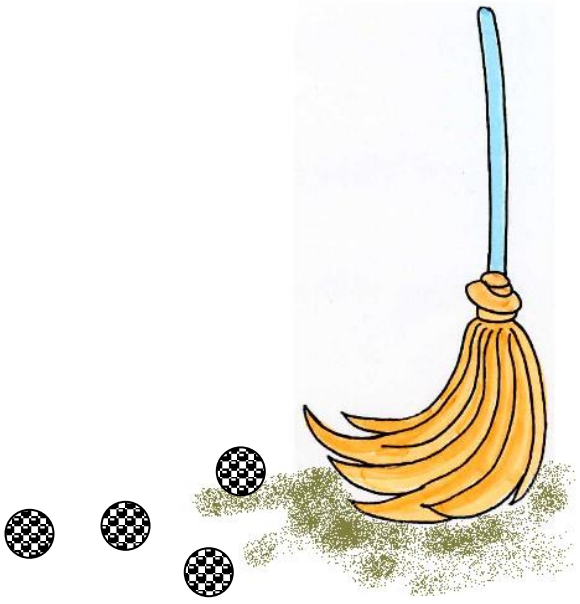
Technical Bulletin

CHROMATOREX

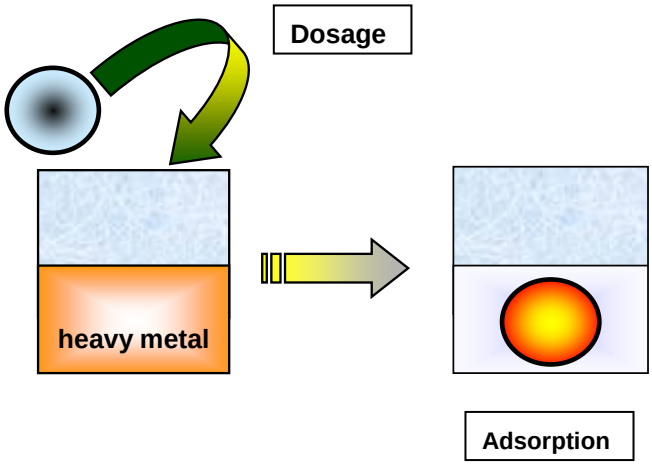
Silica Gels

For Metal Scavenger



Introduction　　Silica gel for Metal scavenger

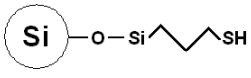
Transition metal catalysts are used in many organic syntheses such as Suzuki-Miyaura reaction. In these processes, removing the residual heavy metals after the reaction is just as important as the development of catalyst reaction process.　One effective process uses a solid scavenger that bonds to the heavy metals. The surface is modified by a functional group to combine specifically with metals on the solid surface in order to remove the metal. We have developed a porous silica-based **metal scavenger** with a high surface area, a high mechanical strength, and high chemical stability compatible with almost all solvents. The silica gel was modified by silane coupling agents which contain special functional groups that have an affinity for heavy metals. We provide **metal scavengers** for removing heavy metals such as palladium. **Metal scavengers** can be used all the way from the small-scale lab bench to large-scale chemical, pharmaceutical, and biological processes.



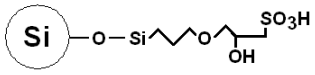
Grade

We supply four kinds of **metal scavengers** with different functional groups.

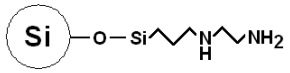
SH　Silica



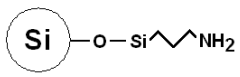
SO3H Silica



Diamine Silica



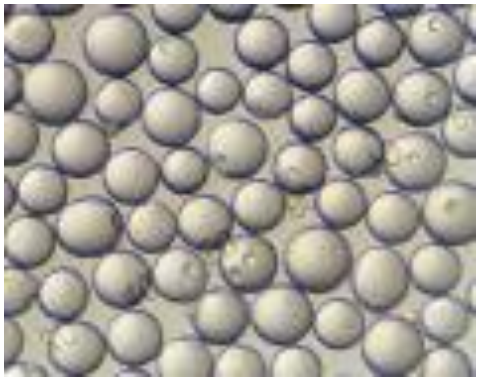
NH　Silica



Properties of the base silica gel

The base silica gel has a spherical shape.

Shape	:	Spherical
Particle size	:	１００μm
Pore size	:	１０ｎｍ（１００Å）

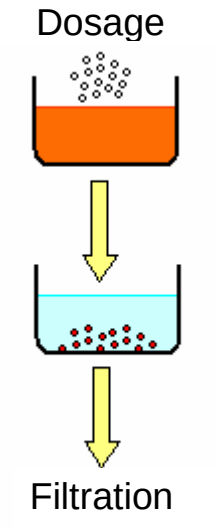


Micrograph of SH Silica 100μm

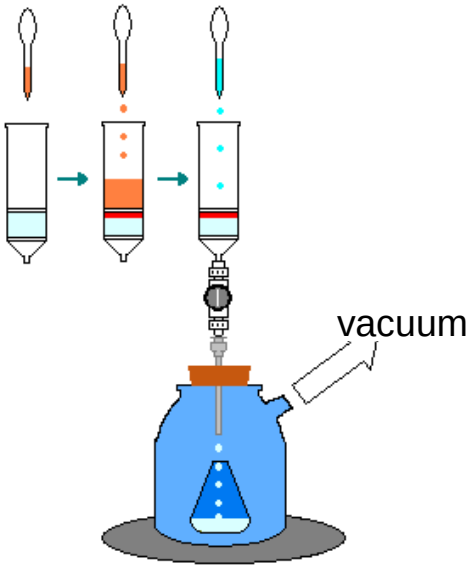
Operation methods

Heavy metal removal can be utilized in both batch and column methods. The two methods are useful for both laboratory experiments and pharmaceutical production.

★Batch method



★Column method



Adsorption capacity

The following experiments demonstrate the adsorption capacity of the metal scavengers. SH Silica and Diamine **metal scavengers** were soaked in a palladium and a nickel solution. After adsorption, the residual metal concentration was measured and changed to the amount of removed metals per gram.

(Experimental condition)

The removal limits were carried out 0.01M of solution and the adsorption capacities were 0.1M of solution.

Pd: Palladium acetate/ chloroform

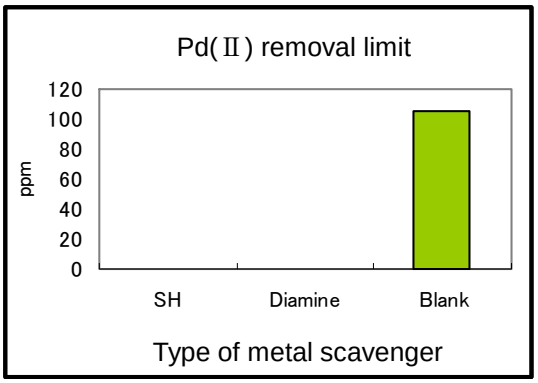
→ Palladium solution + 0.25g of silica gel → stirred 1hr → filter → ICP measurement

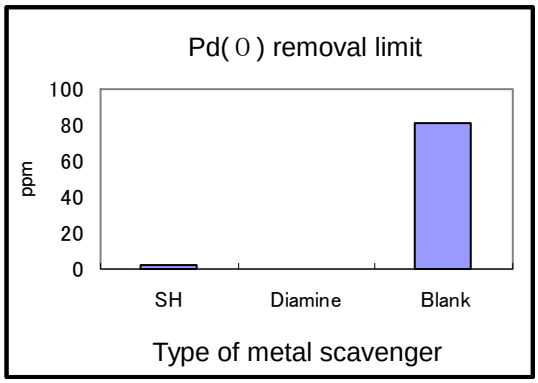
Ni: Nickel acetate/H_2O

→ Nickel solution + 0.25g of silica gel → stirred 1hr → filter → ICP measurement

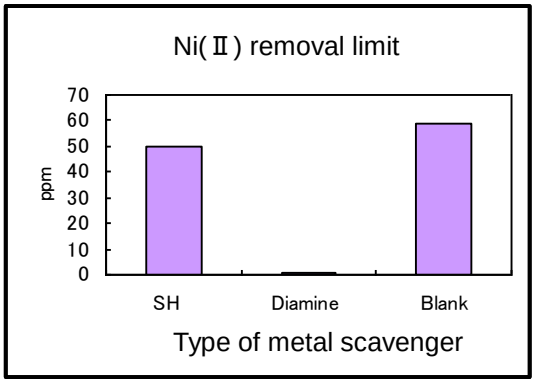
(Results)

Pd removal limit





Ni removal limit



SH Silica and Diamine Silica showed a good adsorption ability for Pd(II). The adsorption ability for Pd(0) was a little lower than Pd(Ⅱ).

Only Diamine Silica showed a good adsorption ability for NI(II).

Exchange capacity

Function	Modification amount (mmol/g)	Exchange capacity (mmol/g)		
		Pd(Ⅱ)	Pd(0)	Ni(Ⅱ)
SH	0.78	0.81	0.19	0.14
Diamine	1.01	0.95	0.48	0.31

Addition and removal limit

The removal limit was tested by changing the amount of added metal **to the scavenger silica**. 25ml of palladium acetate solution (200ppm) was added to 0.125g, 0.25g and 0.5g of the **metal scavenger**. After stirring for 1 hour, the solutions were filtered and the residual palladium was measured by ICP.

	Chloroform	concentration(ppm)
	blank	**197**
◎	SH 0.5g	N.D.
◎	SH 0.25g	N.D.
○	SH 0.125g	0.06
◎	Diamine 0.5g	N.D.
◎	Diamine 0.25g	N.D.
◎	Diamine 0.125g	N.D.

N.D. : less than 0.05ppm

The removal capability of palladium was decreased as decreasing the amount of addition. In this experiment, using only 0.125g of the **metal scavenger** virtually removed all 5mg of the palladium to the detection limit.

Effect of solvent

To confirm the effect of solvents on the metal removal, palladium acetate was dissolved into chloroform, methanol, ethyl acetate, and toluene (200ppm each) and added 0.25 g of the **metal scavenger** to each solution. After stirring, the concentrations of residual palladium were measured by ICP.

(Results)

	Chloroform	concentration(ppm)
	blank	**207**
◎	SH 0.25g	N.D.
◎	Diamine 0.25g	N.D.

	Methanol	concentration(ppm)
	blank	**137**
◎	SH 0.25g	N.D.
△	Diamine 0.25g	1.92

	Ethyl acetate	concentration(ppm)
	blank	**208**
◎	SH 0.25g	N.D.
◎	Diamine 0.25g	N.D.

	Toluene	concentration(ppm)
	blank	**202**
○	SH 0.25g	0.07
◎	Diamine 0.25g	N.D.

N.D.: less than 0.05ppm

Chloroform and ethyl acetate had no influence on the test. There was an influence of Diamine silica with methanol and also showed an influence of SH Silica with toluene.

Adsorption rate

An adsorption rate was measured by the following method. 100ml of 200ppm palladium acetate solution was stirred with 2g of SH Silica. The concentration of palladium in the solution was measured by ICP every 1, 5, 10, 30 and 60min after adding the SH Silica.

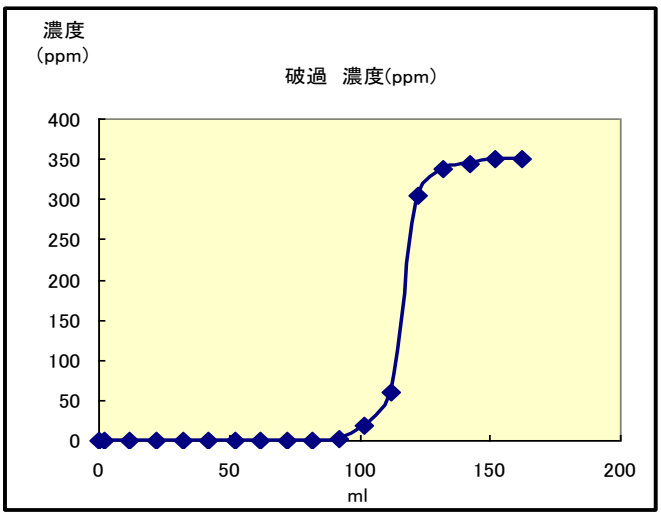
	concentration(ppm)
blank	186
1min later	0.12
5min later	0.03
10min later	N.D.
30min later	N.D.
60min later	N.D.

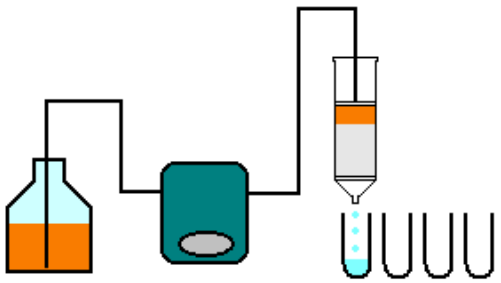
N.D. :less than 0.05ppm

The palladium concentration was less than 1ppm after 1min when adding SH Silica. Most of the palladium was adsorbed completely within a minute.

Column breakthrough test

A breakthrough test was carried out by the following method. A column filled with 0.7g of SH Silica and ran about 350ppm of palladium acetate / chloroform solution with 2.4ml/min. The drain was collected every 10ml and measured the residual of palladium by ICP.





Up to the fraction No.8, the Pd was removed completely. After then, the column reached a breakthrough point and the drain showed a same concentration with the former solution.

Breakthrough capacity:

(5×2.4+10×8)・350/1000=Pd 32.2mg/column= Pd 46mg/SH Silica(g)

Grade and adsorbate

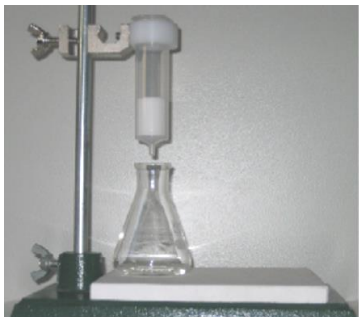
This following table shows the adsorbate that each metal scavenger grade removes.

Grade	Adsorbate
SH silica	Pd(Ⅱ), Pt , Ru , Hg
SO3H Silica	amines
Diamine Silica	Ni(Ⅱ), Pb , Zn , Cd , Ru
NH Silica	acid chlorides, isocyanates

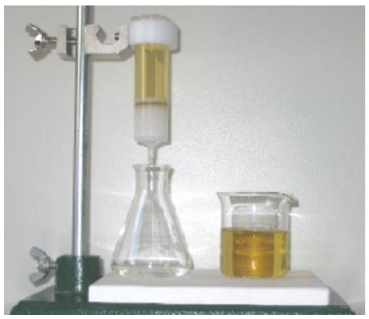
Adsorption and desorption

Here is an example of adsorbed-desorbed palladium recovery operation. More than 95% of palladium could be recovered.

Eluent : 2% of thiourea / 1N of HCl・methanol



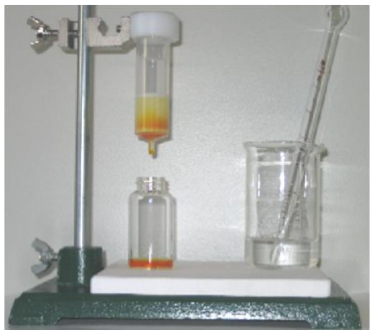
①Set a column



②Flow a palladium contained solution

③Wash the column with a solvent

④Flow the eluent



⑤Recover the eluted palladium

⑥Complete the elution

✱ SH Silica has a strong adsorption force with palladium, therefore it did not elute in this condition

FUJI SILYSIA CHEMICAL LTD.
2-1846 Kozoji-cho,
Kasugai-shi, Aichi-ken,
Japan 487-0013
Phone : +81 568 51 2516
Fax : +81 568 51 8557
E-mail : chromato-jpn@fuji-silysia.co.jp

FUJI SILYSIA CHEMICAL SA
International Chromatography Center
En Budron E 9
CH-1052 Le Mont-sur-Lausanne Switzerland
Phone : +41 21 652 3436
Fax : +41 21 652 4737
E-mail: fuji.silysia.sa@fuji-silysia.co.jp

July 2006