National Institute of Advanced Industrial Science and Technology
AIST

Combined method of scanning electron microscopy and gravimetry for number concentration measurement of nanoparticles in colloidal suspension

Kazuhiro KUMAGAI* and **Akira KUROKAWA**
Research Institute for Material and Chemical Measurement, National Metrology Institute of Japan (NMIJ)
National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba JAPAN
*e-mail: quaz.kumagai@aist.go.jp

Introduction

■ Number concentration (NC) of nanoparticles (NPs)

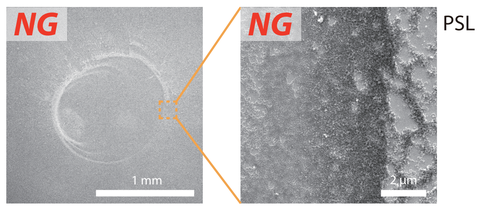
- important in nano-related industry as an ***index for the quality and efficacy*** of products
- For the assessment of the influence of the nanomaterials in the environment, there is a increasing demand for the robust NC measurement.

■ How to achieve reliable NC measurements by EMs?

Electron microscopies (EMs) are ***not*** commonly used for the NC measurements, although EMs have high resolution enough to visualize NPs

- ***Specimen preparation is the key:***
  Simple drop cast method places NPs over a large area on a substrate and often causes hindrance to EM observation such as "coffee ring" effect.

Sample prep. by dropcast with micro pipette



NPs scattered over large area in millimeter scale

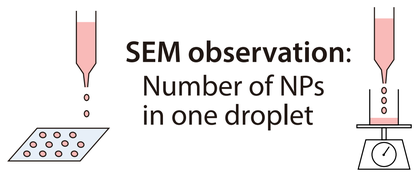
Serious overlapping

This paper presents NC measurement by SEM and gravimetry introducing microdispenser technique to the sample preparation

Experimental

■ Approach

Combination of SEM and gravimetry via microdispenser



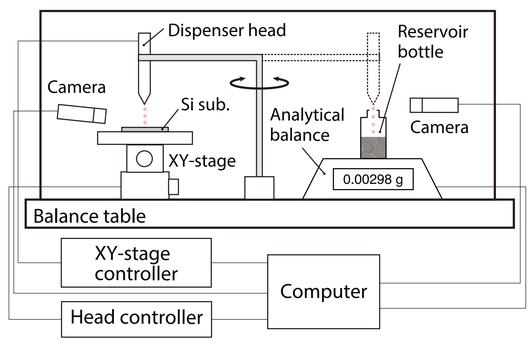
SEM observation: Number of NPs in one droplet

Gravimetry: Weight of one droplet (g)

→ **Number concentration** of Au NP suspension (g^{-1})

■ Experimental setup

SEM sample prep. Gravimetry



Au NP suspension
Water suspension of colloidal spherical Au NPs
Diameter: ~30 nm

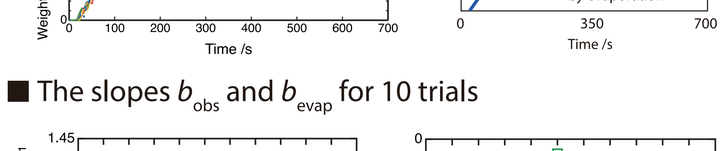
Sample prep. and gravimetry
Microdispenser: IJK-200H & IJHB-30 (Microjet)
Analytical balance: ME215S (sartorius)

SEM observation
SEM: JSM-7100F TTL (JEOL)
V_{acc}: 10 kV, I_p: ~200pA
Detector: ET-SE detector
Image size: 5120 px x 3840 px (3.9 nm/px)
Particle analysis: Image Pro Premier v9.2

Results and discussion

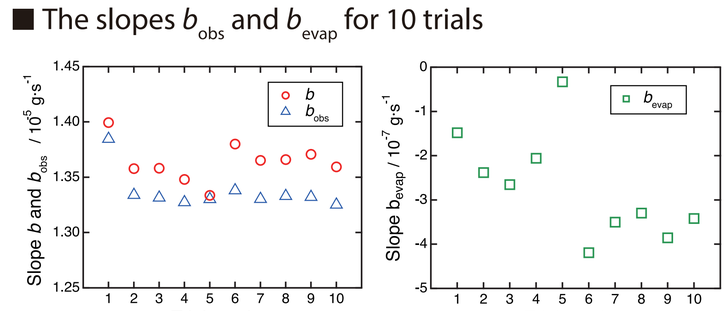
■ Particle number counting via SEM

■ Ejection from the dispenser



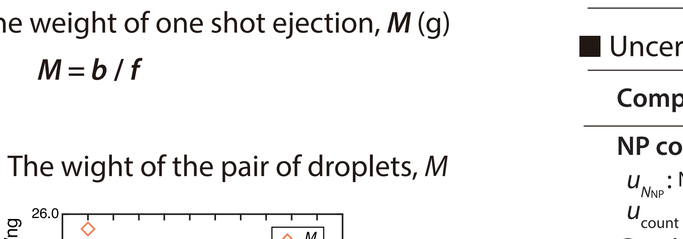
One ejection generated a pair of droplets

■ Image analysis: "catalog of Au NPs"



Checked the detected NPs one by one to remove artifact

■ SEM observation

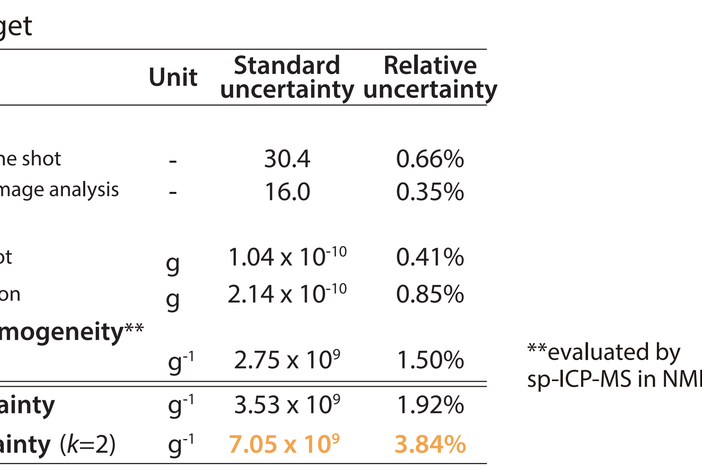


One droplet was examined with 9x11 SEM images to identify all particles

Stitching → Image analysis

■ Image analysis: Position of the detected Au NPs

*Yellow dots are larger than Au NPs to emphasize the position

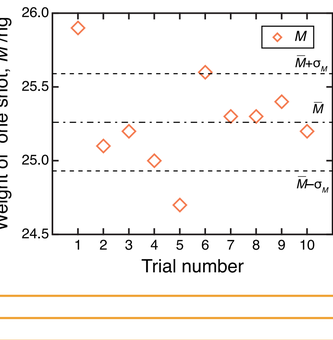


NPs were found within an almost perfect circle, No NPs outside.

→ ***No splash at the landing of the droplets [1]***

Typical SE image

■ Number of Au NPs in 5 pairs of droplets



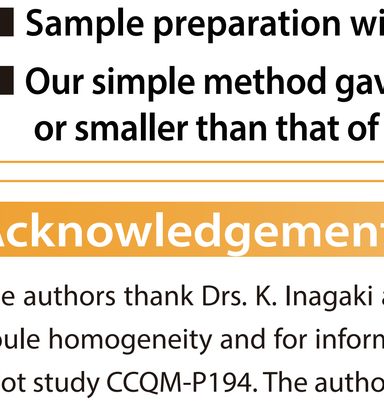
$\bar{N}_{NP}$ = 4635

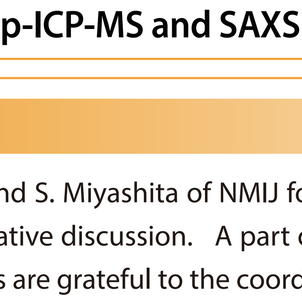
$\sigma_{N_{NP}} = \sqrt{\bar{N}_{NP}}$ = 68.1 (1.5% of $\bar{N}_{NP}$)

Good repeatability of droplet generation

■ Gravimetry

■ Weight variation during continuous ejection at f=540 Hz





Via linear fitting,
Increment by ejection in 1 s, b (g/s)

$$b = b_{obs} - b_{evap}$$

The weight of one shot ejection, M (g)

$$M = b / f$$

■ The slopes b_{obs} and b_{evap} for 10 trials

■ The wight of the pair of droplets, M

$\bar{M}$ = 2.53 (ng)

σ_M = 0.33 (ng)

■ Number concentration and uncertainty evaluation

■ Mean values of measurements

Measurand		Unit	Mean value
Particle number in one shot	N_{NP}	-	4.64 x 10^3
Weight of one shot ejection	M	g	2.53 x 10^{-8}
Number concentration	C_{NP}	g^{-1}	**1.84 x 10^{11}**

■ Uncertainty budget

Component	Unit	Standard uncertainty	Relative uncertainty
NP counting			
$u_{N_{NP}}$: NP number in one shot	-	30.4	0.66%
u_{count}: ambiguity in image analysis	-	16.0	0.35%
Gravimetry			
u_M: weight of one shot	g	1.04 x 10^{-10}	0.41%
u_{cal}: balance calibration	g	2.14 x 10^{-10}	0.85%
Inter-ampoule homogeneity**			
u_{bb}	g^{-1}	2.75 x 10^9	1.50%
Combined uncertainty	g^{-1}	3.53 x 10^9	1.92%
Expanded uncertainty (k=2)	g^{-1}	**7.05 x 10^9**	**3.84%**

**evaluated by sp-ICP-MS in NMIJ

Summary

- **We have developed new method to evaluate NC in NP suspension by combining SEM and gravimetry.**
- **Sample preparation with microdispenser allows us to confine the NPs in a small area without splashing and to identify all particles in a droplet.**
- **Our simple method gave a precise measurement of the NC of Au NPs with a relative expanded uncertainty of <4% (k = 2), which is as small as or smaller than that of sp-ICP-MS and SAXS [2, 3].**

Acknowledgement

The authors thank Drs. K. Inagaki and S. Miyashita of NMIJ for thier evaluation of the inter-ampoule homogeneity and for informative discussion. A part of this study was performed as the pilot study CCQM-P194. The authors are grateful to the coordinators of the pilot study.

References

[1] Xu L, Zhang W W and Nagel S R *Phys. Rev. Lett.* **94** 4 (2005)
[2] Maes J, et al. *Chem. Mater.* **30** 3952-62 (2018)
[3] Shard A *Final Publishable Report Metrology for innovative nanoparticles* (14IND12) EURAMET 27 (2018)