



## Project Summary

# An Evaluation of the Adsorption Properties of Silicalite for Potential Application to Isolating Polar Low-Molecular-Weight Organics from Drinking Water

Colin D. Chriswell, Douglas T. Gjerde, Gerda Shultz-Sibbel, James S. Fritz, and Ikue Ogawa

Isolation is the first step in the determination of many organic species in drinking water. An effective isolation technique is therefore essential to ascertaining whether or not potentially harmful species are present in drinking water. Conventional isolation techniques yield only low recoveries when applied to small, water-like compounds. Because retention of components on a molecular sieve is based primarily on molecular size, studies were performed to determine if low-molecular-weight organic compounds could be isolated from water matrices by adsorption on a hydrophobic molecular sieve.

In this work the chemical and physical properties of the adsorbent known as Silicalite were explored, the utility of this molecular sieve for accumulating analytes from aqueous and gaseous streams was elucidated, techniques were developed for recovering adsorbed components, and an analytical protocol was developed for determining low-molecular-weight compounds such as dichloroacetonitrile in standard samples.

It was shown that Silicalite can be used for the accumulation of a variety of aldehydes, acids, esters, ethers, alcohols, ketones, nitriles, and halogenated species from water. The accumulated components can subsequently be recovered from Silicalite by use of a

simple, convenient, and effective elution procedure using a water-methanol gradient as the eluent. Combining accumulation and recovery techniques into a protocol resulted in recoveries exceeding 80% for compounds as varied as phenol, acetic acid, ethyl acetate, chloroform, crotonaldehyde, propanal, acetaldehyde and butanal which were added to standard solutions. Optimization of the protocol for the determination of dichloroacetonitrile resulted in essentially quantitative recoveries from standard solutions. Tests of the procedure on drinking water samples from Ames and Ottumwa, Iowa were inconclusive. Compounds were recovered having chromatographic properties expected of dichloroacetonitrile, but the levels were below those allowing confirmation by gas chromatography/mass spectrometry. Even though the method should work on drinking water samples when detectable levels of the above compounds are present, applicability to "real samples" has not been established.

*This Project Summary was developed by EPA's Health Effects Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

## Introduction

Hundreds of different organic components have been identified in various drinking water supplies in the United States. Most of these compounds are present only at ultra-trace concentrations and are not believed to pose any threat to human health or to the environment. Some deleterious compounds which have been detected require appropriate control measures to be taken. Obviously before any controls can be instituted, procedures must be available for characterizing and quantitating contaminants in drinking water. Effective techniques are available for most classes of organic compounds found in water. However, no effective procedures are generally applicable to the isolation and concentration of low-molecular-weight, polar organic compounds. Compounds such as aldehydes, ketones, nitriles, alcohols and esters are too water-like in their chemical and physical properties for effective accumulation by conventional procedures, and are present at levels below which they can be determined without resorting to accumulation procedures.

It has been suggested that a hydrophobic molecular sieve introduced by Union Carbide Corporation could be used in the treatment of wastewater for the removal of components such as benzene, phenol, propanol and hexane. It was subsequently demonstrated that this molecular sieve, known as Silicalite\*, is effective for removing chloroform from drinking water and for recovering ethanol from fermentation beer.

Based on the ability of Silicalite to adsorb polar as well as non-polar organic species of low-molecular weight from aqueous solutions, studies were made to determine if this adsorbent could be used for isolating small, polar organic compounds from drinking water prior to their determination.

## Chemical and Physical Properties of Silicalite

Molecular sieves are porous, solid adsorbents having pores of consistent diameters in the range of the solution diameters of molecules. Only molecules small enough to enter the pore structure can be retained by molecular sieves. Interactions between the pore surfaces and adsorbed compounds determine the

degree of retention. Conventional molecular sieves contain metal ions and hydroxyl groups which interact with polar materials such as water. Thus, molecular sieves are commonly used for removing water from organic solvents. In contrast with conventional molecular sieves, Silicalite contains only silicon and oxygen and no polar functionalities. It is hydrophobic and can be used to accumulate organic components from aqueous solution.

The pores in Silicalite are six Angstroms in diameter. Molecules approximately the size of benzene or smaller can enter the pores and be retained. Linear molecules much longer than the six Angstrom pore diameter can enter the pore structure so long as they can assume a conformation such that their diameter in one direction is smaller than six angstroms.

Silicalite is a polymorph of silica and has properties similar to those of quartz. It is stable in the presence of most corrosive agents except for strong bases and hydrofluoric acid. It is unaffected by solvents. Silicalite is stable at temperatures in excess of 1000°C. At about 1300°C it reverts to amorphous silica.

Silicalite is produced as a fine powder with particle sizes of about 20 microns diameter. A binder is used to agglomerate these particles into granules of about 20 to 80 mesh. Various silicate and alumina-silicate clays have been used by Union Carbide as binders. A material designated as LZ-115 which contains 10% of an alumina-silicate clay binder was used in this work.

## Adsorption of Analytes from Water

The primary requirement of an adsorbent is having an affinity for components of interest. The distribution coefficient is a measure of the relative affinity of compounds for an adsorbent. The distribution coefficient,  $D_g$ , is the ratio of the concentration of a species of an adsorbent to the concentration of the same species in water at equilibrium. Distribution coefficients for typical low-molecular-weight organic compounds (Table 1), show a general trend that the most polar compounds such as acetic acid have the lowest distribution coefficients. This is to be expected because such compounds have a high affinity for water. Within a homologous series such as the aldehydes there appears to be an optimum chain length leading to the highest distribution coefficient. Thus, pentanal has a much higher distribution

coefficient than does acetaldehyde which is more polar, and pentanal also has a much higher distribution coefficient than does decanal which must assume a linear conformation to enter the pore structure.

The breakthrough capacity of an adsorbent is the amount of material that is adsorbed before the bed effluent reaches a certain percentage of the influent concentration. Table 2 contains data on the 1%, 10% and 50% breakthrough capacity of Silicalite for selected compounds. The 1% and 10% breakthrough capacities provide an indication of the amount of material that can be accumulated on a bed while retaining 99% and 90% respectively of the analyte. The value for 50% breakthrough is of more interest in water treatment applications than for analysis. In actual use excess capacity must be provided because a minimum bed depth is required for contact, and this minimum is dependent on factors such as flow rate, analyte concentration, and particle size.

## Desorption of Materials from Silicalite

If an adsorption technique is to be useful as part of an analytical protocol, the adsorbed components must be recovered from the adsorbent in a form amenable to their subsequent determination. Solvent elution, Soxhlet extraction, high pressure Soxhlet extraction, adsorbent dissolution, microwave desorption and thermal desorption were investigated as potential techniques for recovering adsorbed species from Silicalite. Of these techniques solvent elution was found to be the most convenient and applicable to the widest range of components.

The elution technique developed consists of using a gradient going from 100% water to 100% methanol in about 15 minutes. During elution, analytes are generally completely retained until the methanol concentration reaches 100%. Despite the fact that analytes are not eluted until methanol concentrations reach 100%, the use of a gradient is critical. This is because the pores in Silicalite are initially filled with air. During adsorption of components from water, some of this air is replaced by the accumulated components, but at the end of a typical adsorption cycle the pores still contain about 5mL of air per gram of Silicalite. This air is displaced during elution by methanol. When gradient elution is used, the air will be displaced slowly and will dissolve in the water which comprises most of the initial

\*Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency

**Table 1.** Distribution Coefficients Between Silicalite and Water

Compound	$D_g$	Compound	$D_g$
Acetic acid	72	Methyl formate	2090
Pyruvic acid	29	Ethyl acetate	4970
Trichloroacetic acid	47	Acetaldehyde	100
Ethanol	65	Acrolein	580
Propanol	250	Crotonaldehyde	1340
Phenol	170	Furfural	1100
Bis-(2-chloroethyl) ether	270	Propanal	1350
Acetone	270	Butanal	88 (>2000)*
Isophorone	1	Pentanal	2800
Methyl isobutyl ketone	2770	Hexanal	940
Acetonitrile	150	Heptanal	440
Dichloroacetonitrile	>600	Octanal	570
Chloroform	1230	Nonanal	130
Acrylonitrile	220	Decanal	240
		2-Chloroacetaldehyde	23

\*2000 based on column equilibrium.

**Table 2.** Breakthrough Capacities for Compounds in Water

Compound	Capacity in mg/g at given % breakthrough*		
	1%	10%	50%
Acetic acid	0.2	3	9
Phenol	18	130	151
Ethanol	120	high	high (<240)
Acrolein	22	29	high (<220)
Crotonaldehyde	7	12	27
Propanal	63	83	high (<240)
Butanal	42	55	81
Pentanal	36	high	high (<240)
Furfural	24	42	58
Ethyl acetate	90	100	110
Acetone	20	29	52
Acetonitrile	150	high	high (<240)
Chloroform	1	3	10

\*10% or 50% breakthrough did not occur with some compounds before the run was terminated. 10% and 50% breakthrough capacities for these compounds are higher than the 1% capacity.

eluent. If, however, the bed is eluted directly with methanol, the air would be displaced rapidly and create air pockets in the bed. The solvent would channel around those pockets and portions of the Silicalite would not be eluted.

Acetonitrile has been found to work better than methanol for recovering decanal from Silicalite.

### Determination of Low-Molecular-Weight Organic Species in Water

A liquid chromatograph equipped with a three solvent gradient elution capability was used for accumulation and desorption of organic compounds from standard water samples. A diagram of the system is depicted in Figure 1. Initially, organic-free, deaerated water is passed through the solvent-selection valve and

the pump to flush the system. A sample is then pumped through a column containing Silicalite where organic materials are accumulated. When a sufficient volume of sample has passed through the Silicalite bed, elution begins with a gradient of water and methanol. The eluate from the Silicalite column passes through a RP-8 chromatographic column, which serves to partially separate the eluted components, and then through a UV detector. Eluate fractions are collected from the detector outlet. Components in these fractions are determined by gas chromatography.

The first test of the applicability of this protocol to the determination of dichloroacetonitrile involved adding dichloroacetonitrile directly to the column and then eluting with methanol. It was found that recoveries were quantitative and it was confirmed by GC/MS that no

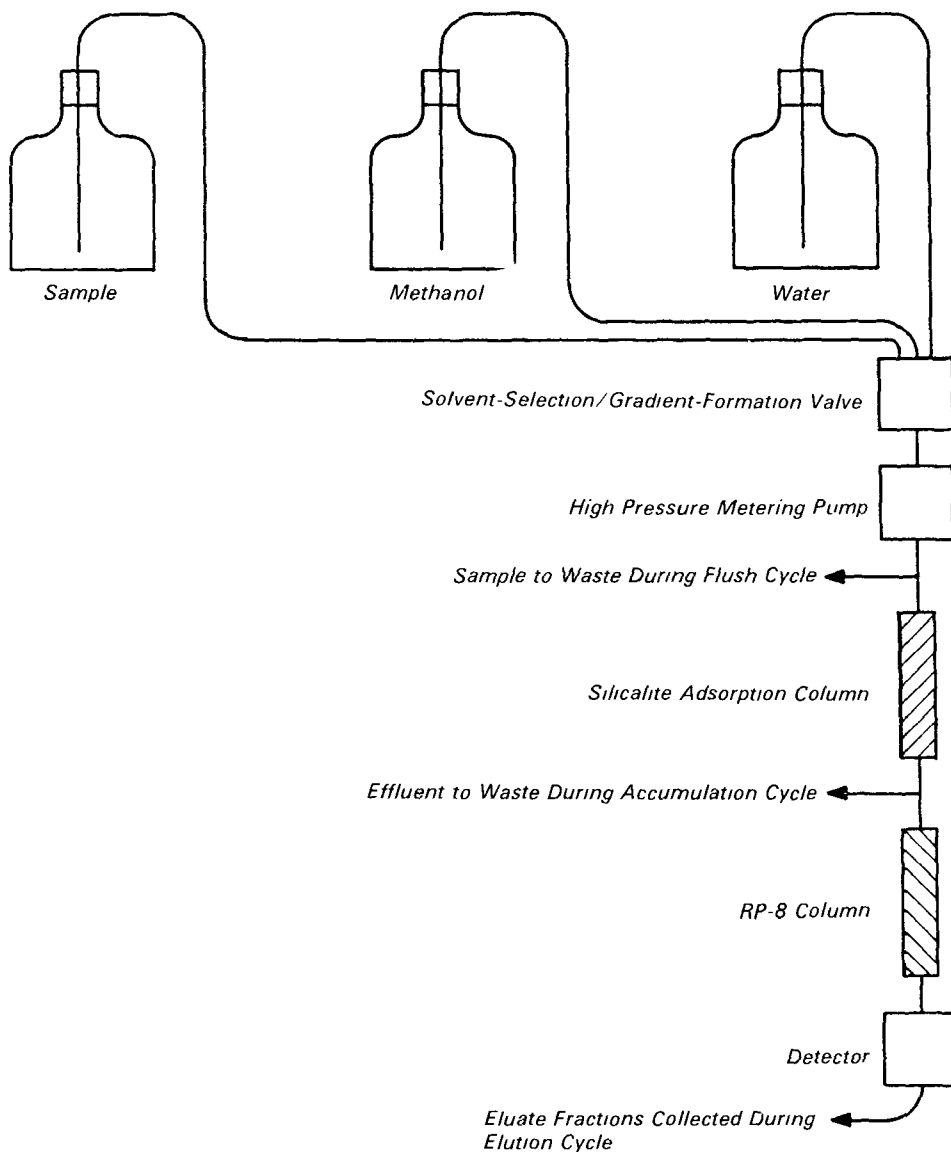
artifacts or degradation products interfered with the determination of dichloroacetonitrile in standard samples. The ability to elute small volumes of dichloroacetonitrile was confirmed in studies in which 100, 10, and 1  $\mu\text{g}$  amounts were loaded on a bed and eluted using a water-methanol gradient. As shown in Table 3, essentially quantitative recoveries were obtained. The total protocol was tested by loading various volumes of water containing various concentrations of dichloroacetonitrile on Silicalite, eluting with a methanol-water gradient, and determining recoveries by gas chromatography. Table 4 shows near quantitative recoveries obtained at concentrations ranging from 10 to 100  $\mu\text{g}/\text{L}$  using sample volumes ranging from 100 to 780 mL.

The procedure was applied to drinking water from Ames, Iowa and indicated a dichloroacetonitrile concentration of 0.1  $\mu\text{g}/\text{L}$ . The amount found is below the detection limit required for confirmation by GC/MS and, thus, the identity of the recovered material as dichloroacetonitrile could not be confirmed.

The protocol was also applied to samples of raw water, finished water at the treatment plant, and finished water in the distribution system in Ottumwa, Iowa. No dichloroacetonitrile was detected in the raw water. Peaks having retention times corresponding to those of dichloroacetonitrile were present in chromatograms of the finished and distribution system water. The identities of those peaks could not be determined by GC/MS. Previous work has shown that dichloroacetonitrile decomposes rapidly at basic pH levels and Ottumwa water has a pH of about 9. Thus, it is unlikely that these peaks are due to dichloroacetonitrile.

Currently the status of application of the protocol to real water samples is simply that the procedures should work if a water supply is located containing detectable amounts of dichloroacetonitrile, although applicability has not been established.

In addition to dichloroacetonitrile, the protocol was applied to standard samples containing chloroform, phenol, ethyl acetate, crotonaldehyde, propanal, acetaldehyde and butanal. In all cases recoveries in excess of 80% were obtained. Decanal could also be recovered, but required the use of an acetonitrile-water gradient in place of the methanol-water gradient for elution from Silicalite.



## Conclusions and Recommendations

The present work has been successful in elucidating the basic properties of the hydrophobic molecular sieve known as Silicalite and has led to the development of what appear to be viable analytical protocols for determining low-molecular-weight organic components in drinking water. However, as is often the case with research, this study has provided more questions than answers. The protocol was applied to standard samples but applicability was not established for drinking water.

Continued development of the use of this adsorbent as an analytical agent should continue and would most likely lead to an entire family of methods for determining low-molecular-weight compounds in real water samples.

Silicalite has been shown to be an excellent adsorbent for a diverse assortment of organic and inorganic gases. The potential utility of this adsorbent for sampling ambient air and gaseous effluents should be explored further.

There is a significant probability that Silicalite could be used in inert gas purging or closed-loop-stripping procedures as a replacement for currently used adsorbents or in combination with them. In this application it is expected that Silicalite would trap materials that are not retained by conventional adsorbents. An evaluation of Silicalite for this application is strongly recommended.

Figure 1. Experimental apparatus

Table 3. Recovery of Dichloroacetonitrile from Silicalite

Amount Loaded, $\mu\text{g}$	% Recovered	RSD
100	96	4
10	99	1
1	98	2

Table 4. Recovery of Dichloroacetonitrile from Standards

Concentration added, $\mu\text{g/L}$	Sample Volume mL	Amount, $\mu\text{g}$ , of Dichloroacetonitrile	% Recovery
100	100	10.	102
100	500	50.	98
100	780	78.	105
10	100	1.	105
10	780	7.8	98

*Colin D. Chriswell, Douglas T. Gjerde, Gerda Shultz-Sibbel, James S. Fritz, and Ikue Ogawa are with Ames Laboratory USDOE, Iowa State University, Ames, IA 50011.*

***W. Emile Coleman** is the EPA Project Officer (see below).*

*The complete report, entitled "An Evaluation of the Adsorption Properties of Silicalite for Potential Application to Isolating Polar Low-Molecular-Weight Organics from Drinking Water," (Order No. PB 83-148 502; Cost: \$8.50, subject to change) will be available only from:*

*National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:  
Health Effects Research Laboratory  
U.S. Environmental Protection Agency  
Research Triangle Park, NC 27711*

United States  
Environmental Protection  
Agency

Center for Environmental Research  
Information  
Cincinnati OH 45268

Postage and  
Fees Paid  
Environmental  
Protection  
Agency  
EPA 335



Official Business  
Penalty for Private Use \$300

PS 0000320  
U S ENVIR PROTECTION AGENCY  
REGION 5 LIBRARY  
230 S DEARBURN STREET  
CHICAGO IL 60604