2P-60

Rapid Removal and Release Ability of DualPore Metal Scavenger in High Flow System

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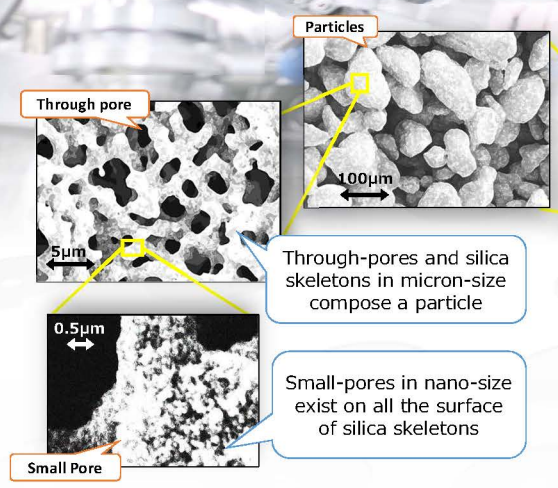
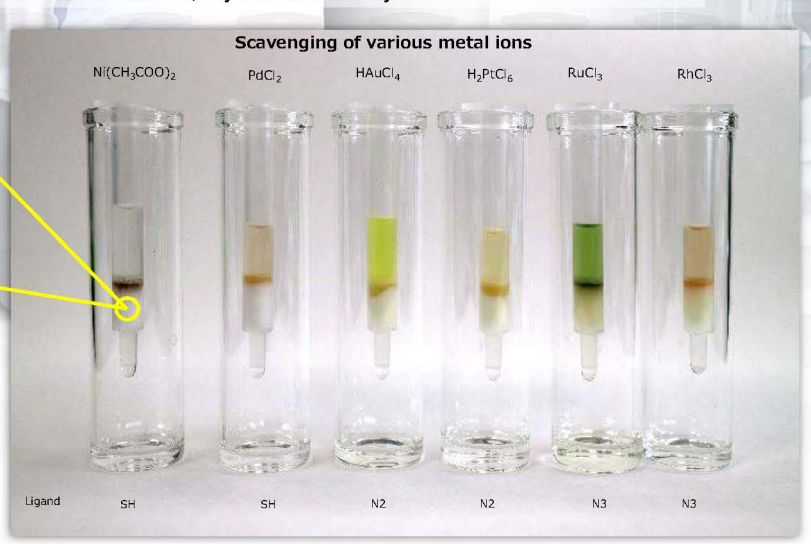
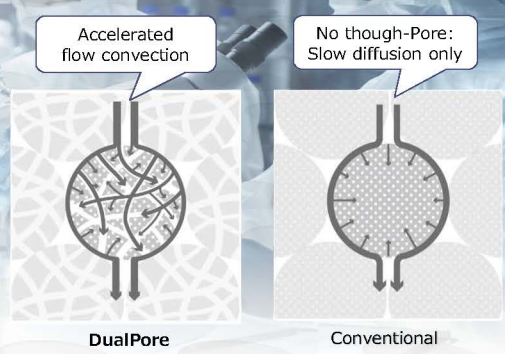


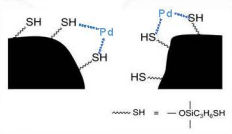


Concept of Perfusion



The DualPore particle has a unique and well-defined bimodal pore structure with through pores and small pores. Therefore, molecules can be diffused deeper inside a particle quickly and the distribution equilibrium is accelerated very effectively, that is called "Perfusion Effect." This phenomenon was already advocated in 1990s by F. E. Reigner but eventually had to wait over 15 years to be proven by DualPore.

IMAGE of metal scavenging



SH modified DualPore silica in a cartridge was applicable to the treatment of residual Pd solution and the Sonogashira coupling reaction. The Pd ions were efficiently adsorbed at a low concentration until 50% of its adsorption capacity as the leaching of Pd.

1) T. Yamada, H. Sajiki, et al., *Org. Process Res. Dev.*, **2019**, *23*, 462−469, DOI: 10.1021/acs.oprd.8b00291

INTRODUCTION: DualPore silica, which consists of a microporous continuous framework structure with small pores in nanometer showing the excellent flow-dynamic adsorption characteristics in column systems by the perfusion effect that accelerates a flow convection into the particle due to the well-controlled macro pore. For efficient removal of metal ions in the purification of medicines or chemicals, a unique metal scavenger, using the DualPore silica immobilized thiol, amino, and carboxy ligands had been developed, that is able to reduce Pd species at 1 ppb or less in rapid processing by flow-through usage. Aiming to utilize the DualPore scavengers on the purification of fine chemicals in ultra-pure grade, here we report the dynamic metal-scavenging characteristics of DualPore in the extremely low concentration of ppt level on ICP-MS/ICP-AES measurement.

1. Excellent scavenging with low back pressure enables high flow treatment exceeding 100 m³ & 100 L/h : Sub-ppm adsorption from lab scale to large processing

1.1 Rapid, efficient, and complete removal on 100 ppm Pd flow study

Excellent dynamic binding capacity: **Residence time (RT) of only 20 seconds was enough to utilize over 70%** of the maximum capacity.

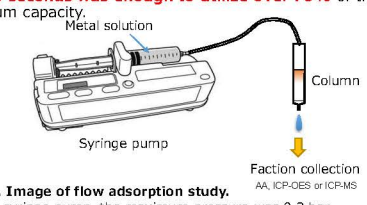


Fig 1. Image of flow adsorption study.
Using syringe pump, the maximum pressure was 0.3 bar.

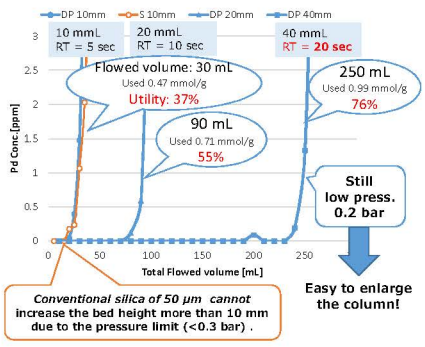


Fig 2. Breakthrough curve on 100 ppm Pd flow adsorption study
100 ppm of Pd $(OAc)_2$ solution in 1% HCl/methanol with flowed through a DualPore or conventional metal scavenger SH packed column (Φ5.5x10 mm) at 3 mL/min (2 mm/sec). Pd concentration in each column outlet was analyzed by atomic adsorption photometer (in collaboration with Hamari Chemicals, Ltd.)

1.2 Extremely low back pressure enables a high flow processing over 100 L/h

DualPore metal scavenger (SH modified) showed **only 1/5 - 1/7 of back pressure** of conventional 50 μm product on the test using an HPLC column. The pressure profiles of the column were linear to solvent viscosity, column length, and the linear velocity.

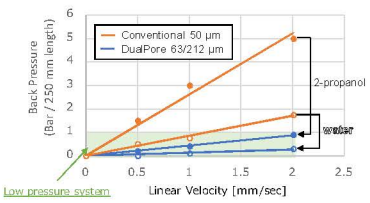


Fig 3. Column back pressure and linear velocity.
Water or 2-propanol was flowed into a column (Φ4.6 × 250 mm) packed with SH modified DualPore or conventional silica using LC-10AD pump at 25℃.

Due to the adequate dynamic adsorption capacity and low back pressure profile, DualPore is versatile to use in combination of any cartridge or flow-through container.

Fig 4. Columns or cartridges for metal scavenging from lab to large processing.

1.3 Flow rate, pressure drops, and lifetime estimate in case of 1 ppm Pd adsorption in each cartridge

Table 1. Design of adsorption cartridges from small to large processing

Purpose	Type	Length [mm]	Diameter [mm]	Volume [mL]	Weight [g]	Capacity [mmol]	Pd Capacity [g]	Waste capacity 1 ppm Pd [m³]
Lab purification	F-40	121	27	69	17	12	1.3	1.3
	F-120	201	36	205	51	36	3.8	3.8
	F-330	203	60	574	143	100	10.6	10.6
Mid. Scale	C-10	185	68	672	168	118	12.5	12.5
	C-10W	185	108	1695	424	297	31.4	31
Large processing	I-3R	200	136	2905	726	508	53.9	54
	I-5R	225	169	5047	1262	883	93.6	94
	I-10R	300	212	10590	2647	1853	196.4	196
	I-20R	350	328	29574	7393	5175	548.6	548

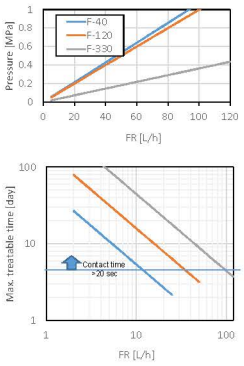


Fig 5. Relations of flow rate, pressure drops, and maximum treatable time in case of 1 ppm Pd scavenging for FLASH cartridges.

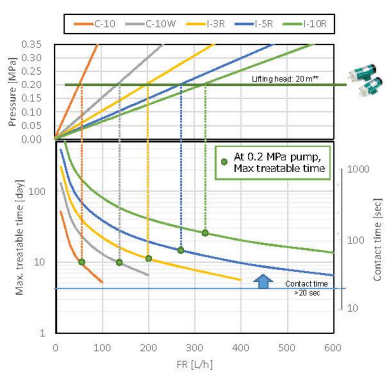


Fig 6. Relations of flow rate, pressure drops, and maximum treatable time in case of 1 ppm Pd scavenging using water purifiers.

2. Ultra purification from ppb to ppt level

Unrecovered metals in a trace concentration < 1 ppm were selectively scavenged by DualPore scavengers and the samples are ultra purified just by passing through the cartridge.

2.1 Removal of Pd from ppb to ppt

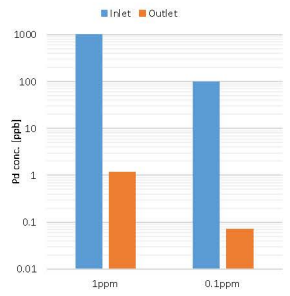
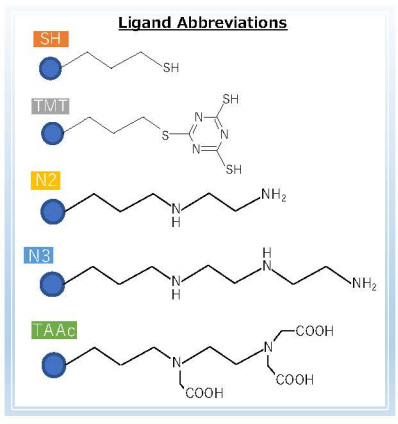


Fig 7. Palladium removal using SH-type scavenger from ppb to ppt
Palladium acetate in 0.1 M HNO_3 4 mL was flowed into a DualPore SH packed column. Flow rate 3 mL/min, Column size: Φ5.5x10mm, SH loading: 1.3 mmol/g, Analyzed by ICP-MS



2.2 Selectivity on transition metals in aqueous solution (pH 1)

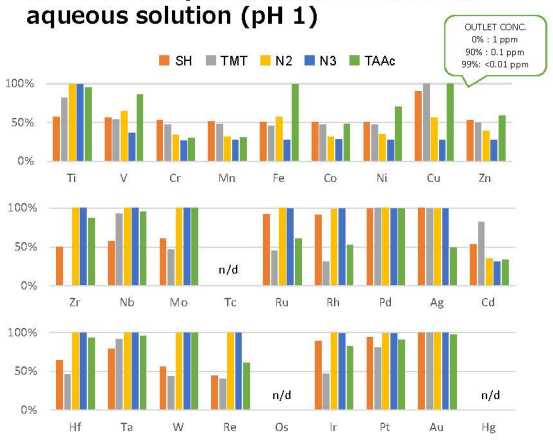


Fig 8. Removal ratio of transition metals from 1 ppm
4 mL ICP-MS standard 1 ppm of each element in 0.5% HNO_3 was flowed in a cartridge (210 mg bed) by ca. 3 mL/min. Concentrations of elements were analyzed by ICP-AES. The detection limit <2-10 ppb depending on the metals. For Ru, Rh, Pd, Ir, Pt, Au, and Hf, the solution was in 1% HCl.

2.3 Selectivity on osmium scavenging

Osmium was completely removed by SH and TMT in the detection limit of < 5 ppb. With N2 and N3, a slight release <2% release was observed (0.2 ppm at outlet). Whereas TAAc was insufficient to remove the Os ion.

Fig 9. Removal ratio of osmium from 10 ppm inlet
10ppm OsO_4 in water 3 mL was passed through the 3mL cartridge / 210 mg bed. OsO4 in 2-propanol solution was diluted in water. Concentrations were analyzed by ICP-AES. The detection limit <5 ppb.

3. Recovery of adsorbed Pd, Pt, Au, etc.

Precious metals adsorbed in a very low concentration can be recovered as a concentrated pure solution (or solid after drying) just by passing the elution solution through the cartridge . Additionally, multiple usage of scavengers is feasible by regeneration by washing with acid.

3.1 Adsorption/release ability of precious metals

Adsorbed precious metals were recovered by the wash by acid or thiourea containing acid depending of the ligand. Additionally, strongly adsorbed metals can be released by a wash with aqua regia.

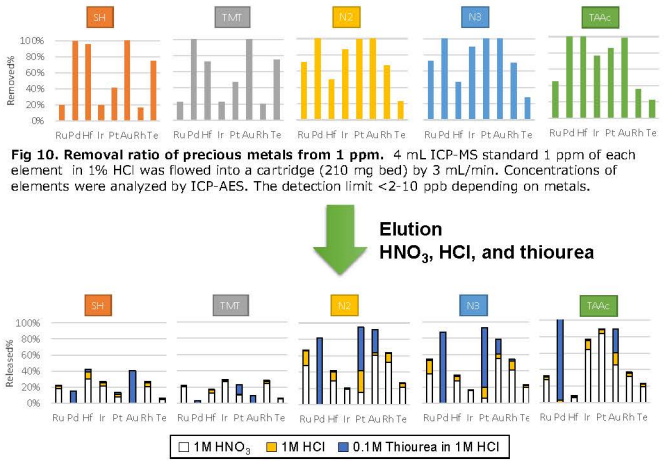


Fig 10. Removal ratio of precious metals from 1 ppm. 4 mL ICP-MS standard 1 ppm of each element in 1% HCl was flowed into a cartridge (210 mg bed) by 3 mL/min. Concentrations of elements were analyzed by ICP-AES. The detection limit <2-10 ppb depending on metals.

Fig 11. Accumulated released ratio. Following to (a), 1M HNO_3, 1M HCl, and 0.1M thiourea solution in 1M HCl (each 3 mL) were continuously flowed into the columns. Concentrations of elements were analyzed by ICP-AES. The detection limit <2-10 ppb depending on the metals.

3.2 Regeneration of scavenger

Fig 12. Multiple usage of the scavenger after adsorbing Pd and the collected Pd as pure crystals. 100 ppm of $Pd(OAc)_2$ solution in 1% HCl was flowed for adsorption. Adsorbed Pd was recovered by flow with 1mL of thiourea solution in 1M HCl to reuse the column.

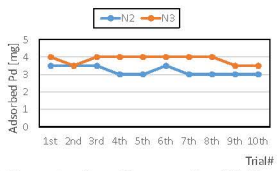


Fig 13. Dynamic adsorption capacity of Pd in regeneration. 100 ppm of $Pd(OAc)_2$ solution in 1% HCl was flowed into each N2 or N3 column (φ5.5x10 mm of scavenger, at 3 mL/min). Dynamic adsorption capacity was determined at which the outlet on the column was >1 ppm.

CONCLUSIONS

DualPore metal scavenger is a unique and versatile solution to remove the trace metal ions to ppb - ppt level and applicable not only to a lab usage, but also to a large process.

Due to the excellent dynamic adsorption capacity only requiring 20 second residential time to utilize over 70% of its maximum capacity as well as the extremely low back pressure profile, DualPore is very suitable and fit with any form of standard cartridges or container in a flow through mode.

Depending on acids, the adsorbed metal ions can be recovered as a concentrated solution or pure crystals. Moreover the scavengers can be regenerated to use over 10 times enabling cost-effective method.

Thus, DualPore metal scavengers can address to the unfulfilled strong need of "polishing" the purity for ultra-pure materials.