# Assessing the Precision and Accuracy of Particle-Size Analysis with a Laboratory Laser-Diffraction Analyzer

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## Introduction

The purpose of this study is to assess the precision and accuracy of laboratory laser-diffraction particle-size distribution (PSD) analysis in support of an effort to formally adopt the method for routine use in U.S. Geological Survey (USGS) sediment laboratories. USGS sediment laboratories analyze the PSD of sediment in support of a wide variety of sediment-transport and water-quality studies from around the United States (US).

The precision of the PSD for a sample can be assessed through replicate measurements, with typical quality control (QC) standards in USGS sediment laboratories requiring that the PSD results from primary and replicate sub-samples differ by no more than five percent finer to meet standards for acceptability (Shreve and Downs 2005). Precision defined in this way captures the combined uncertainty of the subsampling, preparation, and PSD analysis methods used in the analysis.

The International Standards Organization (ISO) defines precision for laser-diffraction analysis in terms of repeatability and reproducibility. To isolate the uncertainty associated with the laser-diffraction PSD analysis method, the ISO standard for laser-diffraction analysis requires the assessment of the coefficient of variation (CV) of the 10th, 50th, and 90th percentile diameters ( $d_{10}$ ,  $d_{50}$ ,  $d_{90}$ ) among at least three repeated measurements of the same material (instrument repeatability) or at least three separate subsamples of the same bulk material (method repeatability) (ISO 13320:2009 6.4). The method used in this study adopts this definition of precision for QC of laser-diffraction PSD analysis.

The ISO standard also calls for method reproducibility checks using the same assessment technique (ISO 13320:2009 6.4). Method reproducibility checks by the ISO definition require multiple measurements of separate subsamples of the same bulk material by different operators using similar instruments (ISO 13320:2009 3.1). Because only one instrument and one operator were available for this study, reproducibility was assessed by measuring separate subsamples of the same bulk material over time.

Instrument accuracy for laboratory laser-diffraction analysis is assessed through the measurement of mixtures of spherical glass beads (ISO 13320:2009 6.5). According to the ISO standard, the best practice is to use nationally-traceable certified reference materials with well-known optical properties and a  $d_{90}/d_{10}$  ratio of at least 1.5 (ISO 13320:2009 6.5). The current protocol requires the measurement of traceable glass bead reference materials as part of the QC for the analysis.

Laboratory laser-diffraction results are reported in terms of the *laser-diffraction diameter*, which is the diameter of a spherical particle that produces the same light scattering pattern as the target particle, using a given optical model. The optical model requires the real and imaginary components of the refractive index (RI) of the particles in the sample as parameters. By this definition, an instrument that has verified accuracy for spherical particles of a known RI produces accurate results.

PSD results produced by laser-diffraction analysis are reported in terms of the percent by volume of sediment in a sample that occurs in various user-defined size classes. This contrasts with sieve and sedimentation methods, which are based on the percent by mass of sediment that is measured in user-defined size classes. Mass-based and volume-based particle-size analysis results can be used interchangeably as long as the particles in each size class have the same average density within a sample.

Different PSD analysis methods use different definitions of the "diameter" of irregularly-shaped particles (Inter-Agency Committee on Water Resources, Subcommittee on Sedimentation, 1957). Consequently, the PSD produced by one method cannot be directly compared to the results from a different PSD method unless the particles are spherical and any other assumptions required by both methods are met. Previous studies of inter-method comparability between laser-diffraction and other PSD analysis methods have mostly concluded that intermethod calibrations are possible for some populations of particles, but that there is no scientific basis for developing universal inter-method calibration functions between laser-diffraction and any other PSD analysis method (Kowlenko and Babuin 2013; Roberson and Weltje 2014). The unpredictable inter-method comparability between laser-diffraction and other PSD analysis methods limits the ability to test the accuracy of the particle sizes measured in laser-diffraction PSD analysis to testing with artificial spherical particles.

Because the purpose of the current protocol is to measure naturally-occurring sediment, a further definition of accuracy has been adopted that allows the laser-diffraction instrument to be tested with geologic materials. Accuracy in this context is extended to include the capacity of a PSD analysis to correctly measure PSD for mixtures of reference materials, each component of which has a well-known PSD for the target method. Under this definition of accuracy, the target of measurement is not the diameter of the particles, but rather the proportion of the sample composed of particles that fall into user-specified diameter ranges. The same method is used to define the accuracy targets and to perform the performance tests. Testing accuracy by this definition demonstrates whether a PSD analysis method is internally consistent without reference to other PSD analysis methods.

### Methods

A single-wavelength Beckman-Coulter LS13320 particle-size analyzer with the Aqueous Liquid Module (ALM) attachment was tested with 1) vendor-supplied reference materials 2) NIST-traceable polydisperse glass bead standards 3) mixtures of commercially-available glass beads 4) mixtures of sands (<1 mm to >0.063 mm) and fines (<0.063 mm). Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Two vendor-supplied reference materials were measured: G15 (Beckman-Coulter), a garnet sample with a mean diameter of approximately 15 microns ( $\mu$ m), and GB500 (Beckman-

Coulter), a population of glass beads with a mean diameter of approximately  $500\mu m$ . The vendor-supplied reference materials were prepared and analyzed according to the instructions provided by the vendor. The results from the LS13320 were compared to the defined targets for mean and standard deviation of the PSD supplied by the vendor.

Three NIST-traceable polydisperse glass bead reference materials were measured: Whitehouse Scientific  $3-30\mu m$  (PS204),  $50-350\mu m$  (PS227), and  $150-650\mu m$  (PS237) standards. All three materials met the ISO requirements for use as an accuracy verification material for laser-diffraction analysis (ISO 13320:2009 6.5).

The 3–30µm material was suspended in a 1:100 solution of chemical dispersant (Guy 1969, p. 29) and de-ionized water (DI). The suspension was physically dispersed for 10–12 seconds with a sonic probe (Sonic Materials Vibra Cell VC375, power level 6, 90% duty cycle).

The coarser two materials (PS227, PS237) were split into two subsamples using a vane splitter (Rickly Hydrological Hydrolgical #505-001). The prepared material was introduced to the ALM and analyzed for three 30-second or 60-second runs following the instructions in the LS13320 user manual (Beckman-Coulter, 2011). The choice of 30-second or 60-second runs was made to explore whether differences in the results were observed based on run duration. The repeatability of each analysis was assessed according to the ISO method (ISO 13320:2009 6.4) using the instrument software. The LS13320 software was used to produce the geometric  $d_x$ values for the average of the three runs under both the glass optical model (RI: real component 1.5, imaginary component 0) and the Fraunhofer model (RI: real component 0, imaginary component 1). The Fraunhofer model is known to be inaccurate for particles finer than about 50µm for transparent particles and about 2µm for opaque particles (ISO 13320:2009 Annex A), however for most naturally-occurring sediment the RI is unknown, so the Fraunhofer model is used to provide a uniform basis for comparison with other results. The measured  $d_x$  values were compared to the target values on the Certificate of Analysis for the reference material. The control limits for the target values were the 95%CI times 1.03 or 1.04 as specified in ISO 1320:2009 6.5.

Internal reference materials (IRMs) of monodisperse commercially-available glass beads and geologic materials were created by measuring replicate subsamples of each IRM in the LS13320 under a variety of analysis conditions (e.g. run duration, pump speed, dilution). Three size ranges of glass beads were used: Polysciences 30–50 microns (Catalog #18901), 150–210 microns (Catalog #05483), and 210–250 microns (Catalog #18902). Six geologic materials were created by dry-sieving material contained in a bag of "Play Sand" (Quickrete, sourced from a local home improvement center) at standard phi intervals (2.0mm, 1.0mm, 0.5mm, 0.250mm, 0.125mm, 0.063mm). The sands were washed and oven-dried at 103°C after dry-sieving; the fines were oven-dried at 103°C after dry-sieving. A second population of fines was dry-sieved from a bed-material sample that had been collected in a stormwater settling basin in California. The fines from the settling basin were finer than the Quickrete fines based on a sedigraph analysis. The settling basin fines are referred to as 'Clayey' fines and the Quickrete fines are referred to as 'Silty' fines. The proportions of the reference materials used in each test mixture are given in Table 1 and Table 2.

At least six scoop subsamples were taken of each IRM. The size of the scoop was sufficient to produce the target 8 to 12 percent obscuration in the LS13320 (Beckman-Coulter, 2011), and varied by the size of the particles (Norton, 2019). The fines were suspended and dispersed as

described above for the polydisperse glass beads, but with 30 seconds of sonication. The subsamples were introduced to the ALM and analyzed according to the instructions in the LS13320 user's manual (Beckman-Coulter, 2011). The volume percent of each subsample that fell into each of the 92 size bins measured by the LS13320 was computed based on the Fraunhofer optical model. The mean and standard deviation of the volume percent in each size bin was computed among all the subsamples of each IRM.

**Table 1.** Percent by mass of each of three glass bead (GB) internal reference materials (Polysciences) used to construct mixtures for accuracy testing of the laboratory laser-diffraction analysis

Mixture	210–250µm	150–210µm	30–50µm
GB-A	20	0	80
GB-B	24	52	24
GB-C	50	50	0
GB-D	5	95	0
GB-E	75	25	0

**Table 2.** Percent by mass of each of six sediment (SED) internal reference materials used to construct mixtures for accuracy testing of the laboratory laser-diffraction analysis.

Mixture	500– 1000µm	250– 500µm	125– 250µm	63– 125µm	Silty Fines	Clayey Fines
SED-A	20	30	20	20	10	0
SED-B	0	10	20	20	0	50
SED-C	39	0	50	0	0	11
SED-D	0	0	0	0	80	20
SED-E	0	0	0	0	50	50
SED-F	0	0	0	0	20	80

Test mixtures of the IRMs were prepared by combining known masses of the individual IRMs to construct test samples with well-known expected PSD results from laser-diffraction analysis. For SED-A, SED-B, and SED-C, two separate test samples were prepared with identical proportions of the IRMs but different total mass. The expected volume percent in each size bin was computed as:

$$p_e = \sum_{i=1}^n \frac{m_i}{m} p_i \tag{1}$$

where  $p_e$  was the expected volume percent in a single size bin measured by the LS13320, n was the number of IRMs used to construct the test sample,  $m_i$  was the mass of a single IRM within the test sample in grams, m was the total mass of the test sample in grams, and  $p_i$  was the mean volume percent in the target size bin for the IRM. Using the mass-based weighted average to compute an expected volume percent depended on the assumption that there was no systematic difference in density among the IRMs that were used to construct a test sample.

The standard deviation of the replicate tests of each IRM was used to compute a standard deviation of the expected volume percent for each size bin using standard methods for propagation of uncertainty:

$$\sigma_{pe} = \sqrt{\sum_{i=1}^{n} \frac{m_i}{m} \sigma_{p(i)}^2}$$
<sup>(2)</sup>

where  $\sigma_{pe}$  was the standard deviation of the expected volume percent in a single size bin measured by the LS13320,  $\sigma_{p(i)}$  was the standard deviation of the volume percent in the target size bin for the IRM, and other symbols were as described above.

The test samples were subsampled, prepared, and analyzed in the LS13320. When sands and fines were included in the same mixture, the fines were separated from the sand by sieving, and each fraction was subsampled and analyzed separately in the LS13320. The sand fractions were subsampled using the vane splitter. The fines were subsampled by either scoop subsampling or aliquot subsampling. Three 60-second runs on the LS13320 were measured at the target 8 to 12 percent obscuration for each subsample (Beckman-Coulter 2011). Other details of the handling and run conditions are documented in Norton (2019). The test results were checked for quality standards, including instrument repeatability and obscuration. The whole-sample volume percent finer was computed according to Equation 1, using the observed mass of sand and fines in the sample. This method of combining results from separate laser-diffraction analysis of multiple fractions in a sample was similar to that used by the USGS Coastal and Marine Geology Laboratory in Santa Cruz, Calif. (Penscil Inc., 2011). Observed results for the volume percent in each size bin from the LS13320 were compared to the expected volume percent to investigate the accuracy of the laser-diffraction PSD analysis for geologic materials.

#### Results

#### **Vendor-Supplied Reference Materials**

The LS13320 produced results for vendor-supplied reference materials that fell within the targets identified by the vendor (Table 1). The passing results indicate that the instrument was installed correctly and was operated in accordance with the instructions provided by the vendor.

Material	Analysis Date	Test statistic	Expected Value (µm)	Control Limits (µm)	Observed Value (µm)	Pass/ Fail
G15	8/10/2017	Mean	14.4	±1.8	14.54	Pass
		St.Dev.	6.17	±2.25	6.383	Pass
GB500	8/10/2017	D10	518	±25.9	518.1	Pass
		D50	578	±17.3	577.9	Pass
		D90	645	±32.2	644.6	Pass
G15	3/12/2018	Mean	14.4	$\pm 1.8$	14.80	Pass
		St.Dev.	6.17	±2.25	6.519	Pass
G15	3/28/2018	Mean	14.4	$\pm 1.8$	14.60	Pass

 Table 3. Results from analysis of two vendor-supplied reference materials in a Beckman-Coulter LS13320 with Aqueous Liquid Module attachment.

		St.Dev.	6.17	$\pm 2.25$	6.371	Pass
GB500	8/10/2017	D10	518	±25.9	518.5	Pass
		D50	578	±17.3	577.5	Pass
		D90	645	±32.2	643.1	Pass
G15	5/21/2018	Mean	14.4	$\pm 1.8$	14.60	Pass
		St.Dev.	6.17	$\pm 2.25$	6.446	Pass

#### **NIST-Traceable Polydisperse Glass Bead Reference Materials**

Tests of the NIST-traceable polydisperse glass bead reference materials demonstrated that the laser-diffraction analysis met the ISO standards for precision, as measured by the repeatability and reproducibility. All the tests except for one passed the ISO instrument repeatability test for the CV of the  $d_{10}$ ,  $d_{50}$ , and  $d_{90}$  values among the 3 runs in each set (ISO 13320:2009 6.4, Norton, 2019). Similarly, the method repeatability among 3 to 8 replicate measurements of each reference material was excellent, with the CV of the  $d_{10}$ ,  $d_{50}$ , and  $d_{90}$  falling within the ISO standards for all but the finest size reported for the finest standard (Table 4, Table 5, Table 6). Details of the analysis conditions and the results from individual tests can be found in the data release that accompanies this report (Norton, 2019).

The LS13320 results for the 3–30um NIST-traceable polydisperse glass beads fell within the certified targets for all but the  $d_{90}$  when the glass optical model was used (Table 4). When the Fraunhofer model was used, the  $d_{10}$  and  $d_{25}$  results were lower than the control limits (Table 4).

**Table 4.** Results from analysis of a 3–30um NIST-traceable polydisperse glass bead reference material (WhitehouseScientific PS205). The control limits for the expected results were computed based on the standards outlined in ISO13320:2009 6.5

 $[d_x:$  the particle size at which x percent of the total sediment volume in the sample occurs in particles of a smaller size than the Dx value; St.Dev.: Standard Deviation; Fraun.: Fraunhofer; CV: Coefficient of Variation]

Percentile Diameter	<b>d</b> 10	<b>d</b> 25	<b>d</b> 50	<b>d</b> 75	<b>d</b> 90
Lower Control Limit (µm)	8.25	10.28	12.55	15.33	18.84
Upper Control Limit (µm)	10.03	11.76	14.51	17.71	21.84
Observed dx (µm), Glass Optical Model	8.848	10.70	13.26	16.75	21.88
Mean of n=3 replicate tests					
Observed dx (µm), Glass Optical Model	0.121	0.18	0.14	0.21	0.58
St. Dev. of n=3 replicate tests					
CV (St. Dev./Mean), Glass Optical Model	1.4%	1.1%	1.1%	1.3%	2.7%
Observed dx (µm), Fraun. Optical Model	1.803 <sup>a</sup>	9.363	13.11	17.04	20.72
Mean of n=3 replicate tests					
Observed dx (µm), Fraun. Optical Model	0.269	0.148	0.21	0.31	0.56
St. Dev. of n=3 replicate tests					
CV (St. Dev./Mean), Fraun.Optical Model	14.9%	1.6%	1.6%	1.8%	2.7%

 $^a$  Only two replicate tests were used for the  $d_{10}$  value because one test did not pass the quality check for instrument repeatability of the  $d_{10}$  value.

The LS13320 results for the 50–350um and 150–650um NIST-traceable polydisperse glass beads fell within the certified targets for some of the  $d_x$  values (Table 5, Table 6). However, the LS13320 consistently measured the  $d_{25}$ ,  $d_{50}$ , and  $d_{75}$  values as coarser than the upper control

limit for the 50–350 $\mu$ m standard (Table 5). Similarly, the LS13320 consistently measured the d<sub>10</sub>, d<sub>50</sub>, d<sub>75</sub>, and d<sub>90</sub> values as coarser than the upper control limit for the 150–650 $\mu$ m standard (Table 6). The excellent reproducibility of the results across a range of conditions (Norton, 2019) indicated that the readings were unlikely to be due to variations in handling, subsampling, or analysis conditions.

**Table 5.** Results from analysis of a 50–350um NIST-traceable polydisperse glass bead reference material(Whitehouse Scientific PS227). The control limits for the expected results have been computed based on the<br/>standards outlined in ISO 13320:2009 6.5

[d<sub>x</sub>: the particle size at which x percent of the total sediment volume in the sample occurs in particles of a smaller size than the Dx value; St.Dev.: Standard Deviation; Fraun.: Fraunhofer; CV: Coefficient of Variation]

Percentile Diameter	<b>d</b> <sub>10</sub>	<b>d</b> <sub>25</sub>	<b>d</b> 50	<b>d</b> 75	<b>d</b> 90
Lower Control Limit (µm)	90.05	117.3	147.9	185.3	232.5
Upper Control Limit (µm)	97.35	119.7	153.7	195.2	245.1
Observed dx (µm), Glass Optical Model	97.98	122.9	157.4	197.1	237.7
Mean of n=8 replicate tests					
Observed dx (µm), Glass Optical Model	0.53	0.5	0.5	0.6	0.8
St. Dev. of n=8 replicate tests					
CV (St. Dev./Mean), Glass Optical Model	0.5%	0.4%	0.3%	0.3%	0.4%
Observed dx (µm), Fraun. Optical Model	97.31	123.8	157.9	197.2	236.9
Mean of n=8 replicate tests					
Observed dx (µm), Fraun. Optical Model	0.60	0.5	0.5	0.6	0.8
St. Dev. of n=8 replicate tests					
CV (St. Dev./Mean), Fraun Optical Model	0.6%	0.4%	0.3%	0.3%	0.4%

**Table 6.** Results from analysis of a 150–650μm NIST-traceable polydisperse glass bead reference material (Whitehouse Scientific PS237). The control limits for the expected results have been computed based on the standards outlined in ISO 13320:2009 6.5

[d<sub>x</sub>: the particle size at which x percent of the total sediment volume in the sample occurs in particles of a smaller size than the Dx value; St.Dev.: Standard Deviation; Fraun.: Fraunhofer; CV: Coefficient of Variation]

Percentile Diameter	<b>d</b> <sub>10</sub>	<b>d</b> 25	<b>d</b> 50	<b>d</b> 75	<b>d</b> 90
Lower Control Limit (µm)	239.9	301.3	356.9	419.4	508.3
Upper Control Limit (µm)	248.1	310.7	368.3	428.6	545.7
Observed dx (µm), Glass Optical Model	253.1	303.4	371.4	458.0	561.3
Mean of n=3 replicate tests					
Observed dx (µm), Glass Optical Model	1.3	1.0	1.5	3.5	6.1
St. Dev. of n=3 replicate tests					
CV (St. Dev./Mean), Glass Optical Model	0.5%	0.3%	0.4%	0.8%	1.1%
Observed dx (µm), Fraun. Optical Model	253.1	303.4	371.4	458.1	561.4
Mean of n=3 replicate tests					
Observed dx (µm), Fraun. Optical Model	1.2	1.0	1.5	3.5	6.1
St. Dev. of n=3 replicate tests					
CV (St. Dev./Mean), Fraun Optical Model	0.5%	0.3%	0.4%	0.8%	1.1%

#### **Internal Reference Materials**

Tests of the IRMs demonstrated that the laser-diffraction analysis with the LS13320 met the ISO standards for repeatability and reproducibility. The instrument repeatability was checked using the ISO standards (ISO 13320:2009 6.4); only two out of 74 tests had a CV of the  $d_{10}$ ,  $d_{50}$ , or  $d_{90}$  that was larger than the ISO target of <3% for the  $d_{50}$  and <5% for the  $d_{10}$  and  $d_{90}$ . (Norton, 2019). When the  $d_x$  values are less than 10µm, the targets can be doubled (ISO 13320:2009 6.4.2). Similarly, the reproducibility among 4 to 6 replicate measurements of each reference material was excellent, with the CV of the  $d_{10}$ ,  $d_{50}$ , and  $d_{90}$  among the replicate tests falling within the ISO standards (Table 7). Details of the analysis conditions and the results from individual tests are documented in Norton (2019).

 Table 7. Reproducibility of the d<sub>10</sub>, d<sub>50</sub>, and d<sub>90</sub> computed from a laser-diffraction PSD analysis among n replicate subsamples of a mixture of internal reference materials. Details of the composition of the mixtures can be found in Table 1 and Table 2. All values were computed using the Fraunhofer optical model.

[S/F: (S)and or (F)ines, the fraction analyzed in the LS13320; Hv: Heavy; Lt: Light;  $d_x$ : the particle size at which x percent of the total sediment volume in the sample occurs in particles of a smaller size than the Dx value; St.Dev.: Standard Deviation; CV: Coefficient of Variation]

Mixture	S/F	n	Mean	St. Dev.	CV	Mean	St. Dev.	CV	Mean	St. Dev.	CV
			<b>d</b> <sub>10</sub>	<b>d</b> <sub>10</sub>	<b>d</b> <sub>10</sub>	<b>d</b> <sub>50</sub>	<b>d</b> <sub>50</sub>	<b>d</b> 50	<b>d</b> 90	<b>D9</b> <sub>0</sub>	<b>d</b> 90
			μm	μm	%	μm	μm	%	μm	μm	%
GB-A	All	4	39.97	0.05	0.1	46.89	0.11	0.2	228.4	1.1	0.5
GB-B	All	4	44.12	0.15	0.3	178.0	0.5	0.3	230.4	0.4	0.2
GB-C	All	4	155.6	1.0	0.6	202.2	0.6	0.3	254.2	0.5	0.2
GB-D	All	4	146.9	0.6	0.4	179.3	0.3	0.1	211.5	0.4	0.2
GB-E	All	4	173.6	0.8	0.5	217.7	0.3	0.1	253.3	0.3	0.1
SED-A Hv	S	6	133.3	0.9	0.7	411.8	8.7	2.1	880.0	22.3	2.5
SED-A Hv	F	4	3.420	0.165	4.8	28.38	0.55	1.9	69.99	1.56	2.2
SED-A Lt	S	6	136.5	2.3	1.7	429.6	10.3	2.4	871.8	1.2	2.1
SED-A Lt	F	6	3.854	0.253	6.6	27.96	1.17	3.9	70.44	18.00	1.8
SED-B Hv	S	6	105.3	0.4	0.4	215.4	2.2	1.0	489.4	3.7	0.8
SED-B Hv	F	5	1.056	0.005	0.5	7.133	0.140	2.0	35.79	0.84	2.3
SED-B Lt	S	5	105.2	1.0	1.0	539.6	1.6	0.7	516.6	3.3	0.6
SED-B Lt	F	4	1.048	0.010	0.9	7.869	0.114	1.6	36.12	0.76	2.1
SED-C Hv	S	6	191.5	1.0	0.5	571.2	10.0	1.7	1028	7	0.6
SED-C Hv	F	4	1.085	0.007	0.6	7.571	0.068	0.9	36.77	0.32	0.9
SED-C Lt	S	6	188.6	2.0	1.1	220.3	30.6	5.7	1021	12	1.2
SED-C Lt	F	4	1.093	0.012	1.1	7.122	0.071	0.9	36.82	0.24	0.7
SED-D	All	4	1.120	0.004	0.3	8.418	0.06	0.7	41.93	0.52	1.2
SED-E	All	4	1.242	0.004	0.3	12.41	0.06	0.5	51.56	0.25	0.5
SED-F	All	4	1.580	0.008	0.5	18.48	0.08	0.4	58.95	0.16	0.3

The difference between the observed volume percent and the expected volume percent in each size class was greater for coarser sizes than for finer sizes for both the glass bead IRMs and the sediment IRMs (Figure 1, Figure 2). The glass bead IRMs did not show a consistent pattern of reading coarser or finer than the expected value for the sand-sized size classes (Figure 1). Rather, the deviation from the expected value varied depending on the test mixture (Figure 1).



**Figure 2**: Difference between the mean observed volume percent and the expected volume percent in each size class for n=4 replicate subsamples of mixtures of internal reference materials prepared from commercially-available glass beads. The composition of each mixture is given in Table 2. Channels outside the range of the sizes of the beads are omitted for visual clarity; no sediment was detected in any of the omitted channels.



**Figure 1**: Difference between the mean observed volume percent and the expected volume percent in each size class for mixtures of internal reference materials prepared from commercially-available play sand. The composition of each mixture is given in Table 2.

For the sediment IRMs, the sand PSD measured in the LS13320 was shifted coarse relative to the expected values (Figure 2). In contrast, the difference between the observed and expected values for the fines was very low (Figure 2). The pattern of coarse-shift for the sands was very similar between the heavy (Hv) and light (Lt) test samples for each of the three mixtures that had two test samples (SED-A, SED-B, SED-C, Figure 2).

## **Discussion and Conclusions**

The laser-diffraction PSD method in this study is precise because it is both repeatable and reproducible. As with any PSD analysis, variation in sample handling can affect the reproducibility of the results. However, the laser-diffraction PSD analysis in this study was reproducible under normal variation in sample handling methods for a single operator in a single laboratory over time.

The observation that laser-diffraction PSD analysis has excellent precision agreed with findings from other studies. Kuchenbecer et.al. (2012) conducted an inter-laboratory study with 31 European labs and found that all were able to meet (or exceed) the ISO method repeatability targets for well-prepared subsamples of three different reference materials. For well-prepared subsamples, the method repeatability of a laser-diffraction analysis can be better than other particle size analysis methods, including the sedigraph (Goossens, 2008; Roberson and Weltje, 2014), the pipet (Beuselinck and others, 1998), and dry sieving (Blott and Pye, 2006). When the results of the laser-diffraction PSD analysis are combined with results from a different method (for example, sieving material too coarse to analyze with laser diffraction), the uncertainty of the combined PSD is dominated by the uncertainty on the least-certain method used for a sample.

The accuracy of the laser-diffraction PSD method in this study was verified for fines. The accuracy of the physical sizing of spherical particles with known optical properties was verified by the tests of the 3–30µm NIST-traceable glass bead standard (Table 4). Further, the accuracy of the observed proportions of different mixtures of fine IRMs was verified by the fact that there was a negligible difference between the observed and expected volume percent in each size class for these test mixtures (Figure 2, SED-D, SED-E, SED-F). While this test cannot verify that results from this laser-diffraction analysis method will match fine PSD results from other methods, it does indicate that the method used to analyze fines in this study is internally consistent.

Knowing that the laser-diffraction PSD analysis method used in this study can correctly detect proportions of mixtures of fines suggests that the method can be used to measure PSDs that can be compared among each other, and further suggests that the method could likely be used to calibrate results to other fine PSD analysis results if an inter-method comparison is required. Careful investigation of the RI of various populations of sediment particles could improve the accuracy of laser-diffraction PSD results by allowing a Mie optical model to be used to compute the results. Such studies would be methodologically challenging, however, and would still require further calibration to relate the laser-diffraction PSD results to the PSD results from sedimentation methods, which have direct hydraulic interpretability for sediment transport studies.

The accuracy of the laser-diffraction PSD analysis method used in this study was not verified for sand. This finding agrees with other observations. Blott and Pye (2006) found that an LS230 (Beckman-Coulter) over-reported the proportion of the coarse component of mixtures of ballotini (glass beads) in the sand size range. They observed that the LS230 may have been over-fitting log-normal distributions to a variety of data sets (Blott and Pye, 2006). The inversion of a light-scattering signal to a PSD is a complex mathematical operation and requires some constraints to produce viable results; however, over-constraint can lead to inaccurately wide PSD results (ISO 13320:2009 Annex A.10). Each model of laser-diffraction PSD instrument and software algorithm likely uses different constraints. The details of the LS13320 algorithm are proprietary, but it is possible that the software is using constraints that produce reasonable-looking, but sometimes inaccurate, PSD results in the coarser size ranges.

Because each laser-diffraction instrument model has different a physical configuration and uses different software algorithms, the findings in this study are not generalizable across all makes and models of laser-diffraction instruments. Particle shape and surface roughness alter the light-scattering pattern produced by natural particles compared to spherical particles (ISO 13302:2009 Annex A). Each instrument make and model is affected differently by irregular-shaped particles and handles the interpretation of the observed light scattering pattern differently, leading to weak expectations of reproducibility of laser diffraction results across different instrument makes and models. Kuchenbecer et. al. (2012) found clear differences among different makes and models of laboratory laser-diffraction instruments in their inter-laboratory study, but also observed good reproducibility among different laboratories using the same make and model laser-diffraction instrument. The techniques used in this study to assess the precision and accuracy of a laboratory laser-diffraction PSD method using a single instrument in a single laboratory can be used by other operators in other laboratories with other instruments to conduct laboratory-specific quality assessments for laser-diffraction analysis.

Further work is needed to evaluate how to incorporate laser-diffraction PSD analysis into the workflow for sediment studies at the USGS and beyond. For fines, laser-diffraction PSD analysis dramatically expands the range of sediment samples for which PSD information can be obtained because the laser-diffraction method typically requires only 0.1-0.3 grams of fines for a reproducible PSD analysis (Norton, 2019). A typical sedimentation method such as the pipet method requires a minimum of 0.8 grams (Guy 1969). For sands, the LS13320 records 37 channels for particles  $63-2000\mu$ m. A similar quarter-phi sieve analysis records 21 size classes. Thus, the laser-diffraction PSD analysis for sands produces higher resolution results than traditional sand analysis methods. The higher resolution should lead to greater precision on  $d_x$  values for the sand fraction than a sieve analysis can produce.

The promise of laser-diffraction PSD analysis will likely best be realized through the use of sediment-population-specific calibrations between laser-diffraction results and results produced by other methods. Determining how to produce, verify, document, and use such calibrations in fluvial sediment projects is likely a next step in incorporating laser-diffraction PSD into the sediment project workflow.

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