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## Silicalite as a sorbent for solid-phase extraction

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### Abstract

A molecular sieve known as Silicalite was used as a sorbent for solid-phase extraction (SPE) of organic analytes from aqueous samples. Silicalite contains an intricate system of channels approximately 6 Å in diameter, but unlike most other molecular sieves the channels of Silicalite are able to retain organic compounds by hydrophobic attraction. Small hydrophilic compounds, such as the lower alcohols, aldehydes, esters and ketones, are well extracted by Silicalite, thus adding a valuable new capability to conventional SPE. Extensive data are presented to define the scope and limitations of Silicalite for SPE. Breakthrough curves were used for several compounds to determine their loading capacity on Silicalite.

*Keywords:* Silicalite; Solid-phase extraction; Stationary phases, LC; Alcohols; Aldehydes; Esters; Ketones

### 1. Introduction

Solid-phase extraction (SPE) is one of the most popular sample preparation techniques for the isolation and preconcentration of organic compounds from aqueous samples. It has many advantages over traditional liquid–liquid extraction. SPE is a multi-stage rather than a single stage process. Organics undergo multiple equilibrations, resulting in a more complete extraction. SPE also uses less organic solvent and is easily automated, saving time and money. It has been shown that modified porous polystyrene–divinylbenzene (PS–DVB) resins containing polar groups are superior for SPE of organic solutes from aqueous samples [1,2]. Most recently, Dumont and Fritz [3] introduced surface sulfonic acid groups to PS–DVB resins. These modified resins displayed excellent surface hydrophilicity and

improved extraction efficiencies. However, these same resins were unable to extract small, polar organics successfully. Therefore, Silicalite was employed for SPE to complement polystyrene and bonded-phase silica adsorbents.

Silicalite is a molecular sieve, first synthesized in the early 1970s [4]. Unlike other molecular sieves, Silicalite is hydrophobic and extracts organic molecules from liquid and gaseous samples. Silicalite is a polymorph of silica with an unusual crystal structure. It has a tetrahedral framework of mostly 5-membered rings of silicon–oxygen tetrahedra. These tetrahedra form a three dimensional system of intersecting channels, 6 Å in diameter, defined by rings of 10 oxygen atoms. The total pore volume is approximately 33% [4]. For sorption, the diameter of a particular analyte must not exceed 6 Å, roughly the kinetic diameter of benzene. Water molecules are not adsorbed because they associate into clusters of 10–12 molecules, producing a total diameter larger than 6 Å [4]. Because of its unique structure, Silicalite

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adsorbs organic analytes through hydrophobic interactions and possesses size exclusion properties.

To date, research involving Silicalite has concentrated on the mechanisms and kinetics of its adsorption and desorption of inert gases [5,6], hydrocarbons [7–17], aromatics [17–26] and alcohols [27,28]. Silicalite has also been used to remove *n*-butanol from fermentation liquors [29], ethanol from beer [30], and sulfur dioxide from stack gas [31]. In other applications, Silicalite has been used as a catalyst [32–35].

Silicalite has been embedded in polydimethylsiloxane, ethylene-propylene, polychloroprene and nitrile butadiene rubbers to form composite membranes. These membranes were used in pervaporation studies of organic solvent/water systems [36–40], separation studies of carbon dioxide/methane and oxygen/nitrogen gas systems [41] and sorption of chlorinated hydrocarbons [42]. Silicalite increased the selectivity of alcohol adsorption and improved the separation properties of the polymers towards gaseous mixtures. Other composite membranes consist of a pure, thin layer of Silicalite on porous ceramic substrates [43,44]. The layer is formed through an in-situ synthesis and composed of highly intergrown Silicalite polycrystals. These membranes were used to study the permeation of single component and binary mixtures of various gases and showed high selectivities for specific conditions.

Silicalite has also been crystallized to form a non-composited membrane on a variety of surfaces, including Teflon [45], silver [45], stainless steel [45–49], Vycor [45], and alumina disks [46,49]. The permeability and selectivity of the membranes were measured for bicomponent gas mixtures [45]. The membranes were also used for pervaporation studies of alcohol/water [46,48,49] and methanol/methyl-*tert*-butyl ether mixtures [47]. Silicalite crystals have also been embedded in silver and nickel matrices [50] and a large, single crystal has been placed in an epoxy resin and mounted in a specially designed permeability cell [51].

An extensive study on the scope and limitations of using Silicalite as a sorbent for SPE is lacking in the literature. Schultz-Sibbel et al. [52] reported distribution coefficients and capacities for the adsorption of a variety of compounds by Silicalite from gas

or water samples. Fritz and Ogawa [53] used Silicalite to concentrate low concentrations of aldehydes and ketones from aqueous samples prior to derivatization and separation by liquid chromatography.

In the present work, Silicalite was used as a sorbent for SPE. Aqueous solutions containing a wide variety of organic compounds were used to determine the extraction ability of Silicalite. Percentage recoveries of various organics extracted by Silicalite were compared with those using a lightly sulfonated porous PS–DVB resin-loaded membrane. Extraction capacities for small, polar organic compounds were also determined using Silicalite.

## 2. Experimental

### 2.1. Reagents and chemicals

Analytes studied were >99% pure and used as obtained from Fisher (Fisher Scientific, Pittsburg, PA, USA) and Aldrich (Aldrich Chemical Company, Inc., Milwaukee, WI, USA). Laboratory distilled water was further purified using a Barnstead Nanopure II system (Sybron Barnstead, Boston, MA, USA). Silicalite from the UOP Inc., was sieved to obtain 5–10  $\mu\text{m}$  particles. Experimental membranes containing these particles [54] were obtained from the 3M company (3M Co., St. Paul, MN, USA). Experimental Empore<sup>®</sup>-type membranes embedded with 8  $\mu\text{m}$  PS–DVB sulfonated resin, 0.6 meq/g sulfonation capacity, were used as obtained from the 3M Company (3M Co., St. Paul) and can be purchased commercially as SDB–RPS.

### 2.2. Procedure for SPE

The apparatus for SPE consisted of a 30 ml glass syringe barrel fitted with a luer tip. A 1.5 ml polypropylene SPE column (P.J. Corbert Assoc., St. Louis, MO, USA) was connected to the glass reservoir via a universal adapter. The Silicalite particles and sulfonated resin-loaded membranes were used as the SPE adsorbents. Towards the end of this study, experimental Silicalite-loaded membranes were available and used to determine the effect of embedding Silicalite particles in a membrane on SPE

efficiency. Each adsorbent was placed between two 20- $\mu\text{m}$  polyethylene frits (P.J. Corbert Assoc.) in the SPE column. Additionally, the Silicalite particles were supported from the bottom with a piece of 2- $\mu\text{m}$  filter paper. The bed heights measured approximately 0.5 cm. Positive pressure was used to force liquids through the adsorbents. Prior to use, 1 ml acetone and 1 ml deionized (DI) water were used to condition each column.

Samples were prepared by adding a 100  $\mu\text{l}$  aliquot of a methanol solution containing 1000 ppm each of 2–3 analytes to 10 ml of DI water. The final concentration of each compound in the sample was about 10 ppm, except for all phenols which were 5 ppm. Air pressure was adjusted to provide a flow of 1–2 ml/min (30–50 p.s.i.; 1 p.s.i.=6894.76 Pa). After loading, the glass reservoir was rinsed with 1–3 ml DI water and air was blown through the column to remove any remaining water. A 1-ml aliquot of acetone was used to elute the compounds into a GC vial. Methanol was the eluting solvent when acetone was an analyte. An internal standard (100  $\mu\text{l}$  of an acetone solution containing 150 ppm toluene) was added to the contents of the vial, which were then analyzed by gas chromatography. A Shimadzu (Kyoto, Japan) GC 14A equipped with an AOC-14 autoinjector, flame ionization detector and a C-R4A Chromatopac data analysis system was used to separate and quantitate the analytes. The GC column was a Supelco SPB-5 column, 15 m $\times$ 0.32 mm I.D. with a phase thickness of 1  $\mu\text{m}$ . Recoveries were calculated as an average of 3 trials by comparing the relative peak areas with standards that were not subjected to SPE.

### 2.3. Breakthrough curve procedure

The HPLC column used was a 10 cm $\times$ 4.6 mm I.D. stainless steel column packed with Silicalite particles. The following packing procedure was used. Silicalite was added to degassed 2-propanol and sonicated under vacuum for 30 min. This step removed any trapped air from within the Silicalite and produced a slurry. A Shandon HPLC packing pump (Shandon Southern, Sewichley, PA, USA) was used at a pressure of 4000 p.s.i. to pack the slurry into the column. The HPLC system consisted of several components. A Gilson (Middleton, WI, USA)

Model 302B HPLC pump equipped with a Model 802B Gilson manometric module and Scientific Systems (State College, PA, USA) Model LP-21 pulse dampener was used for feed solution delivery. Aqueous feed solutions containing 1500 ppm of the organic compounds of interest were pumped through at rates between 0.50 and 1.00 ml/min. The effluent was monitored on-line with a Kratos 783 UV–Vis detector (Applied Biosystems, Ramsey, NJ, USA) or an Erma 7510 Refractive Index detector (Chrom Tech Inc., Apple Valley, MN, USA). Breakthrough curves were recorded by a Hitachi D-200 Chromato-Integrator (EM Science, Cherry Hill, NJ, USA).

## 3. Results and discussion

### 3.1. Particles for solid-phase extraction

Porous crosslinked polystyrene resins have proved to be very effective for solid-phase extraction (SPE) of a wide variety of organic compounds from predominately aqueous samples. Their effectiveness is enhanced by chemical introduction of polar groups, such as acetyl [1] or sulfonated [2,3], on the resin surface. Incorporation of these surface-modified resins into membranes of the Empore<sup>®</sup> type is generally more efficient for SPE than the use of loose resin particles packed into small columns. However, polystyrene resins do not extract, or extract very poorly, small, polar organic compounds such as the lower alcohols, aldehydes, ketones and carboxylic acids. The major goal of this research was to fill this gap by using Silicalite for SPE of relatively small, polar organic analytes from aqueous samples.

Silicalite was expected to have a sieving effect based on the molecular size and configuration of the analytes. Molecules small enough to enter the 6 Å diameter channels would be retained by interaction of the hydrophobic parts of the analyte with the hydrophobic interior of the Silicalite. Molecules that would not fit the channels would be extracted poorly or not at all. However, our early experiments showed that some relatively large molecules were strongly extracted into Silicalite from dilute aqueous solution. Studies by Choudhary and Akolekar [17] have shown that molecular configuration and flexibility

Table 1  
Comparison of percentage recoveries of alcohols using silicalite particles and a sulfonated PS–DVB resin-loaded membrane

Compound	Silicalite	Membrane
Methanol	7	0
Ethanol	54	0
1-Propanol	84	0
1-Butanol	95	10
2-Butanol	94	6
<i>tert.</i> -Butanol	95	87
1-Pentanol	92	99
2-Pentanol	94	85
1-Hexanol	99	91
Cyclohexanol	10	88
1-Octanol	89	94
1-Decanol	82	89
1-Dodecanol	75	89
1-Tetradecanol	58	87
3-Phenyl-1-propanol	73	99
2,2-Dimethyl-3-pentanol	89	86
3-Ethyl-2,2-dimethyl-3-pentanol	94	84
2-Ethyl-1-hexanol	92	90

(compressibility) need to be considered in addition to the critical molecular diameter. For planar molecules, their penetration into the elliptical channels will be easier if the orientation of the analyte molecule aligns itself with the larger axis of the elliptical opening. Some molecules are sufficiently flexible that their bonds can be bent in a direction opposite to that of penetration into the Silicalite channels.

The ability of Silicalite (particles and membrane) and lightly sulfonated polystyrene resins (in a membrane) to extract various organic test compounds from aqueous samples was compared using identical small columns packed with the adsorbents. After the extraction step, the test compounds were eluted with 1.0 ml of acetone and the individual compounds determined quantitatively by gas chromatography. The percentage recoveries were calculated for the test compounds and used as a measure of SPE efficiency.

### 3.2. Extraction of alcohols

Percentage recoveries of alcohols with Silicalite particles and a lightly sulfonated PS–DVB resin-loaded membrane are compared in Table 1. The percentage recoveries of the normal (straight-chain) alcohols are plotted as a function of carbon number in Fig. 1. The most striking difference between the two sorbents is in the  $C_1$ – $C_4$  alcohols which are much more strongly retained by Silicalite. From a maximum around  $C_6$  the Silicalite recoveries decrease gradually with increasing chain length. Recoveries using the sulfonated membrane remain almost constant between  $C_5$  and  $C_{14}$ .

For alcohols with a *n*-alkyl group, increasing the chain length does not increase their effective diameter. The analytes can easily fit into Silicalite with

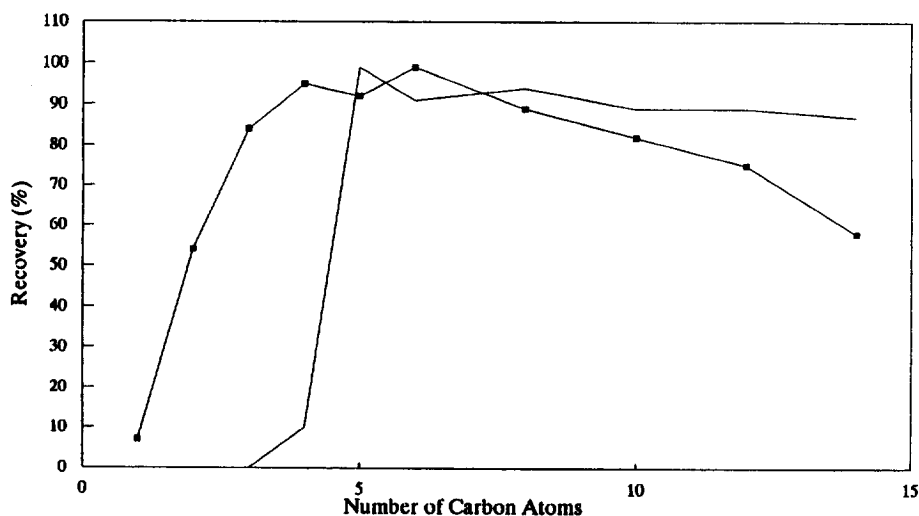


Fig. 1. SPE percentage recoveries of *n*-alcohols using silicalite particles (■) and a sulfonated PS–DVB resin-loaded membrane (solid line).

their hydrocarbon chain parallel to the channels. The increased recoveries are thought to result from an increased interaction between paraffinic hydrogen atoms and the channel walls. As the length of the hydrocarbon chain becomes longer, extraction recoveries of the alcohols decrease. The longer hydrocarbon chain lessens the chance of an analyte directly entering the channels of Silicalite. An analyte will be sorbed if the energy needed to straighten the chain is less than the energy of sorption by Silicalite [52]. Longer molecules need more energy to be straightened and, therefore, give lower extraction recoveries.

The shape of an analyte will also influence its ability to be retained by Silicalite. Alcohols with methyl or ethyl groups as side chains still gave high recoveries. However, cyclohexanol gave only a very low recovery. Not only does cyclohexane have a kinetic diameter larger than 6 Å, but it also has a rigid structure [18]. This rigidity precludes compression of the molecule and prevents entrance into the Silicalite channels.

### 3.3. Extraction of other alkyl compounds

Data for SPE of aldehydes and ketones, esters, carboxylic acids, amines and chlorinated alkanes are given in Table 2. In several instances the lower members of a homologous series are retained much more strongly by Silicalite than by the sulfonated PS–DVB resin-loaded membrane. Examples include acetone, 2-butanone, methyl formate, methyl acetate, ethyl formate, ethyl acetate, propionic acid, butyric acid, propyl amine and *n*-butyl amine.

As might be expected, recoveries of more bulky analyte molecules tended to be lower with Silicalite than with the sulfonated membrane. A good example is *tert*-butyl amine, which gave only 64% recovery using Silicalite compared to 84% using the sulfonated membrane. Tributyl amine, with its bulky three-dimensional structure, gave only 13% recovery using Silicalite compared to 66% recovery using the sulfonated membrane.

### 3.4. Extraction of phenols

Recoveries of phenols following SPE with Sil-

icalite are listed in Table 3. Even phenols with moderately bulky substituents were extracted by Silicalite provided the molecular structure is favorable. Substituents in the 4-position offer the least resistance to penetration into the Silicalite channels. For 4-*n*-alkyl substituents the recoveries for C<sub>1</sub> to C<sub>4</sub> were 100, 98, 98 and 83%. However, recovery was only 27% for the broader 4-*tert*-butyl phenol.

Slight differences in molecular configuration yielded sharp differences in recoveries. For example, recoveries of the cresols in Table 3 depended on the location of the methyl group. In the molecule *p*-cresol, the hydroxyl and methyl groups are attached to the benzene ring on the same axis. The kinetic diameter is very close to 6 Å and *p*-cresol can enter Silicalite with its axis parallel to the channels. In *m*-cresol and *o*-cresol molecules, the two groups are located on two different axes, producing a kinetic diameter larger than the size of the channels [18]. However, these molecules were still extracted by Silicalite. The elastic methyl group in the *ortho* or *meta* position can bend to align with the axis of the channels. The lower recovery of *o*-cresol may be the result of repulsion from the neighboring hydroxyl and methyl groups.

The presence of a large substituent in the 2- or 3-position leads to a much lower SPE recovery. Thus, 2-chlorophenol gave only 33% recovery and 3-chlorophenol gave 39% recovery. However, 4-chlorophenol gave 90% recovery. It is interesting to compare these results with HPLC of chlorinated phenols on a Silicalite column with 35% acetonitrile–65% water (v/v) as the mobile phase [55]. The elution order for monochlorophenols was 2, 3, 4. In addition, pentachlorophenol was completely excluded from the Silicalite and was the very first to elute from the column.

### 3.5. Silicalite in a membrane

Silicalite particles were incorporated into an experimental membrane of the Empore® type. Several circles were cut from the membrane sheets and packed into a small column to the same height as that previously packed with loose Silicalite particles. Results of SPE with the loose particles and membrane column were then compared. The results in Table 4 showed much lower recoveries of ethanol

Table 2

Comparison of percentage recoveries of various test compounds from aqueous solutions using Silicalite particles and a sulfonated PS–DVB resin-loaded membrane

Class	Compounds	Silicalite	Membrane
Aldehydes	<i>trans</i> -Crotonaldehyde	91	24
	<i>n</i> -Valeraldehyde	100	91
	Hexanal	107	85
	Nonylaldehyde	84	74
	Benzaldehyde	89	94
	Salicylaldehyde	54	96
Ketones	Acetone	94	0
	2-Butanone	92	0
	2-Pentanone	90	88
	3-Pentanone	41	68
	4-Methyl-2-pentanone	104	88
	2,4-Pentadione	31	27
	2-Hexanone	93	89
	3-Hexanone	81	89
Esters	Methyl formate	74	0
	Methyl acetate	85	4
	Ethyl formate	83	0
	Ethyl acetate	91	55
	Ethyl propionate	88	61
	Ethyl butyrate	90	75
	Hexyl acetate	79	88
	Methyl benzoate	68	94
Pentyl benzoate	82	70	
Chlorinated alkanes	Chloroform	82	81
	1,2-Dichloroethane	83	77
	1,1-Dichloroethane	80	77
	1,2-Dichloropropane	85	85
Carboxylic acids	Acetic	2	0
	Propionic	62	0
	Butyric	78	13
	Valeric	95	104
Amines	Propyl amine	63	0
	<i>n</i> -Butyl amine	72	52
	<i>tert.</i> -Butyl amine	64	84
	Pentyl amine	78	93
	Pyridine	77	35
	Tributyl amine	13	66

and methyl acetate with the membrane compared to the loose particles. On the other hand, the recovery of cyclohexanol was much higher with the membrane column. In general, results were slightly better with the Silicalite membrane. For the alcohols, excluding methanol, ethanol and cyclohexanol, the average recovery was 90% with the membrane compared to 87% with the loose particles.

### 3.6. Breakthrough curves

Load capacity is another good indication of the extraction ability of Silicalite. Resin load capacity is the total number of moles or weight of analyte extracted by a given amount of resin. In this study, resin load capacities were determined through the use of breakthrough curves. Breakthrough curves

Table 3  
Comparison of percentage recoveries of phenols using silicalite particles and a sulfonated PS–DVB resin-loaded membrane

Compound	Silicalite	Membrane
Phenol	66	84
<i>o</i> -Cresol	53	93
<i>m</i> -Cresol	97	93
<i>p</i> -Cresol	100	87
2-Chlorophenol	33	89
3-Chlorophenol	39	96
4-Chlorophenol	90	95
3-Nitrophenol	56	105
2,5-Dimethylphenol	54	92
2,3,5-Trimethylphenol	27	99
4-Ethylphenol	98	96
4-Propylphenol	98	98
4-Isopropylphenol	89	91
4-Butylphenol	83	95
4- <i>tert.</i> -Butylphenol	27	87

were generated by passing a 1500 ppm aqueous solution of the analyte of interest through a column packed with Silicalite particles until breakthrough occurred. The curves were plotted as a ratio of effluent concentration,  $C$ , to influent concentration,  $C_0$ , versus the volume of effluent. The total number of moles of analyte adsorbed was calculated by multiplying the retention volume,  $V_R$ , by the concentration of the influent [56]. For this study,  $V_R$  was defined as the extrapolated volume from the curve at the point  $C/C_0=0.5$ . Capacities for several small, polar organics were calculated from breakthrough curves and are given in Table 5.

The resin load capacities tended to correlate with the recoveries obtained in the SPE studies. Also, capacities increased as the hydrocarbon chain length increased. The capacities (by weight) increased from methanol, 0.7%, to 1-butanol, 8.5%. Maddox [29]

Table 4  
Comparison of percentage recoveries of various analytes using Silicalite particles and a Silicalite-loaded membrane

Class	Compound	Particles	Membrane
Alcohols	Methanol	7	1
	Ethanol	54	5
	1-Propanol	84	86
	1-Butanol	95	93
	2-Butanol	94	98
	<i>tert.</i> -Butanol	95	100
	1-Pentanol	92	100
	2-Pentanol	94	99
	1-Hexanol	99	99
	Cyclohexanol	10	53
	1-Octanol	89	89
	1-Decanol	82	78
	1-Dodecanol	75	73
	1-Tetradecanol	58	57
	3-Phenyl-1-propanol	73	89
	2,2-Dimethyl-3-pentanol	89	98
3-Ethyl-2,2-dimethyl-3-pentanol	94	98	
2-Ethyl-1-hexanol	92	98	
Esters	Methyl acetate	85	27
	Ethyl formate	83	99
	Ethyl acetate	91	99
Carboxylic acids	Acetic acid	2	0
	Propionic acid	62	5
	Butyric acid	78	84
	Valeric acid	95	100
Phenols	<i>p</i> -Cresol	100	94
	<i>o</i> -Cresol	97	92
	4-Isopropylphenol	89	89

Table 5  
Silicalite loading capacities for various test compounds

Class	Compound	Capacity (mg compound/g)	Pore filling (%)
Alcohols	Methanol	7	5
	Ethanol	18	12
	1-Propanol	69	45
	1-Butanol	85	55
Esters	Ethyl formate	14	8
	Ethyl acetate	119	69
	Ethyl propionate	118	70
	Ethyl butyrate	116	70

showed that Silicalite can adsorb up to 8.5% of its own weight of butanol from fermentation liquors. Silicalite also adsorbed approximately 12.0%, by weight, of the larger esters in Table 5. However, the analytes used in this study occupied only a fraction of the theoretical pore volume in Silicalite of 0.19 cm<sup>3</sup> per gram [4]. This could be caused by hydrogen bonding of the alcohols with water molecules in the aqueous solutions, preventing the alcohols from entering the pores of Silicalite. Also, small analytes may interact with each other to form associates in the sorbed phase. Schultz-Sibbel et al. [52] concluded that Silicalite sorbed various gases in a condensed state. This could prevent the low energy sites of Silicalite from being occupied. In addition, the esters have a relatively rigid structure that may not allow favorable packing inside the channels of Silicalite.

#### 4. Conclusions

Silicalite fills an important gap in solid-phase extraction with its ability to extract relatively small, polar molecules that are not well extracted by sorbent particles used in conventional SPE. Extracted compounds are retained by interaction of the hydrophobic part of the molecule with the hydrophobic interior channels of the Silicalite. Molecules with bulky substituents are partly or completely excluded from these channels due to size restrictions. However, the chemical structure of some large molecules is sufficiently flexible that the molecules may still fit into the channels and be extracted. Positional isomers were extracted in varying degrees, depending on how well they fit into the Silicalite channels.

Large variations in loading capacity were observed. This is further evidence that Silicalite adsorbs organic compounds selectively.

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