

nPSize

Improved traceability chain of nanoparticle size measurements

EMPiR project 17NRM04

Report from A2.4.3 (Part 3)

Report on the homogeneity assessment of bimodal gold materials
(nPSize1 and nPSize2) and particle number concentration by
frequency method

Partner: LGC
Work package/Activity: WP2/A2.4.3
Due: M14
Delivery Type: Activity Report

1. Introduction

The main objective was to assess homogeneity of two bimodal gold materials, namely nPSize1 and nPSize2, containing approximately 1:1 and 10:1 particle number-based ratio of ~30nm and ~60nm particles. Particle number-based concentration within the two size fractions was determined with spICP-MS using the particle frequency method of calibration.

2. Sample Information

2.1. Sample receipt and storage

BMG particle suspensions were prepared and ampouled by LGC using ~30nm and ~60nm particle suspensions purchased from BBI Solution (Cardiff, UK). The vials were stored at 4°C prior to analysis.

2.2. Sample preparation

Vials containing BMG (nPSize1 and nPSize2) samples were allowed to warm up to room temperature. They were then gently inverted several times to ensure homogeneity of the suspensions before opening. Prior to analysis, the materials were gravimetrically diluted using UKAS calibrated analytical balance (with 4 decimal places) approximately 2 000 000 (nPSize2) and 1 000 000 (nPSize1) times with 1mM trisodium citrate buffer (Na₃Ct) and mixed thoroughly. Diluted samples were measured in a single analysis batch performed on the day of preparation.

3. Methodology and Instrumentation

3.1. Instrumentation

SpICPMS measurements were performed using an 8900 ICPMS/MS instrument manufactured by Agilent Technologies. The instrument was equipped with micromist nebuliser operating at a pumping rate at 0.1 rpm, Scott type double pass spray chamber cooled to 2 °C, the MassHunter 4.4 (version: G72dC C.01.03) software and microsecond detection capability, allowing analysis in a single particle mode.

3.2. Methodology

The instrument was tuned daily using 1µg L⁻¹ Agilent Tuning solution containing Li, Y and Tl (part: 5190-0465) in order to verify the instrument's performance. Then, the response factor of the instrument to ¹⁹⁷Au was optimised with 1µg kg⁻¹ (diluted gravimetrically with 1mM Na₃Ct) of elemental Au standard (Romil, #BX645418, 926.1mg kg⁻¹) in order to obtain the best instrument's sensitivity with a minimum background contribution. SpICPMS analysis in fast transient analysis (TRA) mode were performed using a dwell time of 100µs per point, with no settling time between the measurements and using Single Particle Application Module of the ICPMS MassHunter software (G5714A). 'No gas' and a single quad mode was used throughout. Single Particle Application Module of the ICPMS MassHunter software (G5714A), as well as in-house developed Excel spreadsheets, were used for data processing. The instrument was cleaned with 1mM Na₃Ct after each sample. Each sample was measured 5 times under repeatability conditions. Transport efficiency was determined using the frequency method against LGCQC5050 material (~30nm nominal gold particles, diluted gravimetrically approximately 4 500 000 times in 1mM Na₃Ct buffer). Particle concentration (C) in the sample was derived from the following equation:

$$C(\text{NP/g}) = \frac{N \cdot Df}{\eta \cdot V} \quad (\text{Equation 1})$$

, where N is the number of particles detected in time scan (NP/min), Df is the sample dilution factor (a.u.) of the samples, η is transport efficiency (a.u.) and V is the sample mass flow (g/min).

4. Results and Discussion

Particle number present in the 30nm and 60nm size fractions in BMG nPSize1 and nPSzie2 suspensions:

Total of 15 ampoules of nPSize1 and 7 ampoules of nPSize2 were measured in duplicate with spICPMS using the particle frequency method of calibration. Obtained numbers of 30nm and 60nm particles in the BMG materials are shown in **Table 1** along with the average ratio of the two size fractions. Associated measurement uncertainty was calculated in accordance with ISO 17025 and Eurachem/CITAC guidelines and the typical uncertainty budget is shown below.

For quality control purposes, LGCQC5050 material was submitted to the same sample preparation and measurement procedures as the BMG materials. Recovery rates in the range from 97.3% to 102.7% were obtained, indicating good accuracy of the measurement method.

Table 1. Particle number in BMG materials determined by spICPMS (frequency method).

BMG material	30nm size fraction				60nm size fraction				Ratio (%)
	Mean (NP g ⁻¹)	Standard uncertainty (NP g ⁻¹)	Expanded uncertainty, k=2 (NP g ⁻¹)	Relative expanded uncertainty (%)	Mean (NP g ⁻¹)	Standard uncertainty (NP g ⁻¹)	Expanded uncertainty, k=2 (NP g ⁻¹)	Relative expanded uncertainty (%)	
nPSize1	1.9 E10	2.4 E9	4.8 E9	25.7	1.9 E10	2.4 E9	4.9 E9	25.3	1.0
nPSize2	8.9 E10	1.1 E10	2.2 E10	24.9	9.5 E9	1.2 E9	2.4 E9	25.7	9.4

Typical uncertainty budget associated with particle number-based concentration determination with spICPMS (frequency method):

Within day variability:	3.2%
Between days variability:	4.3%
Transport efficiency:	90.7%
Sample intake:	<0.1%
Sample dilution:	1.9%

Material homogeneity:

Material homogeneity assessment was based on the number of particles found per size fraction in each vial of the material (data shown in Table 1 above and Figure 1 below), whilst the uncertainty associated with homogeneity was calculated by combining between unit and within unit variability. Obtained uncertainty values along with the statistical analysis based on one-way ANOVA (p value) are shown in Table 2 below. From the statistical analysis it can be concluded that nPSize2 material is homogenous (p in the range of 0.2-0.3 means no significant differences between the tested units were seen), however some inhomogeneity in the 30nm fraction of the nPSize1 material was observed (p=0.06 is just very close to 0.05 being indicative of significant differences between the vials), but not in the 60nm fraction (p=0.27). These small differences between the nPSize1 units were attributed to low level of agglomerates formed by the 30nm particles.

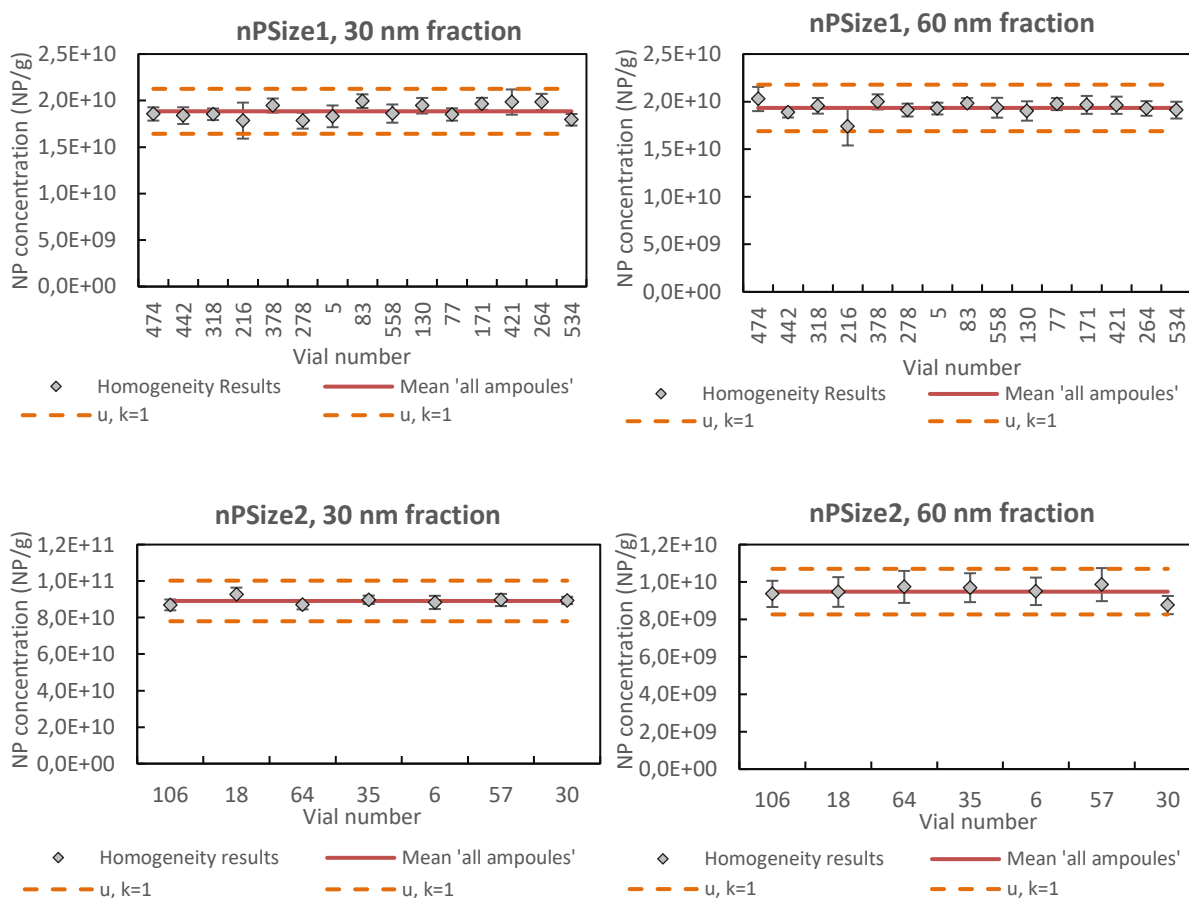


Figure 1. Summary of the homogeneity study on the BMG nPSize1 and nPSize2 materials (error bars associated with data points representing individual vials are stdev from all independent replicate measurements with n=10).

Table 2. Uncertainty associated with the material homogeneity determined by spICPMS (frequency method).

BMG material	30nm size fraction			60nm size fraction		
	Standard uncertainty (NP g ⁻¹)	Relative uncertainty (%)	p* (based on single way ANOVA)	Standard uncertainty (NP g ⁻¹)	Relative uncertainty (%)	p* (based on single way ANOVA)
nPsize1	7.91E+08	4.2	0.06	7.18E+08	3.7	0.27
nPsize2	2.14E+09	2.4	0.21	3.85E+08	4.0	0.33

*where $p < 0.05$ indicates significantly different results

5. Summary

Particle number-based concentration in the BMG (nPsize1 and nPsize2) materials was measured with spICPMS using particle frequency method, obtaining the mean of $1.9 \text{ E}10 \text{ NP}^* \text{g}^{-1}$ for the two size fractions in nPsize1 whilst $8.9 \text{ E}10$ and $9.5 \text{ E}9 \text{ NP}^* \text{g}^{-1}$ for the 30nm and 60nm size fractions, respectively, in the nPsize2 material, with the relative expanded measurement uncertainty of around 25%. BMG nPsize2 material was found homogenous based on a single way ANOVA $p = 0.21$ and 0.33 for the 30nm and 60nm size fractions, with the associated relative standard uncertainty of the homogeneity of 2.4% and 4.0%, respectively. On a contrary $p = 0.06$ associated with the 30nm size fraction within the nPsize1 material can be an indication of some homogeneity issues caused by particle agglomeration, therefore it is not recommended to use this material beyond the project for purposes such as instrument calibration or as a QC. No agglomeration was seen in the 60nm fraction of the nPsize1 material, with $p = 0.27$ and corresponding relative standard uncertainty of the homogeneity of 4.2%.