HORIBA Scientific

Application Note

Particle Size Analysis of Gold Nanoparticles

AN194

Scientific interest in well dispersed suspensions of colloidal gold (or nanoparticles) can be traced back to ancient times. Original uses of colloidal gold included potions, stained glass, and other artistic expressions. Current research using gold dispersions remains quite active and controlling the size and morphology of the particles is critical. Recently, the National Institute of Standards and Technology (NIST) has developed Reference Materials (RMs) of gold nanoparticles that are nominally 10, 30, and 60 nm. This application note describes a procedure and shows results from a study analyzing the NIST RM samples.

Introduction

Colloidal gold, also known as “nanogold”, is a suspension (or colloid) of sub-micron particles of gold in a fluid - usually water. The liquid is typically either an intense red color for particles less than 100 nm (see picture to right), or a dirty yellowish color for larger particles.

Known since ancient times, the synthesis of colloidal gold was originally used as a method of staining glass. Modern scientific evaluation of colloidal gold did not begin until Faraday’s work of the 1850s(1). Due to the unique optical, electronic, and molecular-recognition properties of gold nanoparticles, they are the subject of substantial research, with applications in a wide variety of areas, including electronics, nanotechnology, and the synthesis of novel materials with unique properties.

Gold nanoparticles are typically produced in a liquid by reduction of chloroauric acid ($H[AuCl_4]$), although more advanced and precise methods do exist (2-4). After dissolving $H[AuCl_4]$, the solution is rapidly stirred while a reducing agent is added. This causes Au^{3+} ions to be reduced to neutral gold atoms. As more and more of these gold atoms form, the solution becomes supersaturated, and gold gradually starts to precipitate in the form of sub-nanometer particles. The rest of the gold atoms that form stick to the existing particles, and, if the solution is stirred vigorously enough, the particles will be fairly uniform in size.

To prevent the particles from aggregating, some sort of stabilizing agent that sticks to the nanoparticle surface is usually added. They can be functionalized with various organic ligands to create organic-inorganic hybrids with advanced functionality.

Colloid or Nanoparticle?

The NIST Reference Material (RM) samples discussed in this application note are suspensions of gold particles in the range of 10 – 60 nm. The phrase colloidal gold is sometimes used to describe these samples, but the phrase nanoparticles could also be applied. A colloidal suspension could be defined as any two phase system (dispersed and continuous) where the dispersed phase exists at a length scale from 1 nm – 1 µm. Most people now define nanoparticles as particles at a length scale of 1 – 100 nm. Therefore, the NIST RM samples 8011, 8012, and 8013 are both colloids and nanoparticles and both terms are used in this document.

Materials

Three NIST Reference Materials (RMs); 8011, 8012, & 8013 were analyzed for this study. The RMs were created primarily for evaluating and qualifying instrument performance and/or methodology related to the physical/ dimensional characterization of nanoscale particles often used in pre-clinical biomedical research. The RMs could also be useful for developing and evaluating in vitro assays and interlaboratory test comparisons.

Each sample consists of approximately 5 mL of citrate stabilized Au nanoparticles in an aqueous suspension in hermetically sealed pre-scored glass ampoules sterilized by gamma irradiation. The suspension contains primary particles (monomers) and a small percentage of clusters of monomers. The 8011 sample is nominally 10 nm, the 8012 30 nm, and 8013 60 nm.

The reference values provided on the Report of Investigation supplied with each sample are a best estimate of the true value provided by NIST where all known or suspected sources of bias have not been fully investigated by NIST (5). The reference values and images by SEM and TEM for samples 8011, 8012, and 8013 are shown in Tables and Figures 1, 2 and 3 (6, 7, 8).

Technique	Size nm
Atomic Force Microscopy	8.5 ± 0.3
Scanning Electron Microscopy	9.9 ± 0.1
Transmission Electron Microscopy	8.9 ± 0.1
Differential Mobility Analysis	11.3 ± 0.1
Dynamic Light Scattering	13.5 ± 0.1
Small-Angle X-ray Scattering	9.1 ± 1.8

Table 1: Reference Values for RM 8011

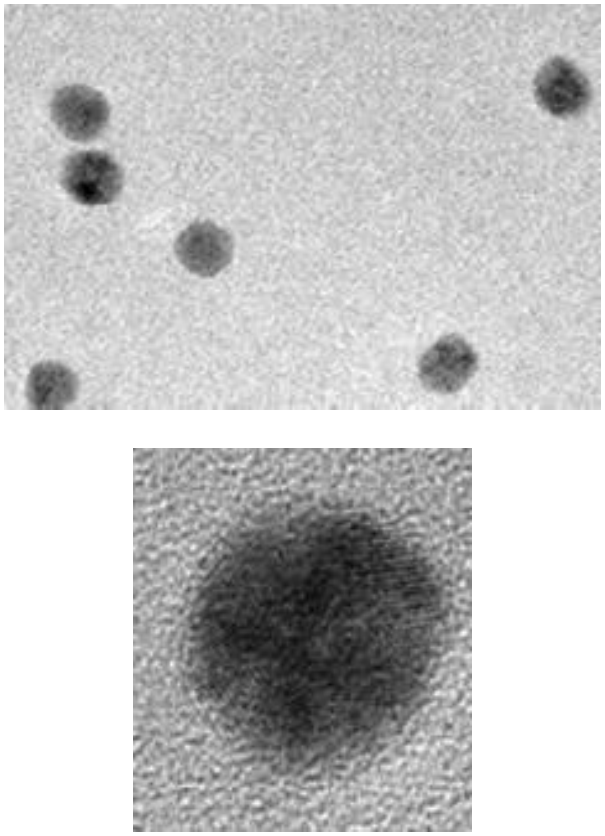


Figure 1: SEM (above) and TEM (below) images for RM 8011

Technique	Size nm
Atomic Force Microscopy	24.9 ± 1.1
Scanning Electron Microscopy	26.9 ± 0.1
Transmission Electron Microscopy	27.6 ± 2.1
Differential Mobility Analysis	28.4 ± 1.1
Dynamic Light Scattering	
173° scattering angle	28.6 ± 0.9
90° scattering angle	26.5 ± 3.6
Small-Angle X-ray Scattering	24.9 ± 1.2

Table 2: Reference Values for RM 8012

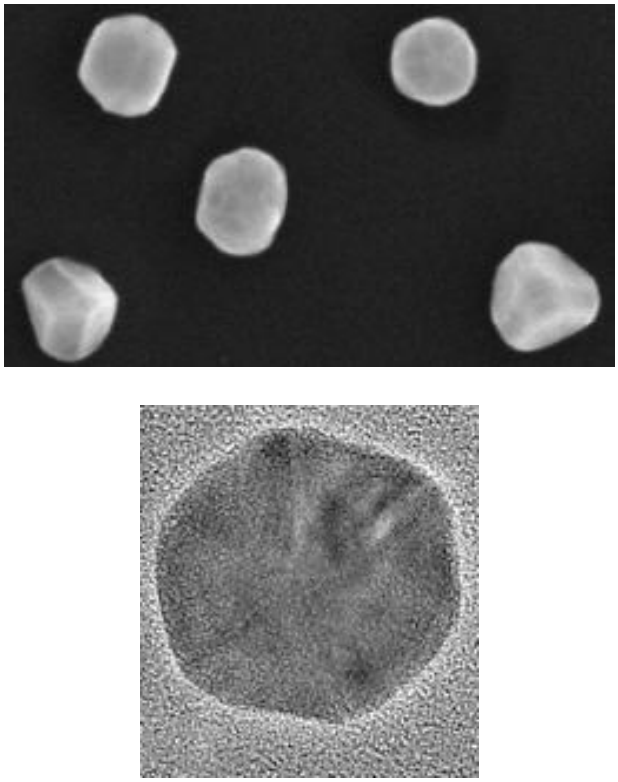
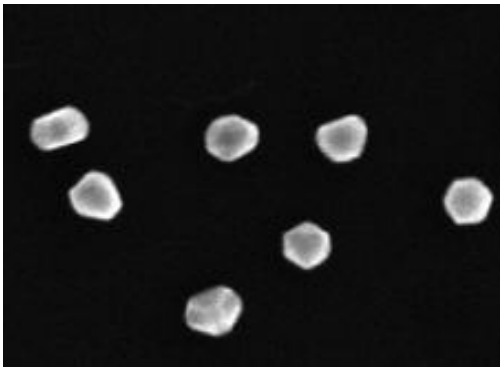


Figure 2: SEM (above) and TEM (below) images for RM 8012

Technique	Size nm
Atomic Force Microscopy	55.4 ± 0.3
Scanning Electron Microscopy	54.9 ± 0.4
Transmission Electron Microscopy	56.0 ± 0.5
Differential Mobility Analysis	56.3 ± 1.5
Dynamic Light Scattering	
173° scattering angle	56.6 ± 1.4
90° scattering angle	55.3 ± 8.3
Small-Angle X-ray Scattering	53.2 ± 5.3

Table 3: Reference Values for RM 8013



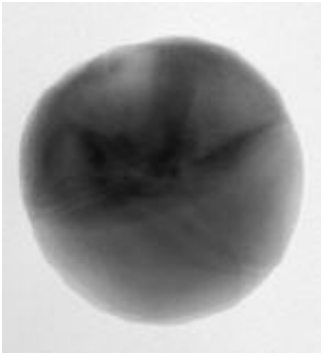


Figure 3: SEM (above) and TEM (below) images for RM 8013

Experimental

The NIST reference materials were analyzed on the HORIBA SZ-100 DLS system (see Figure 4). The following sample preparation and measurement procedure was followed:

- Power up instrument 30 minutes in advance of measurements
- Clean measurement cuvettes w/filtered DI water & dry
- Pre-rinse cuvette w/dilution medium prior to loading sample
- Dilution medium: 50 mL filtered 2 mM (2x10-3 mol/L) NaCl
- Dilute sample 1 part in 10 using dilution medium
- Diluted sample then filtered using 0.45 µm syringe filter
- Set temperature to 20°C
- Perform 5 repeat measurements
- Record the average values of the measurements

Figure 4: SZ-100 Nanoparticle Size Analyzer

Results and Discussion

The results from these measurements are shown in Tables 4-6 and typical graphs shown in Figures 5-7. The HORIBA results shown in row 1 and 2 are reported in Intensity mean (Z average) and polydispersity index (PDI). The third row in each table shows the results from an ASTM interlaboratory study (6) where 13 labs measured the same NIST RMs.

8011		
HORIBA	**Average**	**St dev**
Sample 1	13.4 nm	1.8
Sample 2	12.6nm	1.9
ASTM	**Z ave**	**st dev**
Combined	15.8 nm	4.2

Table 4: DLS results for RM 8011

8012		
HORIBA	**Average**	**St dev**
Sample 1	31.5nm	3.9
Sample 2	32.4 nm	5.9
ASTM	**Z ave**	**st dev**
Combined	31.2 nm	3.6

Table 5: DLS results for RM 8012

8013		
HORIBA	**Average**	**St dev**
Sample 1	57.6 nm	3.5
Sample 2	58.4 nm	3.9
ASTM	**Z ave**	**st dev**
Combined	59.8 nm	5.0

Table 6: DLS results for RM 8013

Conclusions

Gold nanoparticles are of great interest for researchers in many fields. The size distribution of the particles is an important physical characteristic that influences particle behavior. The most common technique to measure the size of gold nanoparticles is DLS. The HORIBA SZ-100 system has proven to be an excellent choice for accurate and reproducible particle size analysis of gold nanoparticles.

References

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