10.2. Hydraulic cement SRM 114 is intended to be used as a reference material. The use of SRM 114 will not permit direct calibration of the instrument, i.e., an instrument correction factor should not be calculated. The scope of the SRM 114 is to provide the means to the operator to develop an appropriate procedure for measuring PSD by optimizing the parameters of the instrument. To use SRM 114, conduct a test using a method as described in section 11. To use these uncertainties to assess agreement with other laboratories, the user should compute the absolute difference in cumulative volume fraction between his or her results and the certified values for SRM 114q for each particle size. These differences

should then be compared to the appropriate expanded uncertainties in columns 3 or 4 of Table 5 in Appendix A of the SRM 114q certificate to determine conformance. If the observed absolute difference between the user's results and the certified values for SRM 114q is always less than the corresponding expanded uncertainty, then the user can conclude that his or her results are in agreement with other laboratories with a confidence level of approximately 95 %. If one or more of the observed absolute differences is larger than the corresponding expanded uncertainty, on the other hand, this is evidence that the user's results are not in agreement with the results of other laboratories and that changes to the measurement procedures are needed.

Note 2: For more details on this methodology see ref [13]

11. Procedure

11.1. Install the desired sample delivery system and select the applicable instrument range, as indicated by the manufacturer's instructions.
11.2. Allow the instrument to warm up for at least 20 min.
11.3. If necessary, establish the correct optical alignment according to the requirements of the manufacturer.

Note 3 – It is advisable that optical alignment be checked upon startup, whenever the sample delivery system is changed and frequently.

11.4. Measure the background in the mode in which the analysis will be conducted. Ensure that the carrier (air or IPA) is flowing through the light path while measuring background. Background values shall not exceed the specifications of the manufacturer. If the background values exceed the manufacturer's specifications, perform the necessary procedures as specified by the manufacturer to bring the background values within acceptable limits.
11.5. Extract a test portion from the cement sample. Refer to the manufacturer's recommendation to ensure that the quantity of test material is acceptable to achieve optimum light scattering conditions. A wide range of sample sizes is acceptable, depending on the median particle size (d_{50}), particle density (mass/volume), refractive indexes and sample delivery system.
11.6. Select the appropriate run time for the test portion. This procedure is very specific to the equipment and material and is generally gauged by the run-to-run repeatability and by the use of SRM 114 (see section 10).
11.7. Select the appropriate refractive indices. Recommended refractive indices of cement are real 1.7, imaginary 0.1; recommended refractive index for IPA: real 1.378, imaginary 0.
11.8. Select the desired data output parameters, according to the manufacturer's requirements. Usually, the PSD reported is the cumulative distribution. To simplify data interpretation, the following particle sizes are to be used: 0.5, 1, 1.5,

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[13] Ferraris, C.F.; Avilés A.I.; Guthrie W.; Peltz M.; Haupt, R.; MacDonald B.; *Certification of SRM 114q; Phase II (Particle Size Distribution)*, NIST SP260-166 (2006).

2, 3, 4, 6, 8, 12, 16, 24, 32, 48, 64, 96, and 128 μm. Other sizes can be reported without affecting the quality of the results.

11.9. Transfer the test portion directly to the sample delivery system. For the wet method, allow recirculation for at least 20 s prior to beginning measurement. For the dry method, engage the sample switch to allow the sample to begin flow past the light source before starting measurement.

11.10. Select the appropriate measurement parameters. For the wet method, parameters such as ultrasonication intensity and time, flow rate, and measurement duration are to be selected. For dry method, parameters such as intensity of vibration applied to the sample feeder, air pressure or vacuum level are to be selected. Refer to the instrument manual for further specifications.

11.11. Perform the sample analysis according to the manufacturer's instructions.

11.12. Collect at least three sets of PSDs and calculate the average value for each particle size on the same test portion of the wet method and on three different test portions for the dry method.

11.13. For the wet method, drain and fill the sample dispersion system in preparation for the next sample analysis. Drain and rinse as necessary, to achieve background values within the acceptable operating limits, as specified by the manufacturer.

11.14. For the dry method, brush or vacuum to remove all particles throughout the sample system. Purge with air or use fine sand to remove particles remaining in the sample system, as described in the manufacturer's instructions.

11.15. Follow the manufacturer's instructions to determine the frequency and the procedure for cleaning the lenses.

12. Report

12.1. Practice E 1617 specifies three levels of detail for reporting PSD data. It is up to the supplier and user of the data to agree on the level of reporting required. As a minimum, report the following information:

12.1.1. The instrument name and model number used and the range selected

12.1.2. The method of dispersing the test portion, i.e., wet or dry

12.1.3. The instrument measurement run time

12.1.4. The parameters selected under 11.10

12.1.5. The number of replicates that were used to calculate the average

12.1.6. The 10 %, 50 % and 90 %, (d_{10}, d_{50} and d_{90} respectively) diameters. These values can be used to calculate the span

12.1.7. The cumulative (volume % versus diameter) PSD. This could be provided in electronic form as well.

13. Precision and Bias

13.1. *Precision statement* – The analysis of the interlaboratory round-robin, sponsored by NIST for the development of the next SRM 114 presented here, was used to develop the precision values.

13.1.1. *Within-Laboratory Precision* — The standard deviation of PSD determinations within a laboratory for a given material, are given in the second column of Table 1. The standard deviations for the different particle sizes, indexed by the cumulative volume fractions observed for this material, are given in the first column of Table 1. Criteria for comparing two PSD values for a particular particle size within a laboratory, the expanded uncertainty of the difference of two cumulative volume fractions, is given in the third column of Table 1. This value gives the acceptable range of two measurements that is likely to be caused by random variation.

13.1.2. *Multilaboratory Precision* — Between laboratory uncertainties are given in the last two columns of Table 1. The standard uncertainties were obtained by taking the standard deviation of the mean PSD values for each laboratory at each particle size.

13.2. *Bias* – This test method has no determinable bias as the values obtained can only be defined in terms of this test method.

14. Keywords

laser diffraction; light scattering; cement; particle size distribution; PSD

Table 1: Standard uncertainties and expanded uncertainties for the difference of two cumulative volume fractions within and between laboratories

Cumulative Volume Fraction (CVF), %	**Standard Uncertainty of CVF's Obtained from a Typical Lab*, %**	**Expanded Uncertainty for the Difference of Two CVF's Obtained from a Typical Lab*, %**	**Standard Uncertainty of CVF's Obtained from Different Labs, %**	**Expanded Uncertainty for the Difference of Two CVF's Obtained from Different Labs, %**
5.075	0.175	0.496	2.511	7.103
8.033	0.281	0.794	3.233	9.144
11.195	0.342	0.969	3.889	10.999
16.286	0.450	1.274	4.526	12.801
21.005	0.530	1.500	5.138	14.532
29.636	0.565	1.598	5.948	16.823
37.573	0.600	1.696	6.191	17.509
51.045	0.603	1.706	6.352	17.967
62.795	0.552	1.561	6.385	18.058
80.823	0.501	1.417	4.982	14.092
91.150	0.384	1.085	3.453	9.766
98.359	0.217	0.614	1.326	3.750
99.695	0.049	0.139	0.565	1.597
99.886	0.003	0.009	0.458	1.295
99.895	0.000	0.000	0.460	1.300
*Note: Different laboratories have significantly different within-lab standard deviations, so some labs will find that smaller differences are statistically significant while others will find that larger differences are not significant.				

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 114q

Portland Cement Fineness Standard

This Standard Reference Material (SRM) is intended for use in calibrating fineness testing equipment according to ASTM Standard Methods. The SRM unit consists of 20 glass vials with plastic caps containing powdered cement (each vial is contained in a sealed foil bag). Each vial contains approximately 5 g of cement.

Certified Values and Uncertainties: A NIST certified value is a value for which NIST has the highest confidence in its accuracy and that all known or suspected sources of bias have been investigated or accounted for by NIST. The certified values for specific surface area and sieve residue are given in Table 1. The certified values for the surface area are the mean of results from analyses performed by cooperating laboratories. The certified value for sieve residue was calculated from a quadratic fit of NIST data using three sieves having openings ranging from 38 µm to 56 µm.

The expanded uncertainties of the certified values for specific surface area were calculated according to the NIST uncertainty policy described in the NIST Technical Note 1297 [1], and are at the 95 % confidence level. The uncertainties include measurement variability within and between laboratories. The surface area uncertainties also include material variability and the uncertainty of the surface area values for the superseded SRM 114p *Portland Cement Fineness Standard*, which was used as the calibrant for this material. The expanded uncertainty for the sieve residue was computed using a Bayesian analysis and is also at the 95 % probability level. The expanded uncertainty accounts for the variability of random measurement effects, sieve calibrations, and material inhomogeneity.

Table l. Certified Values

Measurand	ASTM Method	Certified Value and Expanded Uncertainty		
Specific Surface Area (Blaine)	C 204-96a(a)	3818 cm^2/g (381.8 m^2/kg	± ±	78 cm^2/g 7.8 m^2/kg)
Specific Surface Area (Wagner)	C 115-96a(b)	2183 cm^2/g (218 m^2/kg	± ±	160 cm^2/g 16 m^2/kg)
Sieve Residue (45 µm residue)	C430-96(c)	0.79 %	±	0.19 %

(a) Standard Test Method for Fineness of Portland Cement by Air Permeability Apparatus [Blaine].
(b Standard Test Method for Fineness of Portland Cement by the Turbidimeter [Wagner].
(c) Standard Test Method for Fineness of Hydraulic Cement by the 45 µm (No. 325) Sieve.

Expiration of Certification: The certification of SRM 114q is valid, within the measurement uncertainties specified, until **31 December 2016,** provided the SRM is handled in accordance with the instructions given in this certificate (see "Instructions for Use"). This certification is nullified if the SRM is contaminated or otherwise modified.

Maintenance of Certification: NIST will monitor representative samples from this SRM lot over the period of its certification. If substantive changes occur that affect the certification before the expiration date, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

James St. Pierre, Chief
Materials and Construction Research Division

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

Gaithersburg, MD 20899
Certificate Issue Date: 24 March 2005
See Certificate Revision History on Last Page

The preparation of the material and the coordination of the technical measurements leading to certification were performed by C. Ferraris of the NIST Materials and Construction Research Division.

Statistical consultation on measurement design and analysis of the certification data was performed by W.F. Guthrie and A.I. Avilés of the NIST Statistical Engineering Division.

The support aspects involved in the issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by B.S. MacDonald of the NIST Measurement Services Division.

INSTRUCTIONS FOR USE

Stability and Use: This material is considered to be extremely hygroscopic. Based on measurements in 1993 of several earlier renewals of SRM 114, the properties certified are stable as long as the foil bag remains sealed. The specific surface area of cement changes on exposure to the moisture in air. Therefore, this cement should be used immediately after opening the outer foil bag.

Allow the sealed foil bag to equilibrate to testing temperature before opening. To open the pouch, cut off the end with scissors. Fluff the cement in accordance with ASTM Standard C204, Section 3.4, allow the cement to settle for 2 minutes, and then perform the measurement.

Material Selection and Packaging: The desired properties were determined to be generally the same as those selected for the previous issues of SRM 114; however, in order to better represent current cements, the material selected for SRM 114q consists of a finer particle size distribution than previously issued. The Cement and Concrete Reference Laboratory (CCRL) and NIST identified a plant with suitable cement: Lehigh Cement Company (Union Bridge, Maryland)[14] donated 1300 kg of appropriate cement for this SRM. The material selected was Type I according to the ASTM C 150 Standard Classification and had a mass fraction of less than 8 % tricalcium aluminate (C_3A). The material was collected for shipment to NIST directly from the finish mill process stream into bags. Upon arrival at NIST, the cement was blended in a V-blender (1.68 m^3) and then transferred to 208 L (55 gallon) drums lined with 0.015 cm (6 mil) polyethylene liners to minimize hydration of the cement in storage prior to preparation and packaging. Over the next two days, the cement from each drum was sealed in foil bags, each containing about 16 kg of cement. The foil bags were stored in a climate-controlled area. The contents of each bag were subsequently packaged into vials. The vials were then capped and packaged in boxes of about 500 vials per box. The boxes were sequentially labeled from 1 to 118. About 5 boxes were filled per day. Nearly 59 000 glass vials, each containing approximately 5 g of cement, were produced. Each vial was then individually sealed in a foil bag. Vials were selected from the lot by stratified random sampling [2] for both homogeneity and certification analyses. Selected vials were shipped to the participating laboratories for measurements. The remaining vials were packaged into SRM unit boxes of 20 vials each.

Homogeneity Assessment and Certification Analyses: Homogeneity testing of the material was performed on 48 random-selected samples. Measurements of the loss of ignition (LoI) showed no reversible moisture take-up by the cement during packaging. The data received from the round-robin participants were also checked for laboratory-to-laboratory (or day-to-day in the case of sieve residue) variability, box-to-box variability, and vial-to-vial variability. No significant box-to-box or vial-to-vial variability was detected except for the Wagner or sieve residue tests, and therefore it was determined that the samples were homogeneous for the ASTM measurements. Significant vial-to-vial variability was observed using the Blaine test and the certified values reflect this source of uncertainty.

Certification analyses for specific surface areas using ASTM Standard Test Methods C 115-96a and C 204-00 were performed on two samples at each of the participating laboratories. SRM 114p *Portland Cement Fineness Standard* was used for calibration. Raw data were submitted by each laboratory to NIST for tabulation and calculation of surface areas, which for the Blaine test, assumed a density of 3.15 g/cm^3. The density was measured twice at NIST: the results were 3.255 g/cm^3 and 3.248 g/cm^3.

Certification analyses according to ASTM Standard Test Method C 430-96 for the 45 µm sieve residue were performed at NIST on 40 samples from 20 vials of cement.

Laboratories performing certification analyses are members of the CCRL (http://www.ccrl.us) proficiency program. The full list is provided in the report describing the details of the certification process [2].

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[14] Certain commercial equipment, instruments, or materials are identified in this certificate in order to specify adequately 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.

Information Values: NIST information values are considered to be of interest to the SRM user, but are not certified because insufficient information is available to assess adequately the uncertainty associated with the values or only a limited number of analyses were performed. Information values for SRM 114q are given in Tables 2 and 3. Table 2 provides the approximate chemical composition determined by ASTM Standard Test Method C114-02. The analysis of this cement (CCRL Portland Cement Proficiency Sample No. 150) was performed by 70 to 170 laboratories; the number of participating laboratories depends on the value measured.

Table 2. Information Values for Chemical Composition

Compound	Mass Fraction (%)	Compound	Mass Fraction (%)
CaO	64.0	K_2O	0.70
SiO_2	20.7	TiO_2	0.30
$A1_2O_3$	4.7	P_2O_5	0.12
Fe_2O_3	3.2	Na_2O	0.07
SO_3	2.4	MgO	2.2
Loss on Ignition	1.67		

Table 3 provides the calculation of cement compounds according to ASTM C 150-02.

Table 3. Information Values for Cement Compounds (Calculation from Table 2)

Compound		Mass Fraction (%)
C_3S	(tricalcium silicate)	60
C_2S	(dicalcium silicate)	14
C_3A	(tricalcium aluminate)	7
C_4AF	(tetracalcium alumino-ferrite)	10

REFERENCES

[1] Taylor, B.N.; Kuyatt, C.E.; NIST Technical Note 1297, *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results* (1993).

[2] Ferraris, C.F.; Avilés A.I.; Guthrie W.; Haupt, R. MacDonald B.; *Certification of SRM 114q*; *Phase I*, NIST SP260-161 (2005).

Certificate Revision History: 24 March 2005 (This technical revision corrects the certified values and expanded uncertainties for the measurand); 23 March 2005 (Original certificate date).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet http://www.nist.gov/srm.

Addendum

Standard Reference Material® 114q

Portland Cement Fineness Standard

Particle Size Distribution: The SRM 114q particle size distribution (PSD) was determined using laser diffraction (LD) techniques in a round-robin evaluation. Two LD methods were included in the tests: LD-W, in which the powder was dispersed in a liquid medium (wet) and LAS-D in which the powder was measured in a dry dispersed state as an aerosol (dry). The values given in this addendum were obtained through a round-robin inter-laboratory study by volunteer participants from companies participating in the CCRL certification program. Because the results obtained from the two methods were not found to be statistically different, the results were combined to calculate a mean PSD for LD, shown graphically in Figure 1 and tabulated in Table 4. A complete discussion of the test procedures and statistical analysis is provided in Ref. [3].

This particle size distribution could be used as a reference to validate methodology and instrument operation as described in Ref. [3], notes and Appendix below.

The parameters used to develop the PSD were:

- For LD-D and LD-W: the complex refractive index for the cement used had a real part of 1.7 and an imaginary part of 1.0
- For LD-W: IPA was used as the medium and the refractive index (real) used for IPA was 1.39; the imaginary part was zero.

Table 4. Table 4. Statistical results for the particle size distribution of SRM 114q using LD methodology [3]

Particle Size, µm	1.0	1.5	2.0	3.0	4.0	6.0	8.0	12.0	16.0	24.0	32.0	48.0	64.0	96.0	128.0
Mean Cumulative Volume Fraction, [%]	5.1	8	11.2	16.3	21	29.6	37.6	51	62.8	80.8	91.2	98.4	99.7	99.9	99.9
95 % Lower Expanded Uncertainty Bound [%]	3.8	6.2	9.1	13.9	18.1	26.1	33.8	46.8	57.9	78	89.4	97.4	98.9	99.1	99.1
95 % Upper Expanded Uncertainty Bound [%]	6.5	9.8	13.3	18.8	24	33.3	41.5	55.6	68	83.6	92.9	99.4	100.5	100.7	100.7

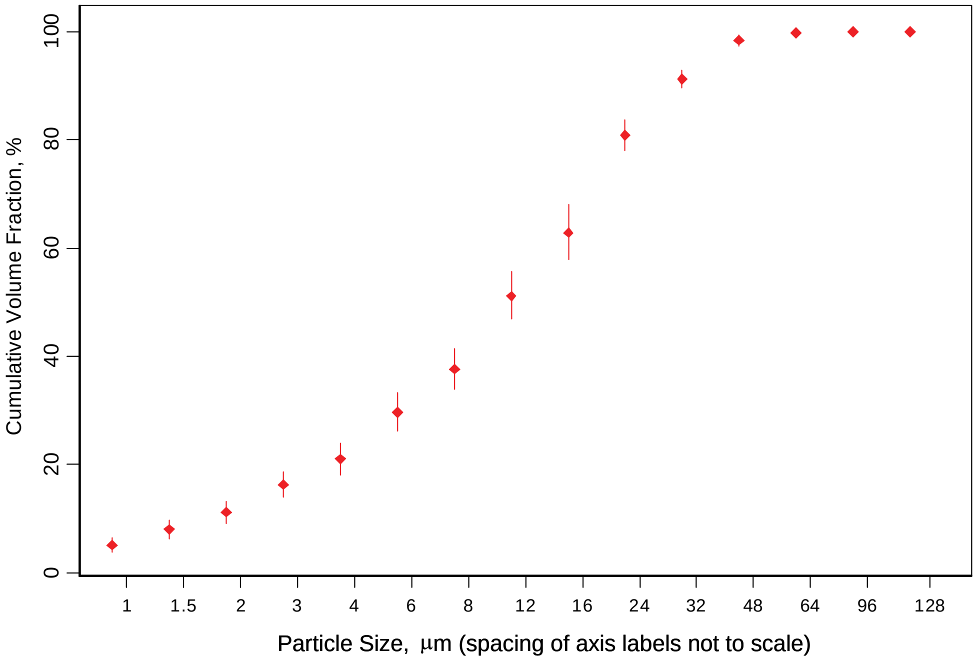

Figure 1. Graphical depiction of the particle size distribution of SRM 114q using LD (either wet or dry dispersion).

NOTES

The purpose of a reference PSD based on an easily accessible reference material is to verify the efficacy of an instrument and the procedure being used.

If the results are found to be statistically different from the SRM certified values, the operator should check the performance of the device, the parameters used (such as the refractive indices) or the procedure used (dispersion, ultrasound, duration of measurement, et cetera). For more details on the procedure, see Ref. [3].

REFERENCES

[3] Ferraris, C.F.; Avilés A.I.; Guthrie W.; Peltz M.; Haupt, R.; MacDonald B.; *Certification of SRM 114q*; *Phase II (Particle Size Distribution)*, NIST SP260-166 (2006).

Appendix: Conformity determination

The operator should start by measuring the SRM 114q at least 3 times using his own procedure and an instrument based on LD. These results can then be used to determine conformity at the following levels:

- General agreement of the results with other laboratories: Because there is no standard test method, a relatively large amount of between-lab variation is allowed in this situation
- Agreement to within-laboratory reproducibility: This level of agreement indicates that the user's results will not differ from the certified value of SRM 114q by more than expected based on the within-lab reproducibility of a typical laboratory.

Table 5: Simultaneous Expanded Uncertainties for Conformance Assessment with SRM 114q

Particle Size, µm	**Cumulative Volume Fraction (CVF) of SRM 114q, %**	**Simultaneous 95% Expanded Uncertainties for the Difference Between a Typical Lab and the Certified Value of SRM 114q, %**	**Simultaneous 95% Expanded Uncertainties for the Difference Between a Typical Lab and the Certified Value of SRM 114q Including Between Lab Variation, %**
1	5.1	2.0	7.6
1.5	8.0	2.8	9.9
2	11.2	3.2	11.8
3	16.3	3.8	13.8
4	21.0	4.6	15.7
6	29.6	5.5	18.2
8	37.6	5.9	19.0
12	51.0	6.7	19.7
16	62.8	7.6	20.2
24	80.8	4.4	15.2
32	91.2	2.8	10.5
48	98.4	1.6	4.2
64	99.7	1.2	2.0
96	99.9	1.2	1.8
128	99.9	1.2	1.8

As stated above, these expanded uncertainty intervals allow for two levels of conformance assessment. The first level indicates agreement with the results typically obtained by laboratories that participated in the interlaboratory study used for certification of the particle size distribution of SRM 114q. Because there is no currently agreed-upon standard test method for obtaining particles size distributions using laser diffraction, a relatively large amount of between-lab variation is allowed for in these uncertainties, given in column 4 of Table 5.

For laboratories that would like to assure tighter agreement with SRM 114q, the uncertainties in column 3 of Table 5 can be used instead. This level of agreement indicates that the user's results will not typically differ from the certified value of SRM 114q by more than the within-lab reproducibility of a typical laboratory.

To use these uncertainties to assess agreement with other laboratories, the user should compute the absolute difference in cumulative volume fraction between his or her results and the certified values for SRM 114q for each particle size. These differences should then be compared to the appropriate expanded uncertainties in columns 3 or 4 of Table 5 to determine conformance. If the observed absolute difference between the user's results and the certified values for SRM 114q is always less than the corresponding expanded uncertainty, then the user can conclude that his or her results are in agreement with other laboratories with a confidence level of approximately 95 %. If, on the other hand, one or more of the observed absolute differences is larger than the corresponding expanded uncertainty, this is evidence that the user’s results are not in agreement with the results of other laboratories and that changes to the measurement procedures are needed.

For more details on how the values were obtained see reference [3].

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