Background Statement for SEMI Draft Document 5297
New Standard: Test Method for Particle Removal Performance of Liquid Filter Rated 20 - 50 nm with Liquid-Borne Particle Counter

Notice: This background statement is not part of the balloted item. It is provided solely to assist the recipient in reaching an informed decision based on the rationale of the activity that preceded the creation of this Document.

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Background Statement

Liquid filters above 50 nm have been evaluated with polystyrene latex (PSL) sphere as traceable standard particle certified by public institution and optical particle counters (OPCs), but OPC is only applicable for approximately above 40-50 nm particle. Currently, there is no test method of below 50 nm-rated filters regarding particle removal capability using OPC.

Verifying various particles, task force confirmed that gold nanoparticle (GNP) has higher refractive index than other particles like PSL and silica particle and has high light scattering capability. Thus, GNP particles could be detected using OPC in the range of 20-50 nm. Also, GNP could be a standard particle for filter testing because that is one of the traceable particle as reference material (RM) released from National Institute of Standards and Technology (NIST).

This document describes a test method for particle removal performance of 20-50 nm-rated liquid filters using GNP and OPC.

The voting results of this ballot will be reviewed by the Liquid Filter Task Force, and will be adjudicated by the Japan Liquid Chemicals Committee at their meeting scheduled on Friday, April 5, 2013 at SEMI Japan, Tokyo, Japan.

If you have any questions on this ballot, please contact the following Task Force leaders or SEMI Staff:

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LETTER (YELLOW) BALLOT

SEMI Draft Document 5297
New Standard: Test Method for Particle Removal Performance of Liquid Filter Rated 20 - 50 nm with Liquid-Borne Particle Counter

1 Purpose

1.1 This document is to provide a standard of mono-dispersed gold nanoparticle (GNP) challenge test for liquid filter rated 20 – 50 nm using optical liquid-borne particle counter.

2 Scope

2.1 This document covers a mono-dispersed GNP challenge test method for 20-50 nm rated liquid filter.

2.2 This document defines a test condition for mono-dispersed GNP challenge test.

2.3 The following areas are to be addressed in this document:

- The test condition such as fluid, flow rate, pressure, GNP concentration, ligand concentration, membrane treatment etc.
- The type of filter evaluated.
- The type of gold nanoparticle (GNP) (reference material).
- The method of membrane treatment prior to the test for decreasing the adsorbing effect.
- The description of the test result.

NOTICE: SEMI Standards and Safety Guidelines do not purport to address all safety issues associated with their use. It is the responsibility of the users of the Documents to establish appropriate safety and health practices, and determine the applicability of regulatory or other limitations prior to use.

3 Limitations

3.1 The test procedure is destructive; the filter cannot be returned into operation.

3.2 Material purity and potential leaching of dissolved contaminants are not addressed by this standard. SEMI F57 does not address this issue for final filters therefore the end user may decide to consider such testing when selecting different types of filters.

4 Referenced Standards and Documents

4.1 *SEMI Standards and Safety Guidelines*

SEMI F63 — Guide for Ultrapure Water Used in Semiconductor Processing

SEMI F110 — Test Method for Mono-dispersed Polystyrene Latex (PSL) Challenge of Liquid Filters

NOTE 1: The SEMI NA Liquid Chemicals Committee is developing Evaluation of the Efficacy of the Filters of Ultrapure Water Distributions Systems intended to be used in conjunction with this Document.

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

5.1 *Abbreviations and Acronyms*

5.1.1 *FM* — flow meter

5.1.2 *GNP* — gold nanoparticle

5.1.3 *LPM* — liter per minute (L/min)

5.1.4 *LRV* — log reduction value

5.1.5 *MSA* — Mercaptosuccinic acid

5.1.6 *NIST* — National Institute of Standards and Technology

5.1.7 *OPC* — optical particle counter

5.1.8 *P* — pressure gauge

5.1.9 *PSL* — polystyrene latex

5.1.10 *T* — thermometer

5.1.11 *UPW* — ultrapure water

5.2 *Definitions*

5.2.1 *background* — the number of OPC count when feeding the water without GNP.

5.2.2 *challenge* — the feed the water including GNP and ligand to test filter.

5.2.3 *efficiency* — particle removal efficiency of filter measured by this test method. It is the effectiveness of the filter in removing the particles, and is measured as (Upstream – Downstream)/Upstream × 100.

5.2.4 *ligand* — ion or molecule (chemicals) that could bind with the surface of gold nanoparticle.

5.2.5 *log reduction value (LRV)* — log reduction value of filter measured by test method. This is measured as logarithmic value of ratio of upstream to downstream particle counts.

6 Summary of Test Method

6.1 This test method describes that test equipment and procedures for determining the particle removal efficiency of liquid filter (20-50 nm) with the water including ligand and GNP by calculating the difference of the number of challenged particle between upstream and downstream. The number of challenged particle is counted with optical particle counter.

7 Apparatus

7.1 *Test Device*

7.1.1 For this test method, use the schematic shown in Figure 1 or Figure 2.

7.1.2 The standard test device shall consist of a pre-filter, flow meters, a particle injection device, pressure gauges, a test filter, a particle counter, flow control valves, a resistivity sensor, a thermometer, and tubing connecting them.

7.1.3 The pore size of a pre-filter shall be equal to or smaller than the pore size of a test filter.

7.1.4 Use a flow meter with an allowable error to less than 5% full scale and of appropriate range.

7.1.5 Use a pressure gauge with an allowable error to less than 1% full scale and of appropriate range.

7.1.6 Use a thermometer with an allowable error to less than 1% full scale and of appropriate range.

7.1.7 Use a tubing with an inner diameter that does not lead to significant pressure loss for the fluid medium used in the test.

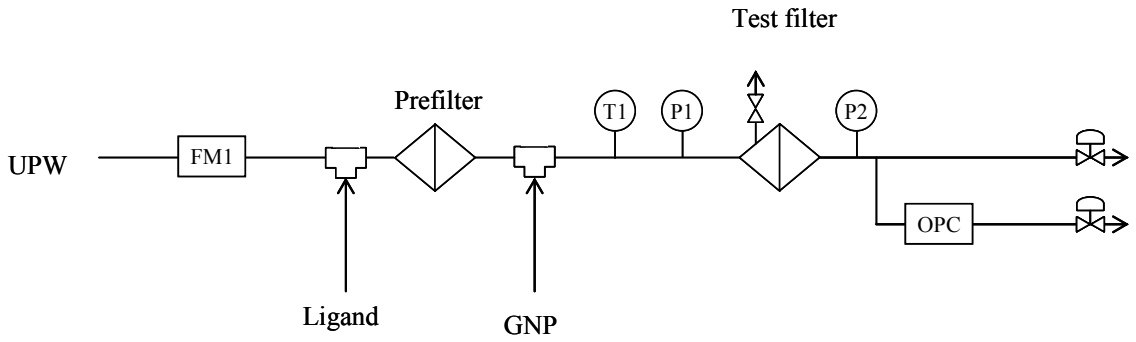

Figure 1
Schematic of Typical Test Setup (Example 1)

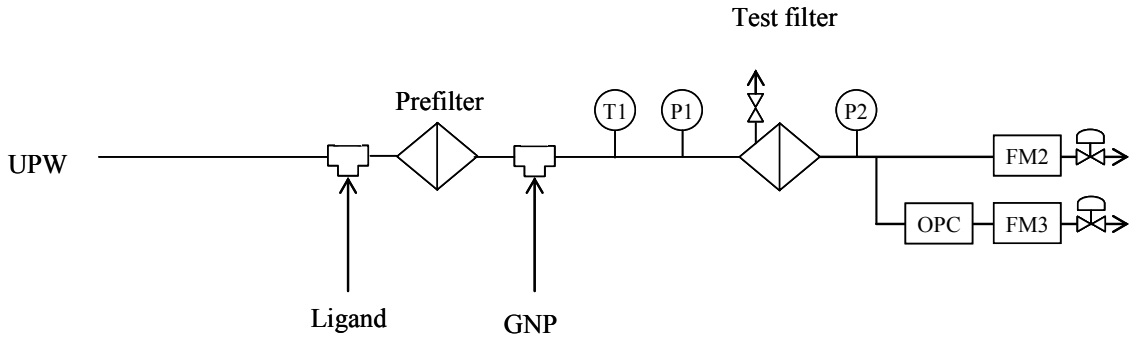

Figure 2
Schematic of Typical Test Setup (Example 2)

7.2 *Particle Injection Device*

7.2.1 Use a particle injection device that can inject a particle at a constant flow rate without a pulsation.

7.3 *Ligand Injection Device*

7.3.1 Use a ligand injection device that can inject a ligand at a constant flow rate without a pulsation.

7.4 *Particle counter*

7.4.1 Use the light scattering method particle counter.

7.4.2 Use a particle counter capable of measuring particle size to smaller than test GNP size.

7.4.3 Use cumulative counts of above minimum measurable particle size with OPC as count value.

NOTE 2: The intensity of scattered light from GNP is approximately 2.5 times of the one of polystyrene latex particle. Accordingly, OPC could detect smaller GNP than PSL. For example, the OPC capable to detect 50 nm particle (calibrated with 50 nm PSL), could detect 20 nm-sized GNP. Please see the Appendix 2.

8 Reagents and Materials

8.1 *Ultrapure Water (UPW)*

8.1.1 Use the supply UPW with the resistivity more than 17MΩ·cm.

8.1.2 Temperature of the UPW shall be adjusted to 25±5℃.

NOTE 3: As some ligands or other surfactants are added to actual challenge solution, there is no need to adhere to the resistivity described in 8.1.1 at challenge test.

8.2 *Gold nanoparticle (GNP)*

8.2.1 Use the mono-dispersed GNP, whose size is as same as the GNP certified by NIST.

8.2.2 The mono-dispersed GNP with 20-50 nm of particle size is used.

8.3 *Ligand*

8.3.1 Use a ligand to make colloidal GNP stably disperse and decrease the interaction between GNP and filter media. (please see the Appendix 1)

9 Test Specimens

9.1 Use a liquid filter from rating 20-50 nm.

9.2 Any size and type of filter, such as disk, capsule or cartridge, can be used in the test.

10 Procedure

10.1 *General Procedures*

10.1.1 The filter is evaluated by the following procedures:

- Testline background
- Filter pretreatment and filter flushing
- Background
- Challenge

10.2 *Testline background*

10.2.1 Background testing is required for every test before installing the test filter into the test line (see Figure 1 or Figure 2).

10.2.2 Set the test condition (flow rate and pressure)

- UPW (Resistivity: ≥17MΩ·cm, temperature: 25±5℃)
- FM1 or FM2 + FM3

  Choose either standard below:

  (1) Filter size standard: n L/min at 25.4*n mm-sized (n inch-sized) filter, (n=1,2,3,4,5….)

  (2) Filter media surface area standard: the flow rate to achieve the flux of 1 ml/min/cm^2.
- P2: ≥100 kPa

NOTE 4: A downstream pressure of at least 100 kPa has to be maintained in order to eliminate air in the system.

10.2.3 Start measurement using the OPC. It is necessary to count and confirm the stable values for more than 30 min.

10.2.4 Record particle levels in at least ten minute intervals.

10.2.5 Continue the particle measurement until the OPC counts become less than 10 counts/mL (≥50 nm).

10.3 *Filter Pretreatment*

10.3.1 Pre-wetting is needed if the test filter is hydrophobic (Follow filter manufacturer's instructions).

10.3.2 Pretreatment fluid is aqueous solution of a ligand used at the challenge test. The concentration shall be same with the concentration at the challenge test.

NOTE 5: The condition of ligand concentration to achieve the lowest adsorbing effect depends on membrane type. Accordingly, it is necessary to optimize it in advance. Please see Appendix 1 in terms of how to set the ligand condition.

10.3.3 Fill the membrane pore with the pretreatment fluid by flowing after installing into the test line.

10.3.3.1 After ¶10.3.3., soak filters in the pretreatment fluid for a minimum of 30 min.

10.4 *Background*

10.4.1 Start UPW flow and ligand injection.

10.4.2 Count the particles at downstream of the filter with the OPC before the challenge testing.

10.4.3 Close the air-vent valve after venting air from the filter upstream.

10.4.4 Set the test condition (flow rate and pressure).

- UPW (Resistivity: ≥17MΩ·cm, temperature: 25±5℃)
- FM1 or FM2 + FM3

  Choose either standard below:

  (1) Filter size standard: n L/min at 25.4*n mm-sized (n inch-sized) filter, (n=1,2,3,4,5….)

  (2) Filter media surface area standard: the flow rate to achieve the flux of 1 ml/min/cm^2.
- P2: ≥100 kPa

NOTE 6: A downstream pressure of at least 100 kPa has to be maintained in order to eliminate air in the system.

10.4.5 Start measurement of OPC.

10.4.5.1 Record particle levels in at least ten minute intervals.

10.4.5.2 Continue the particle measurement until the OPC counts become less than 10 counts/mL (≥50 nm) for more than 30 min.

NOTE 7: If the OPC counts do not become less than 10 counts/mL, terminate the challenge test and re-check test line and other apparatuses. Then, restart the challenge test from 10.4.

10.5 *Challenge*

10.5.1 Prepare the challenge mono-dispersed GNP When the challenge solution is diluted, it is necessary to use UPW characterized at 8.1 and agitate sufficiently. The prepared challenge solution shall be used in the test within 24h.

10.5.2 Install the particle counter directly downstream of the test filter (See Figure 1 or Figure 2).

10.5.3 Set the test condition (flow rate and pressure).

- FM1 or FM2 + FM3

  Choose either standard below:

  (1) Filter size standard: n L/min at 25.4*n mm-sized (n inch-sized) filter, (n=1,2,3,4,5….)

  (2) Filter media surface area standard: the flow rate to achieve the flux of 1 ml/min/cm^2.
- P2: ≥100kPa

NOTE 8: A downstream pressure of at least 100 kPa has to be maintained in order to eliminate air in the system.

10.5.4 Turn on the injection pump which delivers the challenge solution prepared at 10.5.1.

10.5.5 Begin injection at rate to achieve $10^{6\text{-}8}$ particles/mL (calculated actual number diluted from the original GNP number or concentration).

NOTE 9: The challenge level shall be defined in terms of the concentration at the filter after diluting in the main flow. The challenge level shall be lower than the measurable maximum concentration (particles/mL) of the OPC.

10.5.6 Record downstream pressure reading.

10.5.7 Run test for 1 hour.

10.5.7.1 Record particle levels in at least ten minute intervals.

10.5.7.2 Monitor particle levels downstream of the filter.

10.5.8 Close the valve on the particle counter's flow controller.

10.5.9 Without turning off the water or disrupting the injection pump operation, disconnect the particle counter from the downstream port of the test filter housing and re-install the particle counter directly upstream of the test filter in order to stabilize the particle challenge level. (See Figure 3).

10.5.10 Open the particle counter flow controller valve fully to allow air to escape.

10.5.11 Adjust the flow controller to sensor specifications.

10.5.12 Record particle levels in at least ten minute intervals.

10.5.13 Monitor particle levels upstream of the filter. It is necessary to count and confirm the stable values for a minimum of 30 min.

10.5.14 Turn off injection pump.

10.5.15 Turn flow off at inlet valve.

10.5.16 Open drain and vent valves.

10.5.17 Remove test filter.

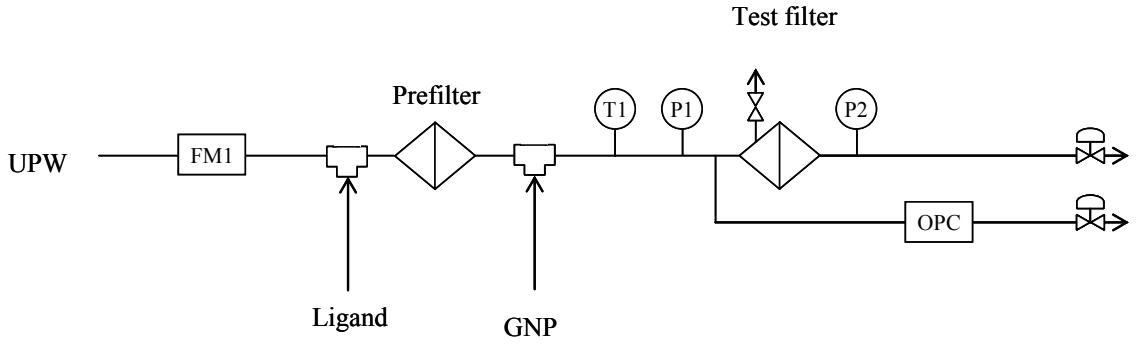

Figure 3
Schematic of Typical Test Setup (Example 3)

11 Calculations

11.1 Particle removal efficiency (%) and LRV are calculated using the average of the data points from 30 min to 60 min for downstream levels and the measured OPC counts as upstream value described at 10.5.13.

$$\% \text{ Efficiency} = (\text{Upstream} - \text{Downstream})/\text{Upstream} \times 100\% \quad (1)$$

$$\text{LRV} = \text{Log}(\text{Upstream}/\text{Downstream}) \quad (2)$$

12 Report

12.1 Include the system setup, which includes the particle data system settings.

12.2 Include calculated efficiencies and LRV, shown in Table 1 (sample data).

12.3 Report resistivity, temperature and flux.

Table 1 Sample Data Format (Example)

Filter / Filter size/ Lot number	A
GNP size *(nm)*	30
GNP manufacturer/ Lot number	A
GNP concentration *(N/ml)*	1E+8
Ligand / Ligand concentration *(mmol/L)*	MSA / 0.3
Flow rate *(L/min)*	0.5
OPC manufacturer/ Model number	A
Background Average *(N/ml)*	0.5
Upstream Average *(N/mL)*	2.0E+7
Downstream Average *(N/mL)*	1500
Efficiency *(%)*	99.99
LRV *(-)*	4.1

#1 Downstream values were calculated by averaging 30 min to 60 min recorded.

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APPENDIX 1

Ligand addition

NOTICE: The material in this Appendix is an official part of SEMI [designation number] and was approved by full letter ballot procedures on [A&R approval date].

A1-1 Purpose of ligand addition

As the GNP used in this standard has very small size, some disturbance such as concentration change, contamination of foreign object, and pH change could easily cause aggregation or sedimentation of GNP. Also, the interaction between GNP and filter media is extremely high and GNP could be adsorbed on the surface of filter media.

In order to stabilize GNP colloidal system and prevent filter media from adsorbing GNP, it is preferable to use ligand technique. Precious metal like gold and platinum can bind with sulfur element and the molecule including amino group with a coordination bond [1)2)]. Thus, the gold surface could be easily modified by molecules including thiol or amino functional groups.

A1-2 Polyethylene filter

For polyethylene filter, a branched or bulky ligand like Mercaptosuccinic acid (MSA) including carboxyl group could reduce adsorbing effect [3)]. Figure A1-1 shows the schematic drawing of atomic configuration of MSA molecule combing with GNP. GNP is entirely covered with MSA ligand by adding the ligand into GNP challenge solution, and the GNP covered with MSA is difficult to approach to filter media surface by steric effect. Furthermore, when the GNP challenge solution including MSA is injected into main line, it is expected that the colloidal system might be instable because MSA concentration is rapidly decreased. Therefore, previously adding MSA ligand into main line at upstream of GNP injection line. Also, it is preferable to use MSA for filter pre-treatment.

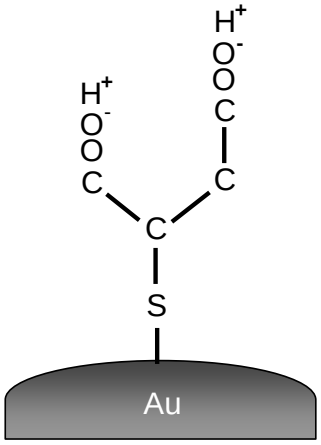

Figure A1-1

Schematic drawing of atomic configuration of MSA molecule combining with GNP. Sulfur element is combined with gold element.

A1-2.2 Investigation of proper ligand concentration

As described in this document, the ligand condition to achieve the lowest adsorbing effect is varied with membrane type. Thus, it is necessary to examine proper condition in advance. Please refer to following example showing particle penetration ratio is varied with MSA concentration.

(Example)

Filter type: Membrane sheet, 47 mm in diameter

Filter rating: 30 nm

Challenge GNP specification : 10 nm – 2.9E+10 pcs/mL

Ligand – MSA 0 – 1.0 mmol/L, MSA solution was added to GNP solution.

Filtration was performed by challenging with GNP solution containing MSA after prewetting the membrane with Isopropyl alcohol at a flow rate of 5 mL/min. Figure A1-2 shows that the penetration ratio of 10 nm GNP through 30 nm-rated polyethylene membrane. The penetration ratio increased with an increase of MSA concentration. On the contrary, the gradual decrease of the penetration ratio was observed at more than 0.3 mmol/L of MSA concentration. In this case, around 0.2 mmol/L of MSA concentration is suitable to achieve the lowest adsorbing effect between GNP and membrane surface.

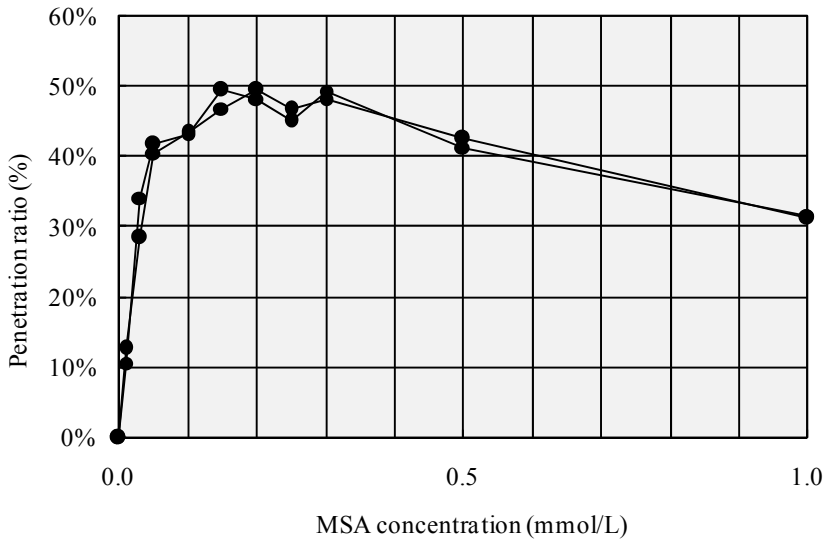

Figure A1-2

The penetration ratio of 10 nm GNP through 30 nm-rated polyethylene membrane. At around 0.2 mmol/L of MSA concentration, the highest penetration ratio could be observed.

A1-2.3 Filter pretreatment

MSA shall be injected into UPW main line. It is expected to have a effect of filter pretreatment decreasing adsorbing effect before GNP challenge test. Also, stabilizing effect of GNP solution could be expected when injecting GNP into main line. Below example shows the comparison between only UPW in main line and UPW+MSA in main line.

(Example)

Filter rating : 50 nm

Filtration area : 660 cm^2

Challenge GNP specification :

30 nm – 1.0E+8 pcs/ml

50 nm – 2.0E+7 pcs/ml

Ligand – MSA 0.1 mmol/L

Flow rate – 500 ml/min

Table A1-1 OPC counts of filter downstream using 60 nm-sized OPC calibrated with PSL

GNP size	30 nm		50 nm
Challenge solution	GNP + ligand	GNP + ligand	GNP + ligand
Main flow	UPW	UPW+ligand	UPW+ligand
	7950	16488	1
	8053	16219	5
	7935	15992	2
	8423	16380	5
	8721	15865	6
	8518	16442	4
	8768	16124	3
	8958	16230	3
	8547	16468	8
	8771	16792	6

Table 2 shows that the count rate of downstream at the condition adding ligand into main line is higher than the one at the condition using no ligand in main line. This result shows that adding ligand into main line causes the reduction of adsorbing effect.

References

1) G. Schmid, “Nanoparticles – From Theory to Application”, Wiley-Vch Verlag GmbH & Co. KgaA (2004).

2) G. T. Hermanson, “Bioconjugate Techniques”, Elsevier (2008).

3) T. Mizuno *et al.*, “A novel filter rating method using less than 30-nm gold nanoparticle and protective ligand”, *IEEE/TSM*, vol. 22, No. 4, (2009) 452-461.

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APPENDIX 2

GNP detection with OPC

NOTICE: The material in this Appendix is an official part of SEMI [designation number] and was approved by full letter ballot procedures on [A&R approval date].

A2-1 Background

Commercialized OPC does not have a capability to detect smaller than approximately 50 nm-sized particle due to the lack of scattered light from the particle. The intensity of scattered light is generally proportional to the 6th power of particle diameter. For example, the intensity of scattered light from 10 nm-sized particle is 1/1000000 of that of 100 nm-sized particle. As the intensity of scattered light is decreased exponentially with a decrease of particle size, it is easily predicted to create a difficulty in counting small particle. If the intensity of scattered light is increased, OPC could detect smaller particles. There are various methods to increase an intensity of scattered light such as increase of the power of incident light, increase of the sensitivity of detector and increase of scattering ability from particle.

GNP has larger refractive index than PSL. The intensity of scattered light from particle depends on the ratio of the refractive index of particles and liquid medium. Thus, it is expected that the intensity of scattered light is larger than that of PSL, and smaller particle could be detected.

However, as commercialized OPC has been calibrated with PSL, it is considered that the detection particle size of GNP differs from the calibration value. In this section, compatibility, detection sensitivity characteristics of the actual measurement of GNP are described.

A2-2 Test diagram and parameter

Actual GNP counting test with OPC was conducted. Figure A2-1 shows that schematic diagram of the test line for GNP counting. The diluted GNP in sample bottle is injected into OPC using syringe sampler, and the number of GNP is counted.

Particle counter (KS-18F, Rion, Japan)

Minimum detectable particle size : 50 nm (PSL)

Effective sample flow rate : 1 ml/min (Sample flow rate : 10 ml/min)

Light source wavelength : 532 nm

Optical angle : 90^{o}

Collecting angle : 90^{o}

Medium : UPW

GNP characteristics

Refractive index : 0.467-2.41i (at 532 nm wavelength) [4)]

Particle : EMGC30 (30 nm) and EMGC60 (60 nm), British Biocell International, UK

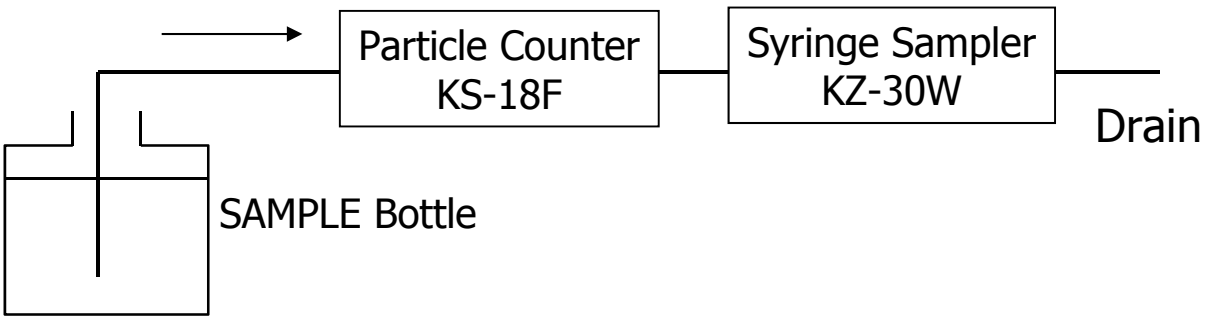

Figure A2-3
Schematic diagram of test line for GNP counting

A2-3 Measurement result of 30 and 60 nm GNP using OPC

Figure A2-2 shows the particle size distribution of 30 nm GNP using PSL-calibrated OPC. The original number of GNP (10,000 pcs/ml) in the solution is calculated from the manufacturer's specification. The peak value of particle size was detected at 70 nm. The number of counts more than 50 nm and 70 nm were estimated at 9,310 pcs/ml and 5,800 pcs/ml, respectively. That is in roughly agreement with original number of GNP.

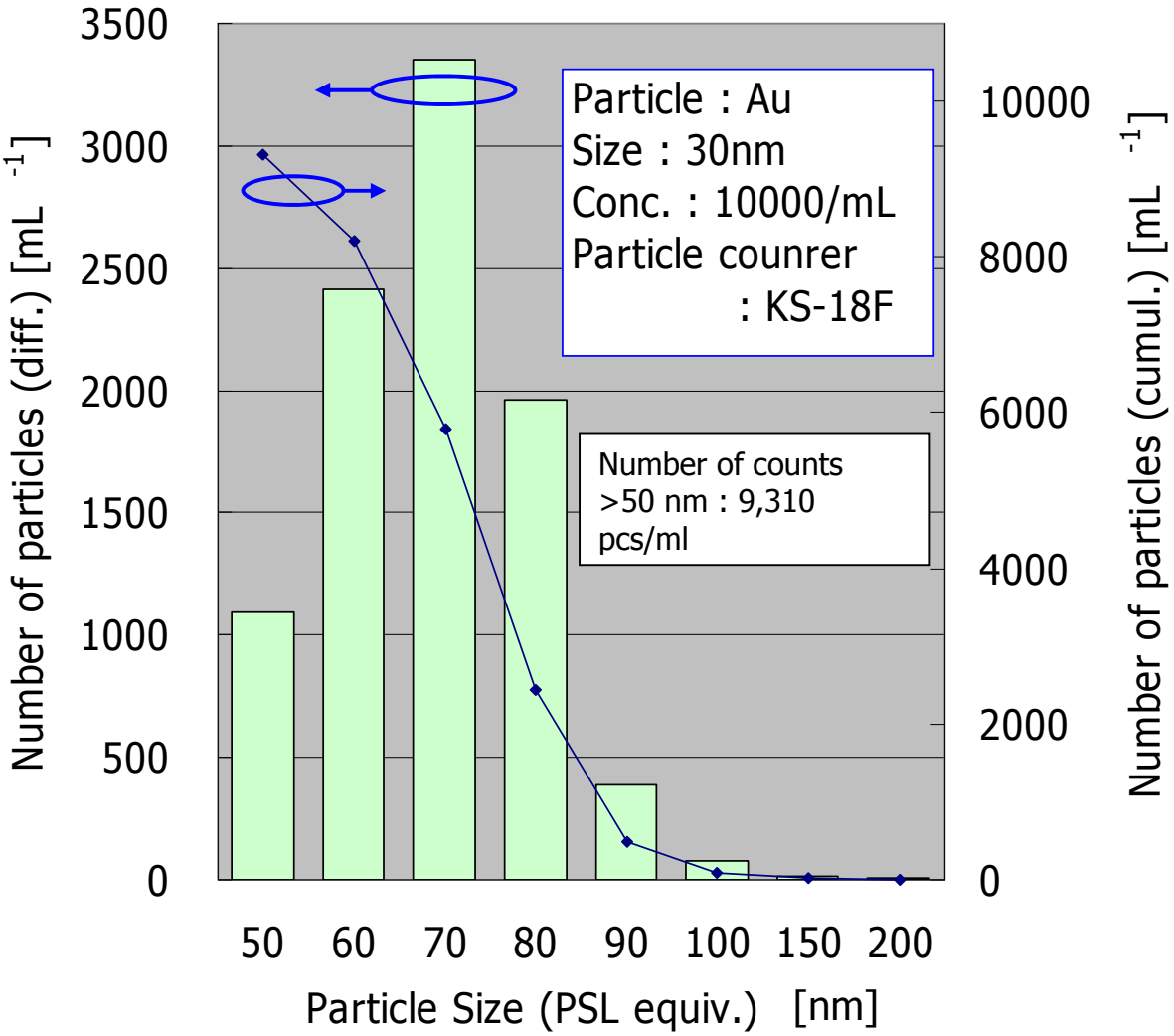

Figure A2-4
Particle size distribution of 30 nm GNP measured with KS-18F (50 nm) OPC

Figure A2-3 shows the result of particle size distribution measurement of 60 nm GNP. The original number of GNP (10,000 pcs/ml) in the solution is calculated from the manufacturer's specification. 170 nm-sized particle was mostly counted. The number of counts more than 50 nm and 170 nm were estimated at 10,470 pcs/ml and 4,770 pcs/ml, respectively. The counting efficiency of 60 nm GNP was about 100%, but several percentages of some smaller particles or contamination were observed.

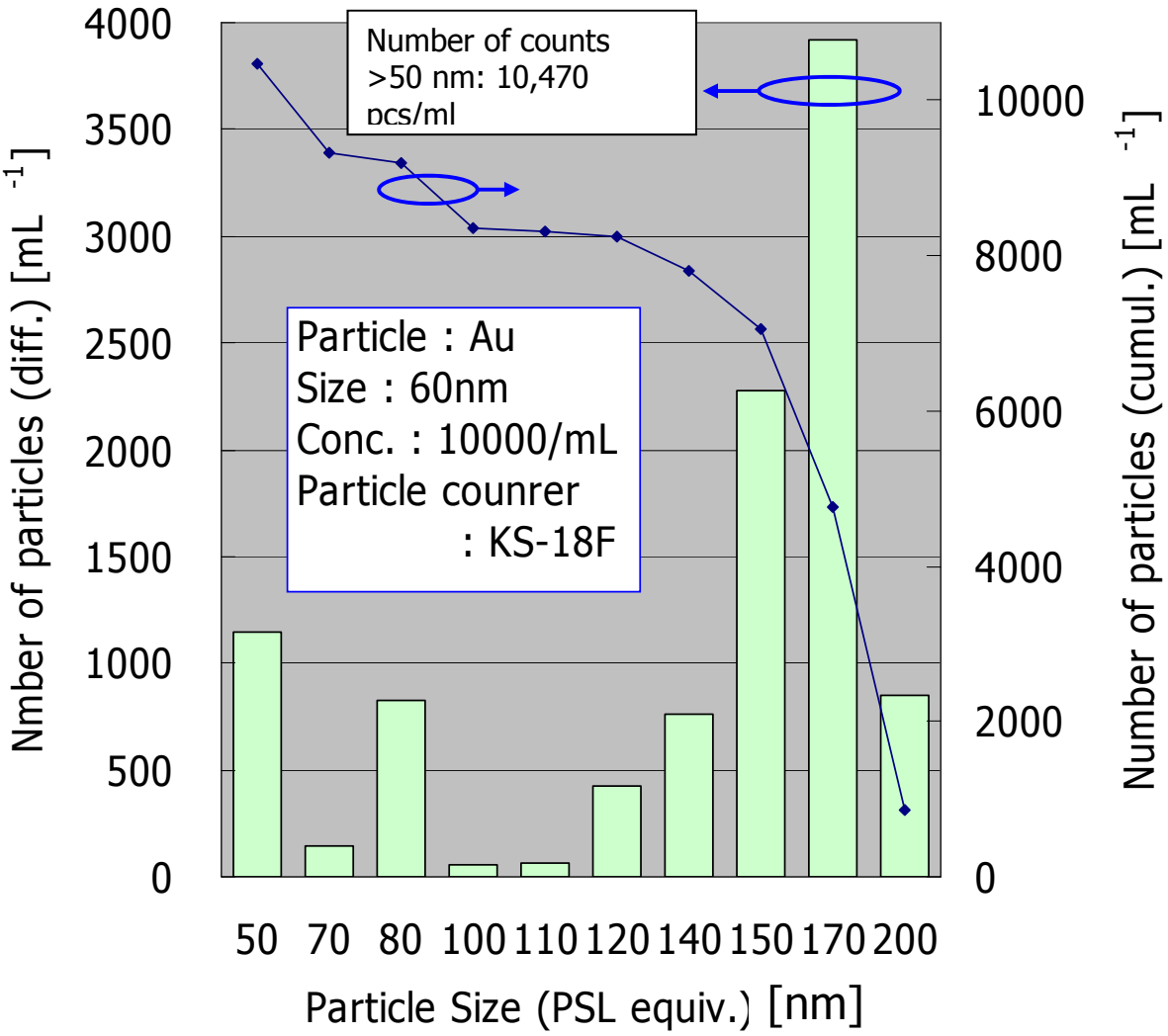

Figure A2-5
Particle size distribution of 60 nm GNP measured with KS-18F (50 nm) OPC

Finally, light scattering intensity (V) of GNP was compared with PSL with a function of particle size each in Figure A2-4. Solid lines mean theoretical light scattering characteristics referring the refractive index 4), and all plots are almost on the theoretical line. Good agreement was confirmed.

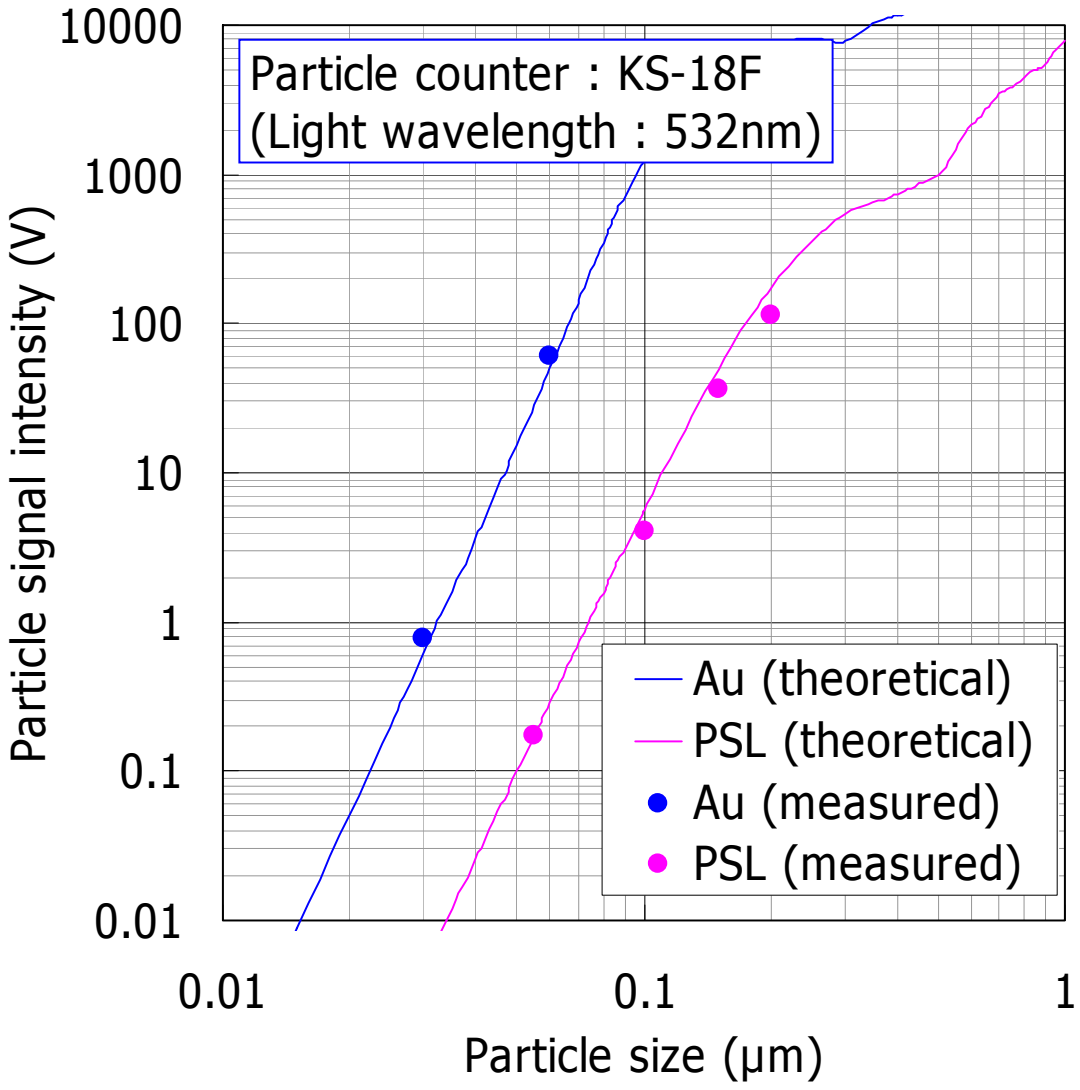

Figure A2-6
Light scattering intensity of GNP and PSL varied with particle size

As a result, the equivalent particle sizes of GNP using theoretical calculation are summarized in Table A2-1 50 nm-sized OPC (calibrated with PSL) could be applied to more than 20 nm GNP challenge test.

Table A2-2 Equivalent size of GNP measured with OPC calibrated with 50 nm PSL

GNP size	Equivalent size (PSL)
20 nm	49 nm
30 nm	74 nm
50 nm	132 nm
60 nm	169 nm

Reference

4) E.D. Palik, Handbook of Optical Constants of Solid, Academic Press (1997)