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Project Summary

Evaluation of Solid Sorbents for Water Sampling

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Based on the results of screening a variety of sorbent/solute pairs, it appears that a combination of two dissimilar resins is the most promising approach to a general purpose sorbent sampling system. In particular, a combination of XAD-2 and XE-347 resins offers the possibility of collection and recovery of both non-polar and polar organic species. This XAD-2/XE-347 system was, for the most part, found to be comparable with solvent extraction in regards to recovery; polar species such as phenols and pyrrole were recovered in higher yield from the cartridge.

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

Introduction

This report describes and presents results of a systematic laboratory investigation of the applicability of macroreticular resins for general and compound specific sampling of organics, based on small scale chromatographic experiments. The objective was to develop screening procedures and a data base that would allow selection of the resin(s) best suited to a particular sampling application and selection of a sampling module size and configuration that gives quantitative collection of contaminants from the aqueous stream of interest.

The Effect of Flow Rate (Linear Velocity)

One important consideration in the design and utilization of a sorbent cartridge is the rate at which the sample passes through the column. The advantage of using a high flow rate is that the sampling time is reduced, for a given volume of sample. High flow rate, however, may have significant disadvantages. A higher flow rate usually produces a higher pressure drop across the column. (This sometimes requires use of higher pressure tubing, such as steel, instead of Teflon). More importantly, high flow rate affects retention.

Flow rate is usually expressed in terms of volume of solution per unit time (e.g., mL/min.). The critical parameter, however, is not flow rate per se, but rather the linear velocity of the solution through the column, because a measurement of linear velocity takes into account the diameter of the column and thus the mechanics of mass transfer, while a measurement of volumetric flow rate does not. Conclusions drawn from observations of a small-scale system can be extrapolated or scaled up, using linear velocity, to a larger scale system.

The effects of linear velocity on adsorption were studied by generating breakthrough curves at various linear velocities. Figure 1 shows breakthrough curves up to the 50% breakthrough point for a particular system at six different linear velocities. Apparent linear velocity (face velocity) was calculated as: $L = F/\pi r^2$, where F is the flow

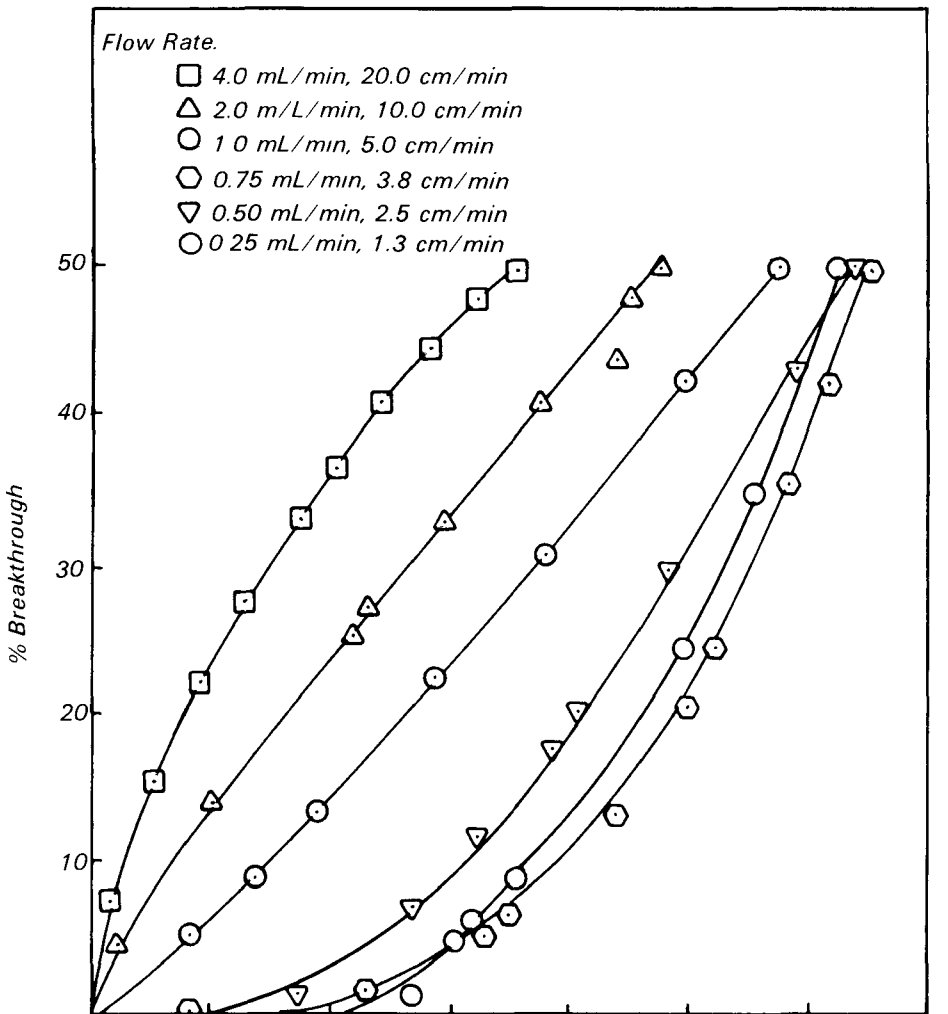

Figure 1. *Normalized breakthrough curves at various flow rates (10 ppm acetophenone on XAD-2 6.2 cm x 0.5 cm I D column)*

rate (mL/min.) and r is the radius of the column (cm).

At low linear velocities (e.g., 4.0 cm/min.) the breakthrough curve is virtually independent of this parameter. This is especially evident in that the value of V_{50} is unchanged with respect to flow rate, and is consistent with the fact that, in elution chromatography, the retention volume of a specific compound is also independent of flow rate (at low flow rates). The breakthrough curve, as the linear velocity is increased, shifts closer to the vertical axis: this means that the solute breaks through sooner. The effect of linear velocity on the shape of the breakthrough curve is an effect which had not been expected. Figure 1 illustrates that at low linear velocities, the breakthrough curve has a distinctive concave appearance while at increased linear velocity, the curve becomes distorted. Since uptake is proportional to the area above the curve, it can be seen that uptake efficiency is greater where the curve is concave than where it is convex. Collection efficiency at the 1/2 V_{50} point is almost 100% at low linear velocities but considerably lower at high linear velocities.

It should be noted that once an appropriate linear velocity criterion has been determined for a sorbent/analyte combination in a chromatographic experiment, it can be used in design of a large-scale sampling system. A sorbent cartridge of at least 3.7 cm diameter would be required, for example, assuming a 4.0 cm/min. velocity criterion and a hour, 10-liter water sampling constrain

Sorbent/Solute Interactions

A systematic study was performed t determine the retention behavior c several sorbents when challenged wit specific model organic compounds a solutes. Because of the demonstrate success of this resin for collection c non-polar compounds, XAD-2 resin wa evaluated using polar compounds o XAD-2. These data demonstrate tha XAD-2 has a significantly lower affinit for polar compounds than non-pola compounds (Table 1). Its affinity fo phenol is so low that in order to sample 10 L sample with 97% collection effi ciency (i.e., at 1/2 V_{50}), a resin bed c 267 cc would be necessary.

Table 1 also shows V_{50} data for th polar model compounds on XAD-7, more polar, acrylic ester resin that ha previously been used for collection o these species. However, V_{50} value within the same range as the XAD- values indicate that neither XAD-2 o XAD-7 is satisfactory for the sampling o polar species. The carbonaceous resin XE-340, XE-347 and XE-348 showe high affinity for the polar compoun tested in contrast to XAD-7. For ex ample, no breakthrough occurred afte 16 hours at 10 mg/L phenol (160 mL/cc)

Comparisons among the XE-34 series resins were made using benzy alcohol as the analyte Table 1 present V_{50} data for some polar compounds o the Ambersorb resins. XE-347 ha slightly greater affinity for benzyl alcoh than XE-348 and significantly greate affinity than XE-340.

The V_{50} values for polar analytes o XE series resins are at least 5-10 time higher (allowing for differences i challenge concentration) than those fo the XAD series. The XE series resins ar moderately polar, indicating fairly stron dipole-dipole interactions in the adsorp tion process. Recoveries of simila compounds are generally lower fron XE-347 than from XAD-2 resin. A pos sible explanation for this is the carbona ceous surface, which may, like carbon show extremely strong solute/sorben bonding.

The ion exchange resins initiall showed promise for polar organics, wit IRA-93 and IRA-904 showing substan tially higher capacity for phenol an benzoic acid in distilled deionized wat than did XAD-2 or XAD-7. However

Table 1. *V_{50} Data for Polar Compounds on Various Resins*

Compound	V_{50} mL/cc XAD-2[a]	XAD-7[a]	XE-347[b]	XE-348[b]	XE-349[b]
Phenol	75	115	584	c	c
Benzoic Acid	101	84	870	c	c
Benzyl Alcohol	99	c	623	582	161

[a]Concentration: 10 mg/L.
[b]Concentration: 100 mg/L.
[c]Not determined.

breakthrough on these resins was virtually instantaneous when the aqueous solution contained as much as 250 ppm of sodium chloride.

Design of the Full Scale Sampling Cartridge (Scale-Up)

No single resin could be used to adequately sample a wide range of chemical classes. XAD-2 has high affinity for non-polar species but fairly low affinity for polar compounds. The best resins for adsorption of polar species were found to be the Ambersorb XE-34 series, with XE-347 exceeding the volumetric capacity of the others. A two-stage cartridge was designed using this information. Samples entering the cartridge would encounter the XAD-2 first. Then any polar materials breaking through the XAD-2 would be adsorbed by the XE-347 stage

Stainless steel was chosen for construction of the cartridge because it is chemically inert to organic species, easy to work with, and rugged enough for field work. The inside diameter of the cartridge was determined by the relationship between the desired sampling rate and the linear velocity criterion established in this work as a constraint for efficient collection.

The minimum length of the resin bed was determined by the retention characteristics of the resins used To obtain satisfactory uptake of the compounds (95% efficiency), it was necessary to use sufficient resin to ensure that the 10 L of sample present added no more than 1/2 V_{50} for any solute of interest. It has been generally accepted that an adsorbent bed should have a length-to-diameter ratio considerably greater than one to avoid channeling and back eddy effects. The requirements for a sampling cartridge are not as severe as those for a chromatographic column. For this reason the length of the cartridge was set at 15 cm, 7.5 cm for each of the two beds (approximately 2.1 length-to-diameter ratio) The cartridge was thus somewhat "overdesigned" compared to the criteria for direct scale-up from the laboratory results.

Use of Full Scale Cartridge

Adsorption of Model Compounds

The first test of the full scale cartridge involved verification of predicted breakthrough behavior of a mixture of seven model compounds A 10 L sample, containing the model analytes at a concentration of 10 ppm, was passed through the sorbent cartridge in 4 hours, at a 4 cm/min linear flow rate. Hourly samples of the effluent of the cartridge were taken to verify that no breakthrough occurred.

Table 2 shows the recovery of seven model compounds from each stage of the sorbent cartridge. The non-polar compounds such as trichloropropane and naphthalene were efficiently adsorbed by the XAD-2 stage and the polar compounds were trapped by the XE-347 stage.

Overall Recovery

Overall recovery of seven model compounds was determined using the full-scale sorbent cartridge and this was compared to recoveries generated by solvent extraction using methylene chloride Table 3 shows data averages for seven and eight determinations for the sorbent cartridge.

At first glance the recovery of dodecane, a strongly hydrophobic compound, appears to be surprisingly low for both methods. However, this is rather frequently reported for aliphatic hydrocarbons and appears to be related to the difficulty of dissolving these species in the water sample. In many cases the dodecane is not in solution at all, but exists rather as micelles and is therefore not available to be extracted

Effect of Solvent on Desorption from XE-347 Resin

Originally, it was thought that methanol, being more polar, would be a better solvent than methylene chloride for recovery of compounds adsorbed on a polar resin (XE-347) However, it was found that the recovery of phenol using methylene chloride was 90% of the

Table 2. *% Recovery of Model Compounds by Batch Extraction*

Compound	From XAD-2 Resin	XE-347 Resin	Total
1, 2, 3-trichloropropane	78	0	78
Naphthalene	84	0	84
Diethylphthalate	89	0	89
Acridine	97	0	97
Phenol	47	27	74
Dodecane	17	0	17
Pyrrole	0	42	42

Table 3. *% Recovery of Model Compounds by Two Methods*

Compound	Sorbent Cartridge Recovery %	SD*	% RDS**	Solvent Extraction Recovery %	SD	% RDS
1, 2, 3-trichloropropane	76%	18	24	75	12	15%
Naphthalene	80	18	23	92	12	13
Diethylphthalate	88	19	22	101	13	13
Acridine	99	15	16	89	21	23
Phenol	76	19	26	17	7	42
Dodecane	18	13	70	41	4	9
Pyrrole	57	24	43	46	9	20

* Standard Deviation.
** Relative Standard Deviation.

recovery obtained using methanol. For this reason, use of the methylene chloride as the solvent for both resins was favored.

Effect of Method of Desorption

A comparison was made between the recoveries obtained using batch extraction versus continuous extraction of compounds adsorbed in the sorbent trap A substantial increase in the recovery of pyrrole was obtained using the continuous extraction method. No significant change was noted in the recovery of the other compounds. The use of a continuous extractor for subsequent samples was favored because of these results and the ease of operation.

Use of Sorbent Cartridge on Environmental Sample

The full scale sorbent cartridge was used to analyze the organic content of 10 L of coal preheater scrubber water obtained from a steel manufacturing firm. This same sample was also subjected to a Level 1 solvent extraction* with methylene chloride.

Conclusions and Recommendations

The chromatographic approach to characterization of sorbent/solute behavior allows rapid, simple quantitative evaluation of resins for water sampling applications. The volumetric breakthrough capacity, V_{50}, as determined in a small scale frontal chromatography experiment, has been shown to be a fundamental property of the sorbent/solute system. At low (< 10 ppm) solute concentrations, uptake of solute by the sorbent is governed by volumetric capacity, rather than by weight capacity, of the resin. Collection efficiency is independent of concentration; a 10 ppb solution can be expected to break through a given sorbent cartridge just as rapidly as a 10 ppm or higher solution.

Values of V_{50} determined in small scale laboratory experiments were valuable in setting design parameters for a full-scale sampling cartridge. The use of such screening studies is highly recommended whenever it is desired to determine the optimum sampling system for a particular organic analyte; of principal advantage is the ability to determine the required data upon small quantities of analyte, thus minimizing worker exposure to test chemicals as well as saving time and money

Uptake is greatly affected by the flow rate through the cartridge. Decreased collection efficiency at high sample flow rates is presumed to be due to mass transfer effects. Therefore, design criteria for full scale sampling systems include a limitation on the linear (face) velocity of the sample through the cartridge. The flow rate must be such that the face velocity (sample flow rate in mL/min. divided by the cross-sectional area of the resin bed) is -4 cm/min. to ensure optimum equilibrium uptake. This constraint combines with V_{50} to determine the size and shape of the resin bed required for any particular sampling application.

A combination of two dissimilar resins is the most promising approach to a general purpose sorbent sampling system based on the results of screening a variety of sorbent/solute pairs. In particular, the XAD-2/XE-347 system was found to be comparable with solvent extraction in regards to recovery of model compounds. Low molecular weight and polar organic species such as phenol and pyrrole were recovered in higher yield from the cartridge than by solvent extraction. High levels of suspended particulate in the aqueous sample will require a slight modification to the sorbent cartridge and/or incorporation of a filter upstream of the sorbent bed.

The mixed bed XAD-2/XE-347 sorbent cartridge is recommended for use for general and for compound-specific sampling of organics from water at levels of 10-100 ppm and below. If an aqueous stream is suspected to contain more than 100 ppm of organics or if its organic loading is unknown, breakthrough may occur before 10 L total sample is collected. Finally, if more than 1 g of organic material is removed from the 3.8 cm by 15 cm XAD-2/XE-347 cartridge, the possibility that the weight capacity limitation could lead to premature breakthrough should be considered.

*Lentzen et al , "IERL-RTP Procedures Manual Level 1 Environmental Assessment" (Second Edition), EPA-600/7-78-201 (NTIS PB 293795), October 1978

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The complete report, entitled "Evaluation of Solid Sorbents for Water Sampling," (Order No PB 81-106 585; Cost. $9.50, subject to change) will be available only from.
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