

Nanometrology for size and chemical analysis of semiconductor process impurity

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Abstract

Impurities in gases and liquids remain on wafer surface during semiconductor processing, and impurities increase in size and quantity along with the process steps, leading to wafer defects and semiconductor device failures. As semiconductor process nodes continue to shrink, the specifications for impurity size and concentration in process gases and liquids become increasingly stringent. With the rapid advancement of the semiconductor industry, the development of nanometrology must keep pace to maintain measurement standards and traceability in the semiconductor field. This project aims to develop nanometrologies for size < 5 nm nanoparticle measurement and ppt-level composition analysis.

Nanometrology

Size measurement

- Electrospray (ES, TSI-3480)
- Differential mobility analyzer (DMA, TSI-3080+classifier TSI-3085)
- Condensation particle counter (CPC, TSI-3776)

Composition analysis

- Metal analysis: Inductively coupled plasma mass spectrometry (ICP-MS, Agilent 8900)
- Anion analysis: Ion chromatography (IC, Thermo Fisher Dionex ICS-6000 HPIC)

Need & Solution & Achievement

Size measurement – lack of reference material with size < 5 nm

- Issues occur when using nanoparticle standards

- Variances in measured size with different preparation methods, including dilution, centrifugation, and heating
- Unsuitableness of size correction equation* for size < 10 nm

$$D_{Au} = D_p \left(1 - \frac{1}{3} \left(\frac{D_r}{D_p} \right)^3 \right)$$

D_{Au} : Diameter of AuNP

D_p : Diameter of NP

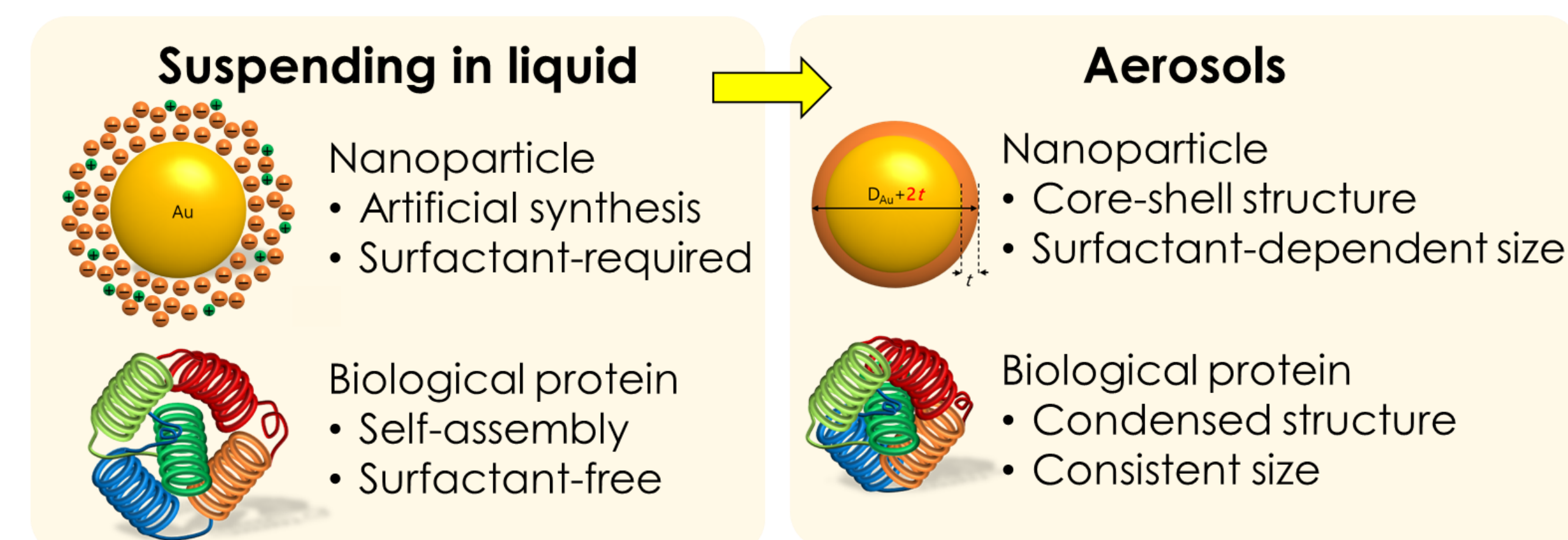
D_r : Diameter of residue particle *J. Res. NIST., 2006

Nominal diameter	Dilution		Centrifugation			Heating		
	0.8x	0.6x	x1	x2	x4	200 °C	500 °C	800 °C
10 nm	12.31	11.51	11.37	12.22	11.89	12.18	12.27	13.77
5 nm	-	7.96	7.85	7.86	7.83	7.98	10.01	9.94

- Formation of surfactant shell covering nanoparticle: surfactant concentration-dependent size of nanoparticle

- Alternative to nanoparticle standards: consideration of self-assembly, surfactant-free biological protein

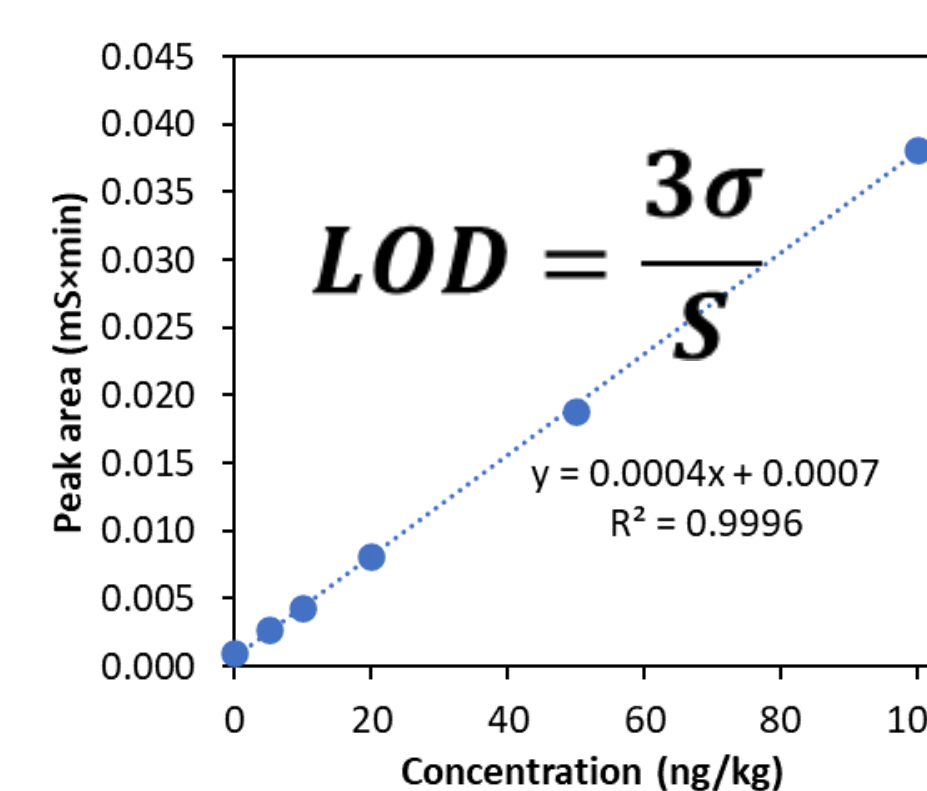
- Suspension in liquid, size variance < 1.2 %
- Long term (~5 months) stability, size variance < 2%



→ A potential reference material with size < 5 nm using biological protein – ubiquitin

Composition analysis – lack of metrology for low concentration < 10 ng/kg (ppt)

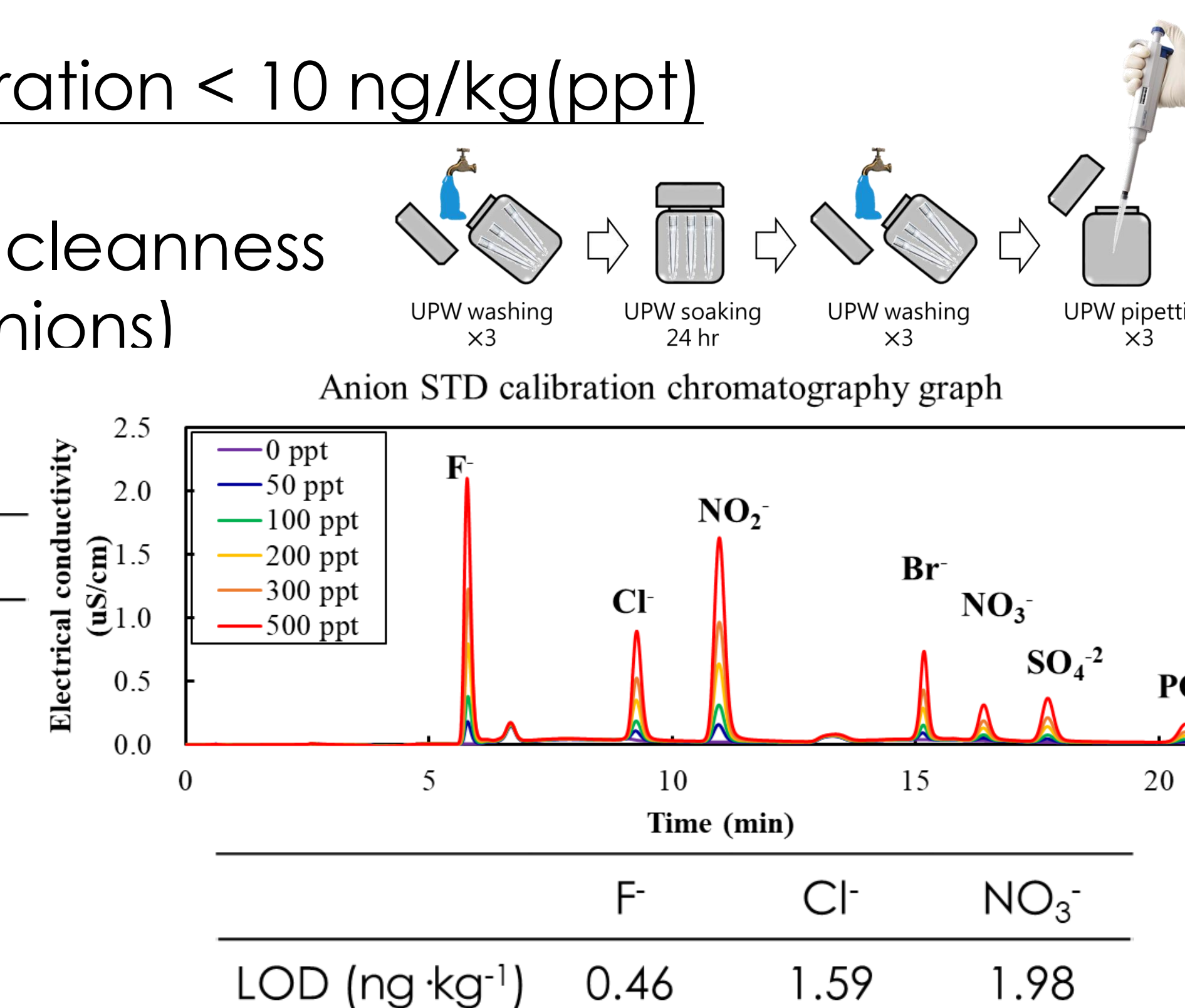
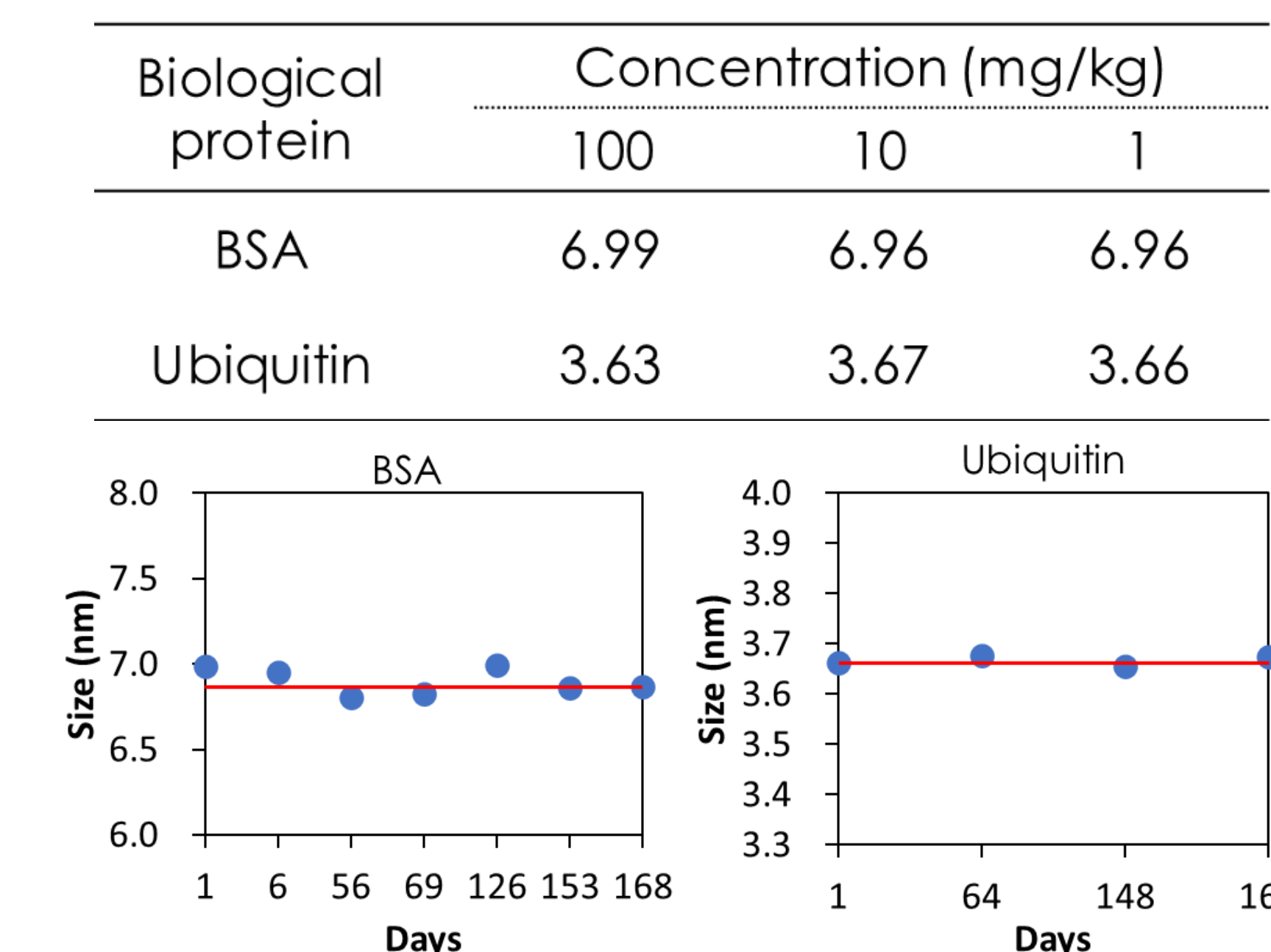
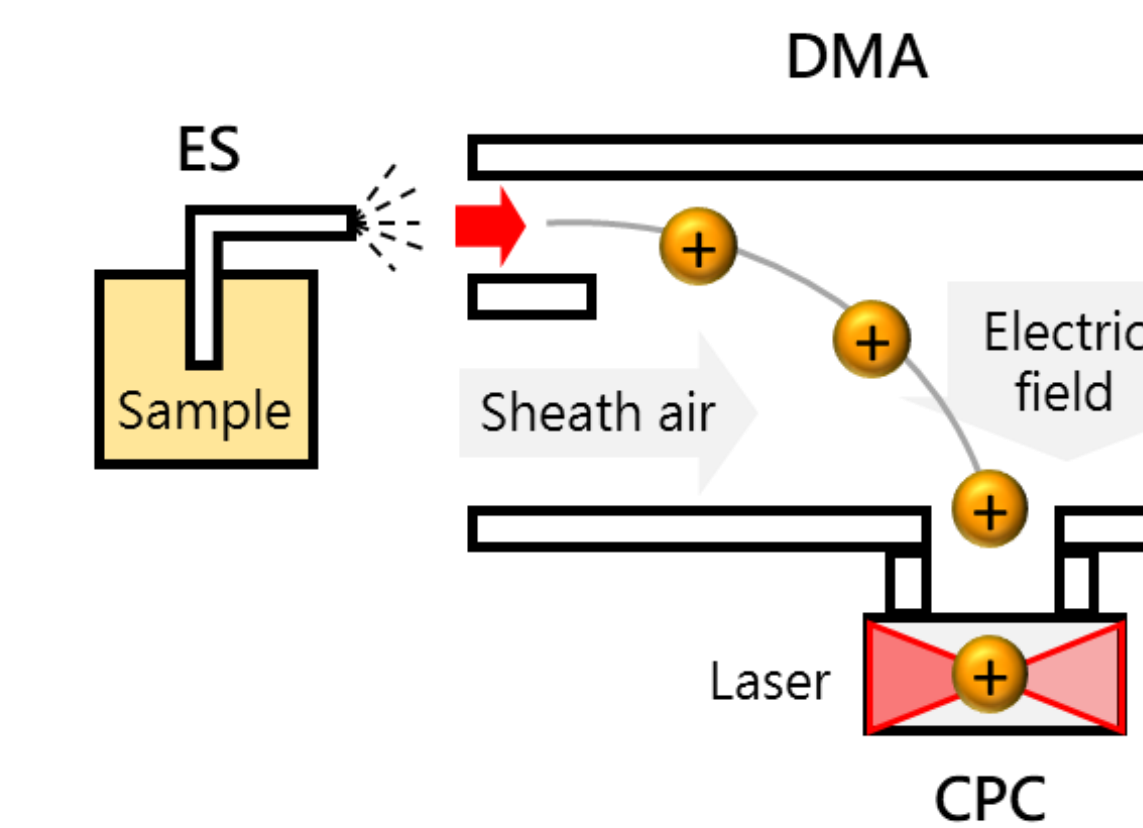
- ICP-MS: tuning optimization
- IC: eluent generator gradient optimization, tip & bottle cleanness
- Preparation of concentration standards (3 metals & 3 anions)
- Calculation of LOD for ICP-MS and IC



LOD: Limit of detect
 σ : Standard deviation
S: Slope of calibration curve

Tuning Parameters	Au	Mg	Fe
Plasma RF Power (W)	1600	1300	1200
Reaction cell gas, H ₂ (mL/min)	-	4.0	3.0
Omega lens (V)	18.5	4.0	4.0
Sensitivity (cps/(ng·kg ⁻¹))	264.92	1087.66	339.16
LOD (ng·kg ⁻¹)	0.23	0.05	0.12

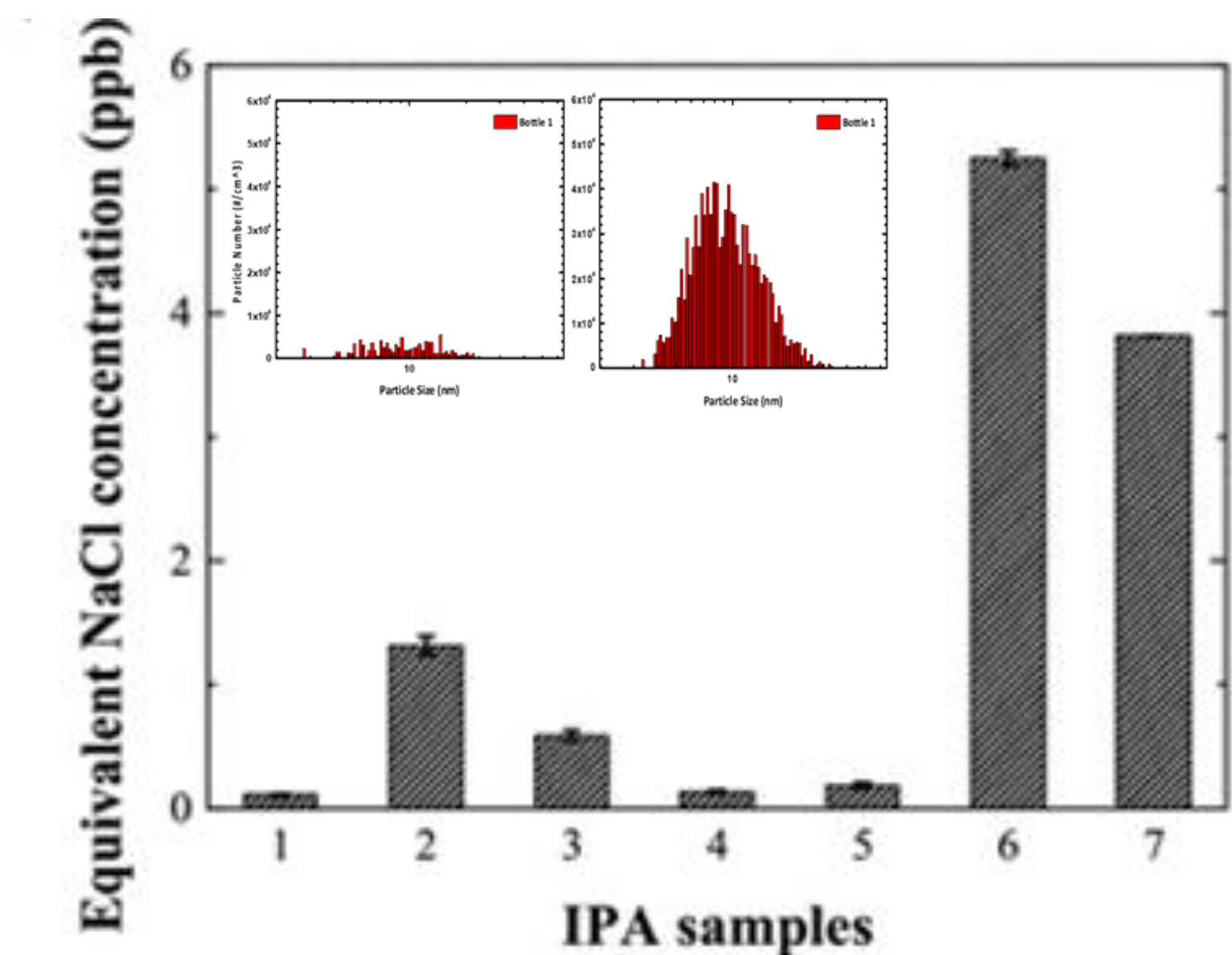
→ Metal & anion analysis for concentration < 10 ppt



Application

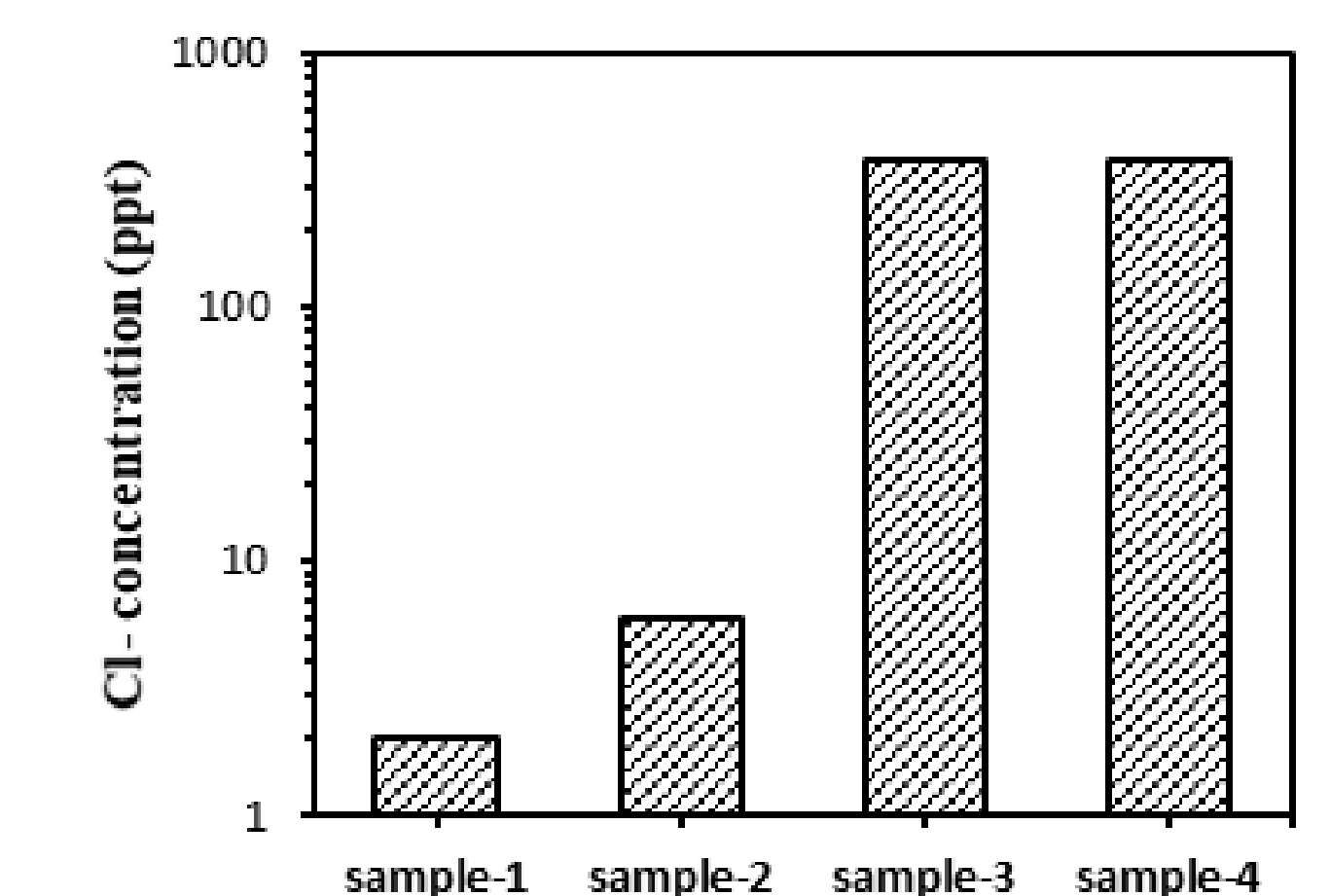
Size measurement

- Ppt-level non-volatile impurity detection
- Recognition of NG batch
- Quality control of chemicals



Composition analysis

- Ppt-level chloride detection
- Quality control of ultrapure water



Conclusion

The achievements of this research include the capability of size < 5 nm nanoparticle measurement and concentration < 10 ppt composition analysis. When applied to industry, this study assists in quality control of semiconductor process chemicals and gases, and fulfills the vision of metrology applications in the industry.