

## **D.5.47 Annex 2**

### **Inter-laboratory comparison on measurand Surface Charge (Zeta Potential) of Silica Particles**

#### **Report of the Results**

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## Abstract

An inter-laboratory comparison on the surface charge, expressed as zeta potential  $\zeta$ , of nanoscaled SiO<sub>2</sub> has been performed using #14 BAM Silica (see D.5.41/5.42) nanoparticles. The comparability of results delivered by participants has been tested.

## 1 Introduction

The Task 5.4 of NanoValid is designed to test, compare and validate current methods to measure and characterize physicochemical properties of selected engineered nanoparticles. The measurand is *Surface charge expressed as zeta-Potential*. The measurements are to be accompanied by estimates of the uncertainties at a confidence level of 95%, deduced from the standard uncertainties. Therefore an uncertainty budget comprising statistical (Type A) and systematic (Type B) errors has to be established and delivered for the measurand. The protocol comprises two Annexes addressing the establishment of uncertainty budgets following GUM. The final goal of the comparison is to identify those methods of measurement which have potential as reference methods in pc characterization of nanoparticles for the determination of a given measurand (Task 5.4 of the NanoValid Project).

## 2 Inter-laboratory Comparison Surface Charge

### 2.1 Objective

The objective of the Inter-laboratory Comparison was to determine the average surface charge of nanoscaled SiO<sub>2</sub> (#14 BAM Silica (see D.5.41/5.42)), expressed as zeta-potential in mV. The participants were free to choose the analytical method, provided it was fit for purpose.

### 2.2 Participation

In the beginning of the NanoValid project partners took part in a survey (Deliverable D5.46) asking for devices and ability to participate in a round robin with measurand surface charge. Members and other interested parties were informed about the organization of the Inter-laboratory Comparison. Individual invitation e-mails were sent to those potential participants

together with a standardized round robin protocol in April 2013 after announcing it at the regular project meeting in November 2012.

Finally, 8 organizations and companies participated in the Inter-laboratory Comparison. There were two Non-EU partners.

### **3 The test material**

#### **3.1 Production**

The test material (#14 BAM Silica (see D.5.41/5.42)) stems from a batch made for the Inter-laboratory Comparison. This batch was produced by BAM in Germany in form of a dispersion followed by dilution to 0.05 wt% and distribution in bottles á 5 ml sample amount. Sufficient material was available that all participants received material not previously used for any measurements except as in 3.2.

#### **3.2 Initial characterisation of the test material**

Material which has been measured is BAM-silica. It has been preliminary tested regarding potential to be developed as a certified reference material by (T)-SEM, TEM and XPS (Deliverable 5.40, Task 5.1). With electron microscopes operated in transmission mode (T-SEM) of two laboratories area-equivalent mean diameters of 14 nm (standard deviation 3 nm) and of 17 nm (standard deviation 2 nm) were determined, respectively. Round robin batch has been characterized with SAXS, (T)-SEM, DLS and zeta-potential. In Deliverable 5.46 suitable methods are documented. For SAXS, curve fitting was performed with a sphere model and assuming a Schulz-distribution and bimodal Schulz-distribution, respectively. Results indicate two size classes present in the dispersion. The first size class comprises particles with a mean diameter of 14.6 nm and polydispersity 0.13. Particles of the second size class exhibit a negligible polydispersity of 0.003 with a mean diameter of 40.6 nm. Particles can be seen in the SEM and T-SEM image, which are displayed in Fig. 1.

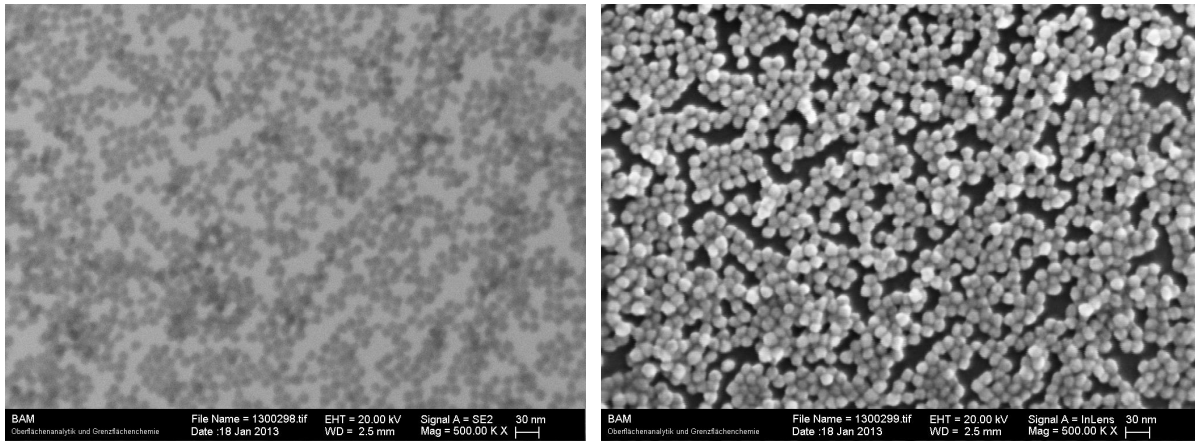


Fig. 1: T-SEM image left and SEM (In Lens) image right and of round robin batch BAM-silica

### 3.3 Sample distribution and deadline for reporting results

Discussions were held with participants concerning their requirements for sample numbers and sizes. Standard sets comprised 1, 2 or even more sample bottles in dependence of type and number of size and zeta potential method(s) chosen by the participants, as the size inter-laboratory comparison was combined with the zeta-potential round robin for practical reasons in order to save money and time in terms of one combined round robin protocol and use of the same test material. Sample bottles together with cover letter were dispatched to laboratories in April 2013 accompanied by the round robin protocol via email. One participant did not receive his sample and others requested more amount of sample, therefore dispatchment had to be repeated in several cases.

The deadline was set to 15 June 2013 initially, which was extended subsequently as due to different reasons several participants delivered their results not before end of 2014.

### 3.4 Instructions to the participants

The shipped package contained

- a 1 page covering letter
- the samples.

The protocol was sent in parallel via email and contained

- a statement of the objectives

- the specific serial codes for each sample
- the timetable
- details of the material, sample handling and any necessary cleaning
- details of issues to report including details of the uncertainty calculation for 95% confidences
- a table to report the size and uncertainties.
- annexes describing sources of uncertainties from literature

## **4 The participants' measurement procedures**

All participants have submitted results. To establish a full uncertainty budget, systematic uncertainties had to be expert-based estimated, except for BAM, who delivered full uncertainty budget and a complete and detailed analysis report. They stated a functional relationship and described the various uncertainty contributions of the uncertainty budget. In the following paragraphs, information as derived from the questionnaire is summarized.

### **4.1 Methods, instrumentation and brief experimental details**

1) IKTS (FhG) used laser doppler velocimetry with a Zetasizer Nano ZS (Malvern instruments) and a He-Ne Laser (633 nm, 5 mW).

2) IUTA used laser doppler velocimetry with a Beckmann Coulter Delsa Nano C (laser wavelength 633 nm).

3) INMETRO used PALS - Phase Analysis Light Scattering with a Zeta PALS (Brookaven, nom. 660 nm laser wavelength, 35 mW).

4) McGill used laser doppler velocimetry with a Mobius (Wyatt) and laser wavelength of 532 nm and power of 52 mW.

5) VN used laser doppler velocimetry with a Zetasizer Nano ZS (Malvern instruments) and a He-Ne Laser (633 nm, 4 mW).

6) BAM used laser doppler velocimetry with a Zetasizer Nano ZS (Malvern instruments) and a He-Ne Laser (632.8 nm).

7) NLAB used laser doppler velocimetry with a Zetasizer Nano ZS (Malvern instruments) and a He-Ne Laser (633 nm).

8) UoB used laser doppler velocimetry with a Zetasizer Nano ZS (Malvern instruments) and a He-Ne Laser (633 nm, 4 mW).

## **5 Results and Discussion**

### **5.1 Results**

Zeta-potential is calculated from the measurement of electrophoretic mobility, which is commonly done automatically with instrument software. The values of the zeta potential and their associated uncertainties at a 95% level of confidence are presented in Table 2 for the inter-laboratory comparison. Except for one participant there were no full uncertainty budgets by the laboratories provided. Nevertheless, all participants delivered A-type measurement uncertainties. There are several reasons hampering the establishment of systematic measurement uncertainties. One of the reasons is certainly the lack of certified reference materials. Instead, participant BAM1.3 used a commercially available reference material, the so-called transfer standard (Malvern, United Kingdom) for determination of a B-type error. Sources of measurement errors are described in ISO 13099-2 [2] and participants had been advised in the round robin protocol to either minimize or avoid these.

**Table 2: Participants' results for the zeta-potential of BAM-silica and 95% uncertainties;  $\zeta$  = zeta potential,  $U$  = uncertainty at 95% confidence.**

BAM-silica dispersion								
Participant	Sample preparation	Measurand Zeta potential (Standard deviation) $\zeta$ / mV	Uncertainties in units of measurand					
			A-type (Standard uncertainty of the mean of measurand), $u_s$	B-type 1: Standard uncertainty $u_1$	B-type 2: Standard uncertainty $u_2$	...more B-type errors	Combined standard uncertainty $u_c^*$	Expanded uncertainty, $U = k u_c$ (Coverage factor for 95 % confidence level, $k = 2$ )
Lab1	Syringe filtered (PES)	-22.0222 (1.6197)	0,6612	2.9903 (Transfer-standard)	0	0	3.0625	6.1251
Lab2 <sup>a</sup>	Syringe filtered (CA)	-24.2 (n.a.)	1.9	0	0	0	0	0
Lab3 <sup>a,b</sup>	As received	-26.71(15.21)	6.8	0	0	0	0	0
Lab4 <sup>a</sup>	As received	-19.6(3.4)	1.388	0	0	0	0	0
Lab5 <sup>a</sup>	As received	-19.75(2.55*)	1.04	0	0	0	0	0
Lab6 <sup>a</sup>	As received	-28.1(n.a.)	2.52	0	0	0	0	0
Lab7 <sup>a</sup>	As received	-37.1(n.a.)	1.25	0	0	0	0	0
Lab8 <sup>a</sup>	Diluted	-24.81(n.a.)	2.48	0	0	0	0	0

<sup>a</sup> No uncertainties of type B were provided

<sup>b</sup> 5 instead of 6 replicates

Note: Lab numbers do not correlate to the sequence in the alphabetical list of participants.



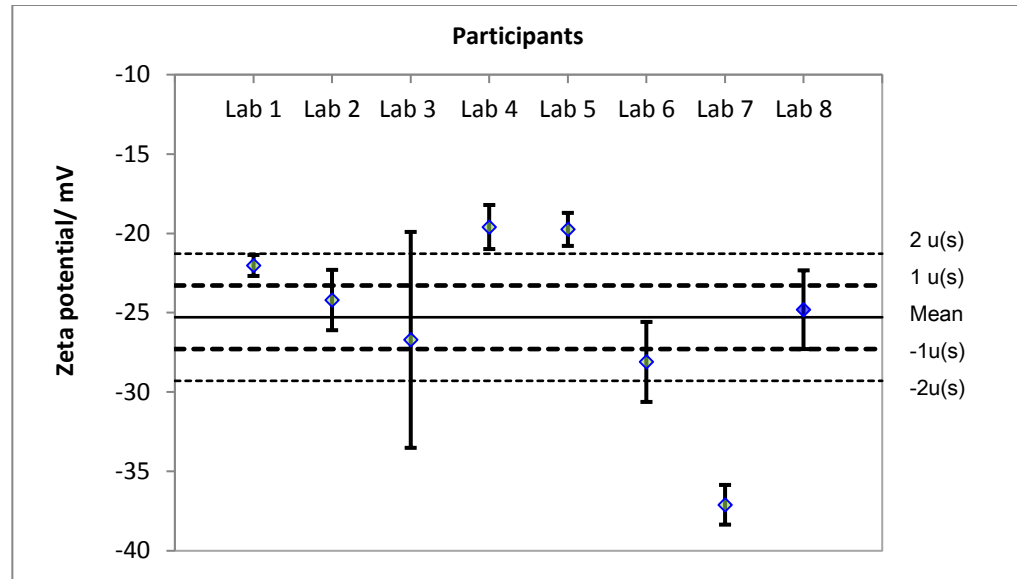


Fig. 2 Mean of zeta potential versus the respective laboratory, error bars indicate standard uncertainty (A-type) and black line represent the mean and dashed lines corresponding standard uncertainties  $u(s)$ .

## **6 Conclusions and Outlook**

Due to the large variability of zeta potential results within laboratories as well as between laboratories it is concluded that the zeta potential method is not recommended as reference method for the analyzed sample #14 BAM Silica (see D.5.41/5.42).

## **7 Acknowledgement**

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## **References**

ISO13099-1, "Colloidal systems — Methods for zeta-potential determination Part 1: Electroacoustic and electrokinetic phenomena," 2012.

ISO13099-2, "Colloidal systems — Methods for zeta-potential determination Part2: Optical methods," 2012.