Method Article

A novel binary pipette splitting sediment subsampling method for improving reproducibility in laser-diffraction particle-size analysis

Zhixiong Shen*, Nicholas Conway, Till J.J. Hanebuth

Department of Marine Science, Coastal Carolina University, Conway, SC 29526, United States

A B S T R A C T

Laser-diffraction analysis has been established as one of the standard methods for particle-size distribution (PSD) measurement. However, the uncertainty when analyzing naturally heterogeneous sediment is poorly constrained for the lack of control on one of its largest error sources simply originating from subsampling. Here, we introduce a novel subsampling method, binary pipette splitting (BPS), and verify its precision by using sediment samples from ten flood-layer deposits that have formed in the wake of Hurricane Florence (2018). The BPS approach avoids extracting from only a fixed part of the suspended fluid but considers all the suspended sediment, resulting in the generation of twin subsamples. The median coefficient of variation (COV) for D10, D50, and D90 of subsamples obtained using BPS is 4%, 3%, and 2%, respectively. These values are significantly smaller than the corresponding values of 18%, 15%, and 13% obtained using the conventional pipette subsampling method. Therefore, the new BPS method represents a significant improvement in producing statistically identical subsamples for laser-diffraction particle-size analysis.

• The binary pipette splitting (BPS) subsampling method dramatically improves the reproducibility of subsampling wet sediment.

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A R T I C L E   I N F O

Method name: Binary pipette splitting

Keywords: Laser diffraction, Splitting, Subsampling, Sedimentology

Article history: Received 17 June 2021; Accepted 17 August 2021; Available online 20 August 2021

* Corresponding author.

E-mail address: zshen@coastal.edu (Z. Shen).

https://doi.org/10.1016/j.mex.2021.101493

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Specifications table

| Subject Area: | Earth and Planetary Sciences |
|---------------|------------------------------|
| More specific subject area: | Geology, Sedimentology |
| Method name: | Binary pipette splitting |
| Name and reference of original method: | Merkus, H.G., Particle Size Measurements: Fundamentals, Practice, Quality. Particle Technology Series. Vol. 17. 2009: Springer, Dordrecht. |
| Resource availability: | N.A. |

*Method details*

**Background**

Particle-size distribution (PSD) analysis is fundamental to sedimentary geology and has been used for investigating sedimentation processes [e.g. 1–4], paleoclimate [e.g. 5–7], and guiding soil classification [e.g. 8], for instance. Recent development in unmixing PSD [e.g. 9,10] revitalizes PSD analysis for paleoclimatic [e.g. 11,12] and paleohydrological studies [e.g. 13,14,15]. Laser-diffraction analysis has been established as one of the standard methods for PSD measurement because it has high precision, reduces measurement time, and works with a small sample size (<1 g) that enables, for example, ultrahigh-resolution (mm-scale) stratigraphic studies. The laser-diffraction method takes particle size as the diameter of an assumed sphere that scatters monochromatic coherent light at the same forward angle as the particle does. PSD is then obtained based on the intensity of the forward diffracted light at all detectable angles during the sample's solid suspension is circulated through the measurement cell in front of laser beams.

Previous studies have investigated many factors that could potentially affect the accuracy of laser-diffraction analysis, including sample preparation, the applicability of the Fraunhofer diffraction and Mie scattering theories, and the optical properties of particles [e.g. 16–21]. However, little has been done to address the fundamental issue of obtaining representative subsamples (aliquots) from wet, heterogeneous sedimentary material that was regarded as almost impossible yet [16]. Miller and Schaezel [8] found that subsampling is the primary source of error in laser-diffraction analysis even for relatively homogenous loess samples, and the sampling error increases with a coarser sediment texture. A mechanical splitter or riffler is often used to subsample dry material [22], yet natural sediment samples are often notoriously heterogeneous, i.e., containing a poorly sorted mixture of particle-size sub-populations, and prepared in wet. Pipetting from suspension or subsampling with a spatula from a thick sediment paste has been recommended [22–25]. However, these methods suppose that the sediment particles are well-mixed with each other, an assumption that is questionable. Fisher et al. [18] used the dispersion and circulation unit of a Mastersizer 2000 creatively to split wet samples, but this method is not recommended by the machine manufacturer and does not apply to differently designed laser-diffraction analyzers.

Here, we introduce a novel binary pipette splitting (BPS) method to overcome the difficulty of obtaining representative subsamples from a sediment suspension and verify the reliability of the method on ten sediment samples freshly collected from young flood-layer deposits that have formed during the Hurricane Florence event that hit South and North Carolina in fall 2018 [26]. Because it is almost impossible to particularly keep the sand fraction homogenously suspended, conventional pipette subsampling methods recommended pipetting from a certain depth in the vial carrying the sediment suspension while stirring the suspension [24,25] (Fig. 1A), which is operationally impractical. We designed the BPS method according to the principle that a representative subsample should consist of material collected from the entire suspension over discrete times, instead of over a fixed part of it continuously [cf. 22]. To achieve this goal, we continuously pipette the agitated suspension to create a virtually outward stream flow of sediment. The pipetted content is then alternately re-combined to create two new twin-subsamples that represent an equal 50% split of the original sample. Each subsample may undergo repeated similar binary splits if needed until the desired small sediment mass is obtained (Fig. 1B).
Fig. 1. Schematic diagrams of (A) the conventional pipette and (B) the novel binary pipette splitting (BPS) subsampling methods to extract a suitable quantity of particles for laser-diffraction particle-size analysis. In both methods, the sediment suspension is maintained by continuous stirring or shaking. In conventional pipetting, a random subsample is pipetted out of the suspension and transferred directly into a laser analyzer. In BPS, the suspension is binarily split repeatedly into two equally sized twin-subsamples until the desired quantity of sediment is obtained in the subsamples. Each subsample is expected to be identical to all other subsamples and can, subsequently, be transferred to a machine.

Method details

Materials and instrument

We used ten sediment samples of recent flood layer deposits that have resulted from the widespread and severe 2018 Hurricane Florence inundation [26], to develop and verify the PBS method. These samples were collected from the bottom of three oxbow lakes along the Great Pee Dee River and at two sites in the Winyah Bay estuary (both in SC), into which the river drains. A few grams of each sediment sample were prepared with the following procedure.

1) Place the sample in a 50 ml beaker and add 5 ml 30% hydrogen peroxide (H₂O₂) to digest the organic matter. If the chemical reaction is too strong, dilute the suspension-hosting solution with deionized water to slow it down.
2) Wait for about 1 hr for the reaction to stabilize and fill the beaker with deionized water up to 50 ml so that the sample does not dry out while leaving overnight to complete the reaction. If organics remains after 24 h through visual examination, add another 5 ml 30% H₂O₂ to complete the reaction.
3) Boil the suspension-hosting solution for about 2 min using a hotplate to remove any residual H₂O₂.
4) Add 3 ml 0.1 M sodium hexametaphosphate (‘Calgon’) to the beaker for supporting particulate dispersion, and let the beaker cool to room temperature before starting the subsampling procedure.

Carbonates and diatom frustules may be removed with additional chemical treatments if needed. A CILAS 1190 was used for all PSD measurements in this study. The CILAS 1190 uses a tri-laser technology, with a 5 mW/635 nm, a 1.5 mW/830 nm, and a 2 mW/830 nm laser, to measure particles...
in the 0.04 to 2500 μm particle size range in liquid mode. The particle size range coverage is subdivided into 100 bins. The accuracy of the instrument was verified using a Whitehouse Scientific 10–100 μm polydisperse glass microsphere standard. The Fraunhofer theory was used because the particles of this study were mostly much larger than the laser wavelengths.

**Binary pipette splitting (BPS) protocol**

1) Transfer a chemically prepared sediment sample into a 500 ml beaker and fill the beaker with deionized water up to about 100 ml.
2) Arrange two additional 50 ml beakers on a nearby workbench for receiving the new subsamples.
3) Manually shake the 500 ml beaker in a circular motion to get all sediment into suspension and continue with this suspending motion during the entire pipette splitting.
4) Take a 5 ml plastic transfer pipette and repeat extracting 5 ml each time from the bottom of the suspended fluid and transfer the extract alternatingly into one or the other of the two 50 ml beakers until the 500 ml beaker is emptied. This step creates two new twin-subsamples.
5) Repeat Steps 1 – 4 for each of the two subsamples obtained at Step 4.
6) Test one of the subsamples for obscuration value, a measure of the quantity of particles in the subsample, to decide either to start with the PSD measurement if the value is acceptable, to remerge subsamples if the value is too low, or to continue with a further BPS round of subsample generation if the value is still too large.

The tip of the 5 ml transfer pipette may need to be cut back, so that its opening is at least three times the size of the largest particles [22]. The BPS method can split a sample into 2 to 8 subsamples, i.e., 1 to 3 subsample generations, within a few minutes, depending on the manual skills of an operator. We recommend the PSD of all subsamples to be analysed when starting to practice BPS for the first time for controlling the quality of the split operation, and 1–2 subsamples to be measured if the desired precision can be consistently achieved by a skilled operator.

**Method validation**

The ten flood-layer samples varied from sandy mud to sand, mostly having a multimodal PSD (Fig. 2). The diameters at 10%, 50%, and 90% cumulative percentage (D10, D50, and D90) of the particles ranged from 4 – 90 μm, 30 – 180 μm, and 75 – 380 μm, respectively.

**Fig. 2.** Particle-size distribution of the ten flood-layer sediment samples exemplarily used in this study.
Acknowledgments

Fig. 3. Coefficient of variance (COV) of D10, D50, and D90 for the ten flood-layer sediment samples subsampled using the conventional pipette (P) method and the newly proposed binary pipette splitting (BPS) method. Each circle represents a sample analyzed, and box plots of the COV are placed next to the samples.

The precision of the BPS method was measured by the coefficient of variation (COV = standard deviation / mean × 100) of D10, D50, and D90 of all generated BPS subsamples (2 to 8 subsamples for each sample) for each of the ten flood-layer samples. The COV fell from 1 to 6%, with one single outlier at 25% for D10, from 2 to 7% for D50, and from 1 to 5% for D90. The median COV was 4%, 3%, and 2% for D10, D50, and D90, respectively (Fig. 3). For comparison, we measured the precision of the conventional pipette method (Fig. 1A) using newly prepared material suspensions derived from the ten flood-layer samples. The prepared material resulted in 3 to 6 subsamples for each sample. The median COV of D10, D50, and D90 using the conventional pipette method was 18%, 15%, and 13%, respectively (Fig. 3). These significantly different COV values between the two subsampling methods clearly indicates that the novel BPS approach presents a major improvement in subsampling sediment in suspension and helps to produce highly representative subsamples.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The samples used in this study were collected with the support of NSF RAPID EAR-1901818. JT Durica and M. Fink helped with the sample collection in the field.

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