COLLOIDAL SILICA AS A PARTICLE SIZE AND CHARGE REFERENCE MATERIAL

Frequent system verification should be an integral component in the use of any particle characterization effort using any instrumental technique. Various particle size standards and reference materials can be used for the verification process. LUDOX silica is a well known and characterized colloid that has been studied using various particle size analysis techniques including acoustic spectroscopy, laser diffraction, and dynamic light scattering. The results from these studies indicate that LUDOX silica is an appropriate sample to use as a reference material.

Verification vs. Calibration

Many analytical instruments require calibration both before first use and on a regular basis in order to assign proper values to measured responses. The process of calibration in the field of particle characterization typically involves challenging the instrument with a series of known samples (typically standards) and creating a calibration curve that associates measured response to particle size. Techniques that require calibration include electric sensing zone, light obscuration, and other counting techniques. Instruments based on acoustic attenuation and light scattering are "first principle" techniques that do not require calibration, but should be subjected to verification tests on a regular basis. Verification in this sense involves challenging the system with a known sample and comparing the calculated result with the expected value. If the calculated vs. expected result varies beyond the determined maximum deviation, then the system typically requires service attention (alignment, source or detector replacement, etc.) to return the system to proper operating condition.

Types of Reference Materials

Different nomenclature can be used when discussing materials used to calibrate or verify particle characterization instruments. Terms used include standards, reference materials, and certified reference materials. For the purposes of this document the terminology defined by ISO guide 30(1) will be used.

A *Reference Material* is "sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process".

A *Certified Reference Material* is "characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability".

Using these definitions, then what many people refer to as a standard is a certified reference material since this includes a certificate of analysis and statement concerning traceability. A reference material can be any particulate sample meeting the defined conditions of being homogenous, stable, and established to be fit for a given use.

The current supply of certified reference materials available for use in particle characterization can also be further classified as either monodisperse or polydisperse. Monodisperse (or monosized) reference materials are typically polystyrene latex spheres with extremely narrow distributions. An example distribution may be 1.020 µm ± 0.022 µm. These materials are so narrow that typically only a mid point (such as the mean) to the distribution is used for calibration or verification. Polydisperse reference materials have a broader distribution so that other points of the distribution (such as the d10 and d90) can also be cited and used during the verification process. Many polydisperse reference materials are glass beads (2,3) with certified values including the d10, d25, d50, d75, and d90.

Although several standard practice documents (4,5) suggest using polydisperse reference materials "over one decade of size" (1-10, 10-100, etc.) for the verification process, in practice none of the available materials meet this criteria. The NIST standard reference material (SRM) 1003c may be the best characterized sample of this type and would be accepted as appropriate by any regulatory or enforcement agency. The NIST certificate for 1003c provides certified diameters from the d5 to d95 in five percent increments ranging from 18.9 – 43.3 µm, hardly a 10-100 µm spread.

LUDOX Silica

LUDOX ® is a trademark first issued to DuPont, later acquired by Grace in 2000, for a stable colloidal silica suspension. Scientific references to the particle size of LUDOX dates back to the 1960's (6). LUDOX is used for a variety of industrial applications including coatings, ink receptive papers, metal casting, refractory products, catalysts, and as a clarifying agent. The suspension is electrostatically stabilized, preventing agglomeration over time and assuring easy mixing.

LUDOX TM silica has been used by particle characterization manufacturers and end users for many years due to several unique properties of this material including:

- Availability and low cost
- Extremely long shelf life
- Understood particle size (30-34nm) (6,7)
- Understood zeta potential (near -37 mV)
- Known concentration (50% by weight)

Until recently, very few well characterized materials in the 30 nm size range were available. For all of these reasons instruments based on acoustic spectroscopy have been using LUDOX TM as a particle size and zeta potential reference material for over 20 years.

Experimental: Instrument Techniques

Several batches of LUDOX TM-50 were prepared and analyzed on three different techniques: acoustic spectroscopy, dynamic light scattering, and laser diffraction. Instruments used in this study were:

- Dispersion Technology DT-1201
  Acoustic spectrometer
- HORIBA LB-550
  Dynamic light scattering system
- HORIBA LA-950
  Laser diffraction analyzer

Experimental: Sample Preparation

The LUDOX TM-50 was first diluted from 50 to 10 weight percent using the following procedure:

- Prepare 1 liter 0.01 M KCl by adding 0.745 g KCl into 1 liter vol. flask and fill to 1 liter w/DI water
- Tare 250 mL beaker on balance
- Add 25 g of 50% LUDOX concentrate
- Dilute to 125 g total wt. using 0.01 M KCl

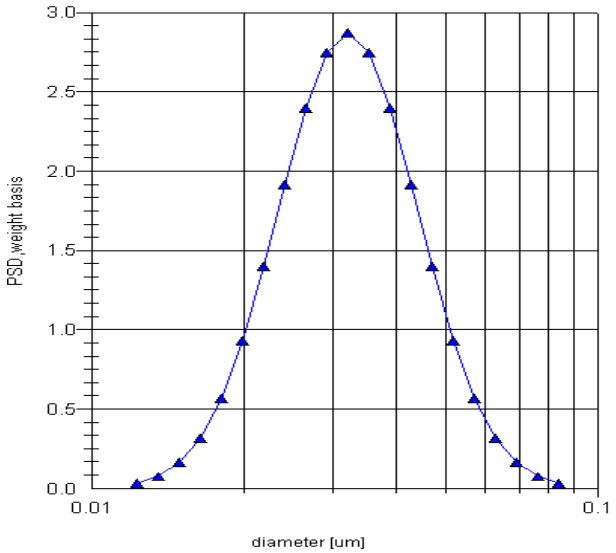
The 10 weight percent sample was measured in the DT-1201 without further dilution. Both the LB-550 and LA-950 instrument techniques require additional dilution for measurement. The only input required for the DT-1201 measurements was the weight percent of the sample.

Five drops of the 50 wt% sample were added to a standard DLS cuvette containing 3 mL of the 0.01 M KCl solution. The particle size analysis is calculated on a volume basis using the refractive index for colloidal silica: 1.45 real, 0.0 imaginary. The sample is dilute enough so as to approximate the viscosity of water.

The 50 wt% sample was added to the LA-950 with a disposable pipette until the blue light transmittance level (T%) was between 97-90%. The LA-950 measured the sample using RI values of 1.45, 0 in 1.33, iteration number 150.

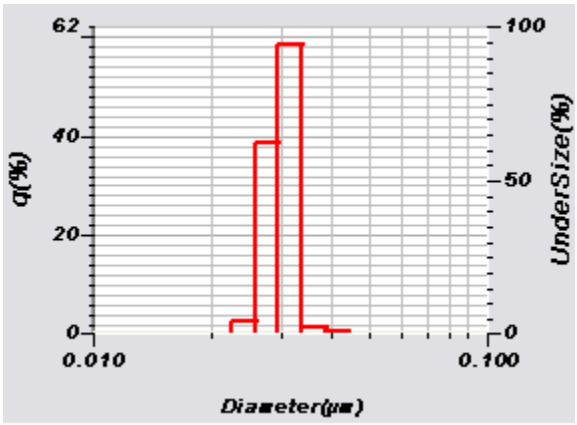
Results: Particle Size

The particle size distribution of LUDOX is fairly narrow, although not nearly as narrow as a latex reference material, with a span (d90-d10/d50) near 0.5 or standard deviation near 0.1. For this reason, only mean values are reported for this study. Results from the measurements on the three techniques are shown below in Figures 1-3.



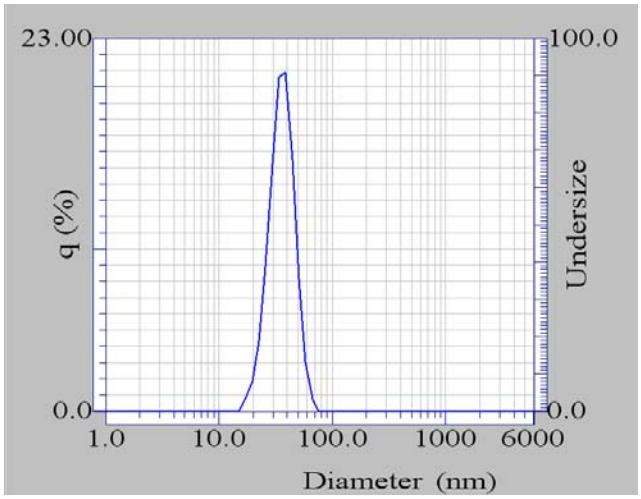
Mean Size : 0.0321(µm)

Figure 1: Typical particle size analysis for LUDOX TM on the DT-1201



Mean Size : 0.02990(µm)

Figure 2: Typical particle size analysis for LUDOX TM on the HORIBA LA-950



Mean Size : 34.1(nm)

Figure 3: Typical particle size analysis for LUDOX TM on the LB-550

Results: Zeta Potential

The zeta potential of the sample was also measured on the DT-1201 system, again without further dilution. The results from multiple measurements are shown below in Figure 4.

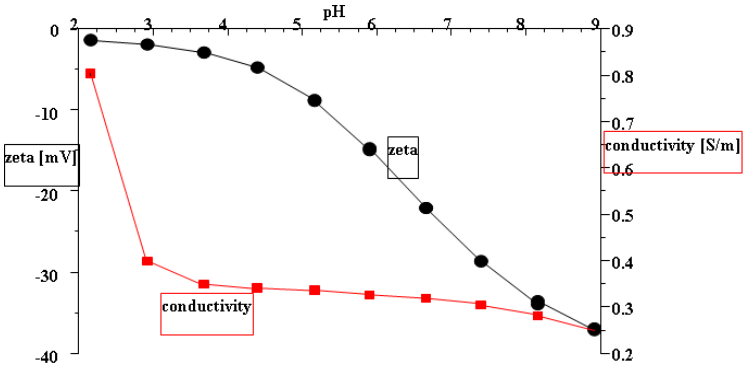


Figure 4: The pH titration curve for zeta potential and conductivity of LUDOX TM

Conclusions

For most cases the results created by different particle characterization techniques can generate a wide spread of mean values. LUDOX appears to be the very rare sample where multiple particle sizing techniques generate very similar results. Reasons for this could include the nature of the particles themselves (round, narrow size distribution) and the stability of the suspension at various concentrations. This unique combination of availability, low expense and similar results using multiple techniques suggests that LUDOX could be used as a nearly universal particle size reference material in many industries. It should be noted however that most other commercially available laser diffraction systems do not have the sensitivity to detect 30 nm materials.

References

1. ISO Guide 30:1992(E)/Amd.1:2008 Terms and definitions used in connection with reference materials
2. Example: NIST 1003c Standard Reference Material, see https://www-s.nist.gov/srmors/tables/view_table.cfm?table=301-1.htm for a listing of NIST particle size Standard Reference Materials
3. Example: Whitehouse PS202 material, see www.whitehousescientific.com for a listing of Whitehouse particle standards
4. ISO 13320, Particle size analysis -- Laser diffraction methods -- Part 1: General principles
5. USP <429> Light Diffraction Measurement of Particle Size, USP30, NF25
6. Deželić, G,Wrischer, M, Z. Devidé, Z, Kratohvil,J Electron microscopy of Ludox colloidal silica, Colloid and Polymer Science, Volume 171, Number 1,July, 1960
7. Bergna, H., Roberts, W. Colloidal Silica: Fundamentals and Applications , CRC Press, 2006 ISBN 0824709675

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