CCQM-P194 'The determination of number concentration of colloidal nanoparticles'

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CCQM-P194 ‘The determination of number concentration of colloidal nanoparticles’

D I Belenkii, T M Magomedov, D M Balakhanov

All-Russian Scientific Research Institute of Physical-Technical and Radiotechnical Measurements

Abstract. The paper describes pilot comparisons of P194 ‘The determination of number concentration of colloidal nanoparticles’, measurand, measurement methods and principles. Preliminary results of comparisons and additional measurements of particle sizes and zeta potential of the provided samples are presented. Conclusions are drawn about the possibility of using this sample as a reference material.

1. Introduction
Nanotechnology is actively used to solve scientific and industrial problems. Measurements of the nanoparticles concentration in colloidal suspensions are of great interest for a wide range of industries, including pharmaceuticals, cosmetology, food and microelectronic industries. However, to date, the methods used to determine the concentration of nanoparticles in liquids are not standardized. Within the framework of the IAWG, it was decided to carry out the CCQM-P194 comparisons, since this task meets the requirements of the strategic program of pilot comparisons for new and challenging measurands. During comparisons, participants determined the concentration of gold nanoparticles, according to their chosen method.

2. Measurand
The sample is colloidal spherical gold nanoparticles (stabilized by citrate buffer) with an average diameter of approximately 30 Nm suspended in water. The nominal number of particles is in the range 1-2.5E11 NPs/g. the suspension of nanoparticles (approximately 5 ml) is contained in a sealed ampoule of amber glass, flushed with Ar-gas and sterilized by gamma irradiation. Up to 5 vials of CCQM sample with freeze and 30 + indicators were sent out to all participants. To measure the concentration of gold nanoparticles, the laboratory coordinator recommended the use of dilutions (depending on the measurement method) in a 1mM citrate buffer. NIST provided one ampoule of PM 8012 (30 Nm gold nanoparticles) to each participant to control sample quality and determine transport efficiency using the spICPMS method. 300 µl sub-aliquots of this sample were sent to each participant. A certificate of analysis for this material with instructions for use is also sent to each participant. The monodispersity of the sample was tested by the LGC coordinator laboratory.
The concentration of gold nanoparticles in 15 ampoules was measured for 8 hours by particle tracking analysis (PTA, Malvern Panalytical NS500). During one measurement, there were five repeated measurements of the instrument per sub-sample.

Concentration of gold nanoparticles in 15 ampoules was measured for 8 hours by Particle Tracking Analysis (PTA, Malvern Panalytical NS500). During one measurement, there were five replicate instrument measurements per sub-sample.

According to the results of measurements homogeneity uncertainty was 2.49%.

Stability testing by LGC using PTA-samples stored at temperatures up to 60 °C for 1 day and two weeks (fig.1).

3. Measurement methods used by VNIIFTRI

Participants were free to use any suitable method. A full uncertainty budget also had to be included with results. During discussion of spICPMS measurements at the IAWG it was noted that this is a very new method and a key aspect of the pilot study is to gain experience of the measurements and investigate consistency between different laboratories/instruments. In order to facilitate this, the coordinating laboratory has provided information on aspects of the methodology which have been found to assist reproducible measurements.

For spICPMS measurements, the dwell time recommended for this study depends on the in house capabilities and practice experience of each participant. Overall, dwell time resulting in baseline separation between background signal and particles population are recommended.

Transport efficiency should be determined following the procedure developed by each participant but as specified in PD ISO/TS 19590:2017, but it is recommended to assess transport efficiency at the start, middle and at the end of the measurement batch to be able to assess the within batch variability of this parameter.

Figure 1. Sample stability tests
During the comparisons we used two methods to measure the concentration of gold nanoparticles:
  — The method of dynamic light scattering (DLS);
  — Inductively coupled plasma mass spectrometry (sp-ICP-MS).

### 3.1 Dynamic light scattering

Dynamic light scattering method [1] is used to measure the size of nanoparticles. In this method, the diffusion coefficient of dispersed particles in a liquid is determined by analyzing the characteristic time of fluctuations measured in the intensity of scattered light. The diffusion coefficient is used to calculate the hydrodynamic radius of nanoparticles. Thermal (Brownian) motion of particles causes fluctuations of their local concentration. In turn, these fluctuations lead to local inhomogeneities of the refractive index of the medium. When a laser beam passes through such a medium, part of the light is scattered on these inhomogeneities. The fluctuations of the scattered light intensity correspond to the fluctuations of the local concentration of dispersed particles. Information on the particle diffusion coefficient is contained in the time-dependent correlation function of the intensity fluctuations.

Particle size measurements are made according to the Stokes-Einstein equation (1):

\[
d = \frac{kT}{3\pi\eta D}
\]

Where:
- \( k \) = Boltzmann constant;
- \( T \) = Absolute temperature;
- \( \eta \) = Solvent viscosity;
- \( D \) = Diffusion coefficient.

To calculate the concentration of particles, data on their size, optical properties (imaginary and real parts of the refractive index), polydispersity index and count rate (number of photons per second) are used.

### 3.2 Inductively coupled plasma mass spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) [2] is a type of mass spectrometry that uses an inductively coupled plasma to ionize the sample. The sample, an aqueous suspension, is introduced continuously into a standard ICP-MS system that is set to acquire data with a high time resolution (i.e. a short dwell time is used). Following nebulization, a fraction of the nanoparticles enter the plasma where they are atomized and the individual atoms ionized resulting in a cloud of ions. This cloud of ions is sampled by the mass spectrometer and since the ion density in this cloud is high, the signal pulse is high compared to the background signal if a high time resolution is used. The number of pulses detected per second is a directly proportional to the number concentration of nanoparticles in the aqueous suspension that is being measured. To calculate concentrations, the nebulization efficiency has to be determined first using a reference particle.

Particle concentration measurements are made according to the equation (2):

\[
C_p = \frac{C_m}{m_p}
\]

Where:
- \( C_p \) = particle number concentration;
- \( C_m \) = mass concentration of the particle suspension;
- \( m_p \) = mass per particle.
Individual particle mass is calculated according to the equation (3):

$$m_p = \frac{I_p t_d}{RF_{ion}} \cdot \frac{V \eta_n}{60} \cdot \frac{M_p}{M_a}$$

(3)

Where

- \(m_p\) = particle mass;
- \(I_p\) = particle signal intensity in the sample;
- \(RF_{ion}\) = ICP-MS response for ion standard;
- \(t_d\) = dwell time;
- \(V\) = sample flow rate;
- \(\eta_n\) = nebulization efficiency;
- \(M_p\) = molar mass nanoparticle material;
- \(M_a\) = molar mass analyte measured.

4. Results and discussion

The results of the comparison presented in the preliminary report are shown in figure 2.

![Figure 2](image_url)  
**Figure 2.** The results of the comparison. Measurement uncertainties are given at \(k=1\), the uncertainty of the median value was \(0.124\times10^{11}\) g⁻¹

However, we have carried out additional measurements of the size and zeta potential of the particles, as the values of the concentration varied from vial to vial within 15%.

According to the results of particle size measurements, the average particle diameter was 30 nm, and the polydispersity reached 21% (fig. 3).

![Figure 3](image_url)  
**Figure 3.** Gold nanoparticles size and polydispersity index
According to the results of measurements of the Zeta potential of the particles, the average value was about 50 mV, and the deviation reached 27 mV (fig.4).

![Gold nanoparticles zeta potential](image)

**Figure 4.** Gold nanoparticles zeta potential

Summing up all the obtained measurement results (size, counting concentration, zeta potential), the use of gold nanoparticle samples provided by the coordinating laboratory as reference material is questionable.

5. References.

[1] ГОСТ Р 8.774-2011 "ГСИ. Дисперсный состав жидких сред. Определение размеров частиц по динамическому рассеянию света"

[2] H E Pace, N J Rogers, C Jarolimek, V A Coleman, C P Higgins and J F Ranville 2011 Determining transport efficiency for the purpose of counting and sizing nanoparticles via single particle inductively coupled plasma mass spectrometry *Anal. Chem.* 9361–9369