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## Elution of organic solutes from different polarity sorbents using subcritical water

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### Abstract

The intermolecular interactions between organic solutes and sorbent matrices under subcritical water conditions have been investigated at a pressure of 50 bar and temperatures ranging from 50 to 250°C. Both polar and nonpolar organics (chlorophenols, amines, *n*-alkanes, and polycyclic aromatic hydrocarbons) and five different sorbent matrices (glass beads, alumina, Florisil, silica-bonded C<sub>18</sub>, and polymeric XAD-4 resins) were used. From the same matrix, the polar solutes always eluted at lower temperatures, while the moderately polar and nonpolar solutes only eluted at higher temperatures. Similar to matrix effects previously observed using supercritical carbon dioxide, the sorbent type greatly influenced the elution efficiency under subcritical water conditions. Lower temperatures are sufficient to elute a particular solute from glass beads, alumina, and Florisil, but higher temperatures (less polar water) are needed to elute the same solute from silica-bonded C<sub>18</sub>. The highest temperatures were required to elute aromatic organics from XAD-4. These matrix effects demonstrate that, while low temperature water can break inert or dipole interactions between solutes and glass beads, alumina, and Florisil, higher temperature water is required to interrupt the van der Waals attractions between solutes and silica-bonded C<sub>18</sub>, and even higher temperatures needed to overcome the  $\pi$ -electron interactions between aromatic solutes and XAD-4. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Mobile phase composition; Stationary phases, SFC; Extraction methods; Chlorophenols; Amines; Polynuclear aromatic hydrocarbons; *n*-Alkanes; Water, subcritical

### 1. Introduction

Water at ambient conditions is too polar to solvate most organic pollutants. However, the polarity of liquid water can be controlled over a wide range by changing temperature under moderate pressures to maintain water in the liquid state (so-called 'subcritical' water). For example, increasing the water tem-

perature to 200–250°C causes a similar change in solvent polarity (measured by dielectric constant), as is achieved by the common HPLC method of mixing methanol or acetonitrile with the water to a concentration of 100% (Fig. 1). At elevated temperatures, liquid water acts more like organic solvents so that the solubility of organics is dramatically increased. For example, the solubility of benzo[*e*]pyrene at 350°C has been reported to be 10 wt%, an increase of 25 million-fold over its solubility at ambient conditions [1,2]. While little solubility data is available in the literature for organics in

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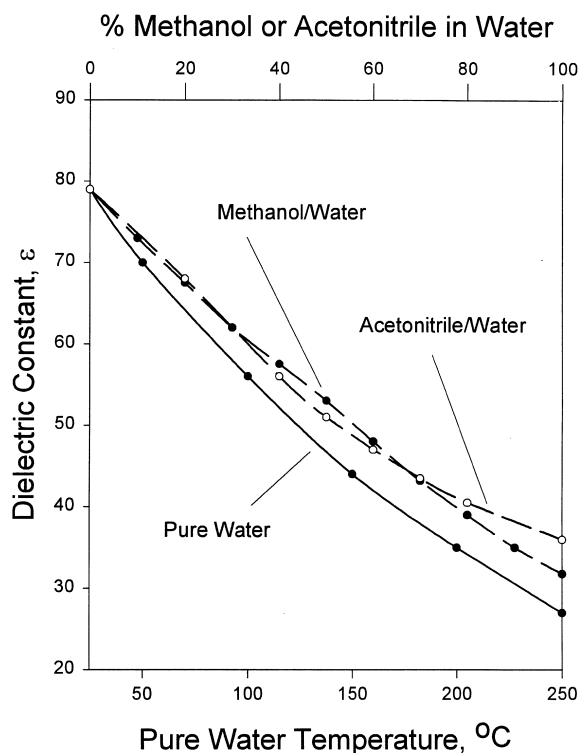


Fig. 1. Control of solvent polarity (dielectric constant) by changing temperature (at 50 bar) with pure water compared to mixing water with methanol or acetonitrile at 25°C and ambient pressure. Water data was adapted from [4], and the mixed solvent data from [18].

subcritical water, we have recently demonstrated that increases in solubility of  $10^4$ – $10^5$  are typical for moderately- and nonpolar organic compounds by raising water temperature from 25 to 200°C [3]. For example, the solubility of the polycyclic aromatic hydrocarbon (PAH) anthracene increases by ~20 000-fold when the temperature is raised from 25 to 200°C. Similarly, the solubility of the pesticide chlorothalonil increases by 130 000-fold over the same temperature range [3]. Moderate pressure changes (e.g., 50 to 100 bar) have no significant effect on solubility as long as the water remains liquid, presumably because pressure has little effect on the dielectric constant of liquid water [4].

The concept of using subcritical water to extract organic compounds with a wide range of polarities has been used in our laboratory [5–9]. Polar organics (e.g., phenols and amines) are efficiently extracted at lower temperatures (50–100°C), while nonpolar

organics including PAHs and polychlorinated biphenyls (PCBs) are efficiently extracted at higher temperatures (200–250°C) [5–9]. Since matrix effects have previously been shown to control many extractions with supercritical carbon dioxide [10–14], the development of a better understanding of matrix effects during subcritical water extraction would be useful for the further development of this technique.

A second recent application of subcritical water is to achieve reversed-phase separations by using pure water at elevated temperatures [15–17]. Water is normally mixed with organic solvents to serve as the mobile phase in reversed-phase liquid chromatography (LC) [18,19]. However, the polarity of water can be controlled over a similar range by simply heating pure water with enough pressure to maintain the liquid state (Fig. 1). Two additional mobile phase parameters which control liquid phase separations are the solvent surface tension and viscosity [18], where lowering the surface tension reduces retention (for reversed-phase separations), and lowering viscosity results in better mass transfer, thus achieving better chromatographic efficiencies. While water at ambient conditions has very high surface tension and fairly high viscosity, increasing the temperature (again while maintaining enough pressure to keep the water in the liquid state) reduces surface tension and viscosity. Heating water to 250°C reduces its surface tension about the same as solvent programming to 100% methanol or acetonitrile (Fig. 2), and reduces the viscosity of water even more than solvent programming to 100% methanol or acetonitrile (Fig. 3). Thus, mobile phase polarity, surface tension, and viscosity can be controlled by simply heating pure water (in the liquid state) over the same ranges achieved by conventional solvent programming to 100% methanol or acetonitrile (Figs. 1–3).

In the present study, pure water was used to elute organic solutes from different types of stationary phases at elevated temperatures. The intermolecular interactions between solutes and packing materials under subcritical water conditions were investigated to evaluate the matrix effect on water extraction efficiency, as well as to understand chromatographic separation mechanisms. Phenols, amines, *n*-alkanes, and PAHs were used as organic solutes. Different packing materials were used to investigate the ability

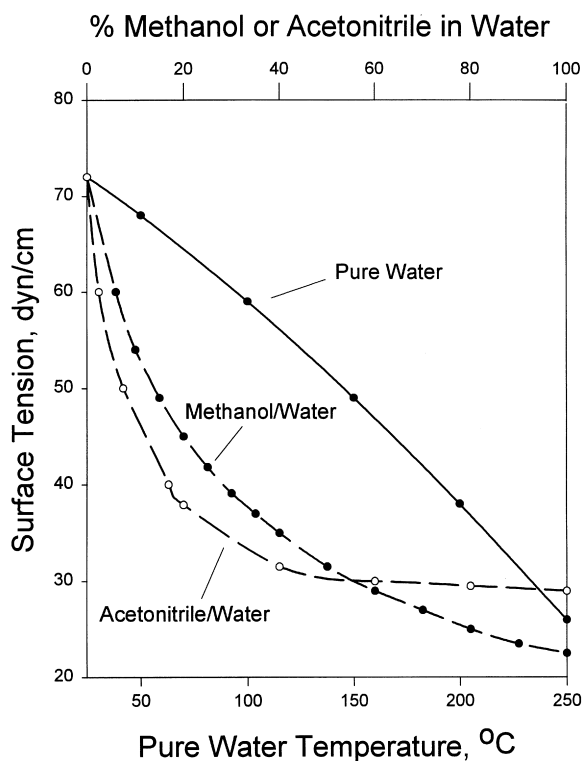


Fig. 2. Control of solvent surface tension by changing temperature (at 50 bar) with pure water compared to mixing water with methanol or acetonitrile at 25°C and ambient pressure. Water data was adapted from [4], and the mixed solvent data from [18].

of subcritical water to disrupt intermolecular interactions including dipole interactions (alumina and Florisil), Van der Waals attractions (silica-bonded  $C_{18}$ ), and  $\pi$ -electron interactions (XAD-4) between the solutes and the stationary phases.

## 2. Experimental

### 2.1. Solutes and sorbents

Chlorophenols, amines, *n*-alkanes, and PAHs were chosen for test organic compounds. Nonporous glass beads (3M, 40  $\mu\text{m}$ ), basic alumina (60–325 mesh), and Florisil (60–100 mesh) were purchased from Fisher Scientific (Pittsburgh, PA, USA). The silica-bonded  $C_{18}$  (5  $\mu\text{m}$ ) and polymeric XAD-4 resins (polystyrene–divinylbenzene, 250–850  $\mu\text{m}$ ) were supplied by Supelco (Bellefonte, PA, USA).

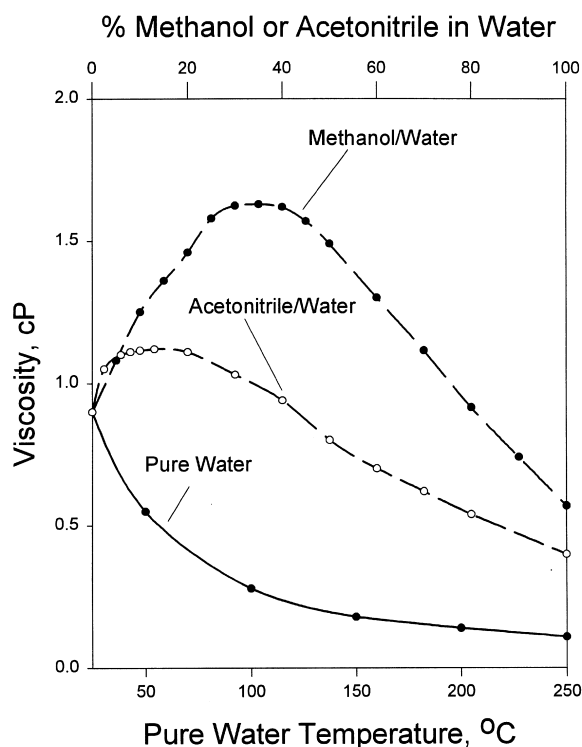


Fig. 3. Control of solvent viscosity by changing temperature (at 50 bar) with pure water compared to mixing water with methanol or acetonitrile at 25°C and ambient pressure. Water data was adapted from [4], and the mixed solvent data from [18].

### 2.2. Solute elution process

The sorbents were dry packed into a stainless steel column (50 mm height  $\times$  4.6 mm I.D., from Keystone Scientific, Bellefonte, PA, USA). The mixture of the test analytes (20  $\mu\text{l}$  containing  $\sim$ 100–200  $\mu\text{g}$  of each test compound) was spiked onto the inlet of the packed column. HPLC-grade water (Fisher) was purged using nitrogen to remove dissolved oxygen. The spiked column was eluted using the oxygen-free water (with a flow-rate of  $\sim$ 1 ml/min) at 50 bar and sequential column temperatures of 50, 100, 150, 200 and 250°C (water remains in the liquid state at temperatures up to 250°C at 50 bar), and 250°C steam (at  $\sim$ 5 bar) for 10 min at each condition. Temperatures were controlled by placing a 1-m preheating coil and the packed column in a Hewlett-Packard 5730 GC oven as previously described [5–7]. An ISCO 260D syringe pump (ISCO, Lincoln,

NE, USA) was used as the water pump and operated at a constant pressure of 50 bar so that the water remained in the liquid state at temperatures up to 250°C. For the steam extraction (250°C and ~5 bar), the constant flow-rate (1 ml/min) mode was used. The eluates were collected in 2 ml of methylene chloride (cooled by placing the collection vial in an ice bath) as previously described [5–7]. An internal standard (*n*-hexadecane) was then added to the collection vial. After shaking the vial in a rotator for 30 min, the methylene chloride was removed from the collection vial. The water eluate was extracted with an additional two washes (0.5 ml each) of methylene chloride, and then the three methylene chloride fractions were combined for analysis. Since the pH of the water eluate was ~8–9 from alumina and Florisil, the pH of these eluates were lowered to ~4 to efficiently transfer the acidic solutes from the water phase to the methylene chloride phase prior to GC analysis.

### 2.3. Eluate analysis

All of the analyses were performed by a Hewlett-Packard Model 5890 II gas chromatograph equipped with a flame ionization detector (FID), using a 25 m×0.25 mm I.D. (0.17- $\mu$ m film thickness) HP-5

column. The initial oven temperature was 40°C (held for 3 min) and was then increased to 320°C at 6°C/min. Autosampler injections were performed either in the splitless mode for 0.3 min or in the split mode with a ratio of ~1:30 depending on the analyte concentration. The individual phenols, amines, anilines, PAHs, and *n*-alkanes were quantified using standard calibration curves generated from appropriate dilutions of a mixture containing a known amount of test compounds (also compared to the internal standard).

## 3. Results and discussion

### 3.1. Recoveries of the eluted solutes

The elution system was tested by determining the recoveries of the solutes from glass beads, alumina, and Florisil using sequential extraction at 50, 100, 150, 200 and 250°C with liquid water. Overall recoveries were determined by adding the recoveries of the five fractions, and were acceptable (from 81 to 124%) considering the fact that recoveries were based on the sum of five fractions, as shown in Table 1. However, *n*-decane and the high-molecular-mass PAHs (benzo[*a*]pyrene and benzo[*ghi*]perylene) re-

Table 1  
Total recoveries of five-step sequential liquid water extractions (50 to 250°C at 50 bar) from glass beads, Florisil, and alumina

Compound	Recovery <sup>a</sup> %, (R.S.D., %) <sup>b</sup>			
	Glass beads	Florisil	Alumina	
<i>o</i> -Chlorophenol	109 (9)	95 (7)	101 (4)	
3,4-Dichlorophenol	103 (5)	96 (9)	99 (15)	
2,3,5-Trichlorophenol	91 (3)	96 (5)	117 (1)	
Nitrosodipropylamine	120 (7)	103 (5)	90 (4)	
4-Chloroaniline	124 (8)	104 (3)	91 (6)	
1,2,4,5-Tetrachlorobenzene	91 (8)	92 (8)	85 (4)	
4-Chlorodiphenylether	93 (5)	89 (8)	89 (4)	
9-H Fluorenone	103 (6)	104 (10)	93 (3)	
<i>n</i> -Decane	87 (12)	69 (32)	83 <sup>c</sup> (12)	60 (32) 80 <sup>c</sup> (20)
Naphthalene	101 (8)	98 (8)	81 (8)	
Anthracene	94 (7)	88 (6)	88 (4)	
Pyrene	99 (4)	82 (23)	85 (9)	
Benzo[ <i>a</i> ]pyrene	93 (8)	90 (28)	71 (22) 93 <sup>c</sup> (29)	
Benzo[ <i>ghi</i> ]perylene	77 (18) 98 <sup>c</sup> (39)	50 (40)	83 <sup>c</sup> (35)	63 (33) 104 <sup>c</sup> (32)

<sup>a</sup> Sum of five fractions at 50, 100, 150, 200, and 250°C (10 min for each temperature) under liquid conditions.

<sup>b</sup> R.S.D.s are based on triplicate five-step sequential extractions and analyses.

<sup>c</sup> The second recoveries were obtained using 20-min extractions at 250°C.

quired an additional 10 min at 250°C for efficient extraction (Table 1).

The reasonably good recoveries of the test solutes demonstrate that this system is reliable for elution studies. For a second test of the extraction efficiencies, each sorbent residue (after water extraction) was mixed with sodium sulfate and sonicated overnight using methylene chloride to detect any incomplete elution of the solutes. If none of a given solute was found in the methylene chloride extract, then this solute was defined as 100% eluted by subcritical water. For the sake of clarity, all subsequent discussions are based on this definition of percentage eluted.

### 3.2. Influence of temperature on solute elution

As discussed in Section 1, increasing temperature should enhance the elution of organic solutes. Previous studies on soils and sludges [5,7] have demonstrated that lower temperature water (e.g., 100°C) extracts polar organics with high solubility in ambient water, while higher temperature water (e.g., up to 250°C) is required to extract moderately and nonpolar organics with low water solubility at ambient temperature. In the present study, the temperature effect (50 to 250°C) on the elution of organics was studied using glass beads, alumina, Florisil, silica-bonded C<sub>18</sub>, and XAD-4. Figs. 4–7 show the elution efficiencies versus water temperatures. R.S.D. values ( $n=3$ ) are similar to those shown in Table 1.

#### 3.2.1. Elution from normal phases

The elution-temperature trend is very similar for glass beads, alumina, and Florisil, although there is a small shift to higher temperatures for some compounds on alumina and Florisil compared to glass beads. All of the polar solutes (phenols and amines) were quantitatively eluted at 50°C from these three matrices. However, most of the moderately-polar and nonpolar solutes still remained on the column at 50°C because of their low solubility in water (Fig. 4). For example, efficient elution required temperatures of ~150–200°C for 1,2,4,5-tetrachlorobenzene, 4-chlorodiphenylether, and 9-H fluorenone, while quantitative elution of *n*-decane can only be reached at 200–250°C (middle plot in Fig. 4). As would be expected based on their ambient water solubilities,

the temperature required to elute PAHs increases with their molecular mass. For example, while naphthalene ( $M_r=128$ ) was quantitatively eluted at 100°C, elution of the higher-molecular-mass PAHs (benzo[*a*]pyrene,  $M_r=252$ , and benzo[*ghi*]perylene,  $M_r=276$ ) was only achieved at 250°C.

The effective elution temperature apparently correlates to the solute solubility in ambient water. The lower the solubility of a solute in ambient water is, the higher the temperature required is to reach efficient elution of a particular solute from glass beads, alumina, and Florisil. For example, the amines and phenols (top of Fig. 4) have ambient solubilities ramping from ~1000 mg/l to 30 000 mg/l and are effectively eluted at 50°C. The remaining solutes have ambient solubilities ranging from a high of 30 mg/l for naphthalene to a low of 0.003 mg/l for benzo[*ghi*]perylene, and require increasingly higher water temperatures for elution.

#### 3.2.2. Elution from reversed-phase packings

Compared to the normal phases (Fig. 4), all of the solutes required higher temperatures for elution from the C<sub>18</sub> and XAD-4 columns (Figs. 5 and 6). Polar acids and bases were easier to elute than the moderately-polar and nonpolar solutes from reversed phases, even though the elution of a particular solute required higher temperatures from reversed-phases than from normal phases. As shown in Fig. 5 for the silica-bonded C<sub>18</sub>, all of the phenols and amines were eluted at 100–200°C compared to only 50°C required from the normal phases (Fig. 4). Elution of tetrachlorobenzene, 2-chlorodiphenylether, and 9-H fluorenone required 200–250°C, while *n*-decane was eluted only with 250°C steam. PAHs also required higher temperatures to elute from the silica-bonded C<sub>18</sub>. For example, naphthalene and anthracene required 100–150°C higher temperatures to elute from C<sub>18</sub> than the same compounds required from the normal phases. The effective elution of benzo[*a*]pyrene and benzo[*ghi*]perylene from C<sub>18</sub> was achieved only using 250°C steam.

Elution from XAD-4 (Fig. 6) is very similar to that of C<sub>18</sub> (Fig. 5), except the effective elution temperature was shifted ~50°C higher for each solute. Phenols and amines were eluted at 200–250°C, however, 250°C steam was required to elute tetrachlorobenzene, 2-chlorodiphenylether, 9-H

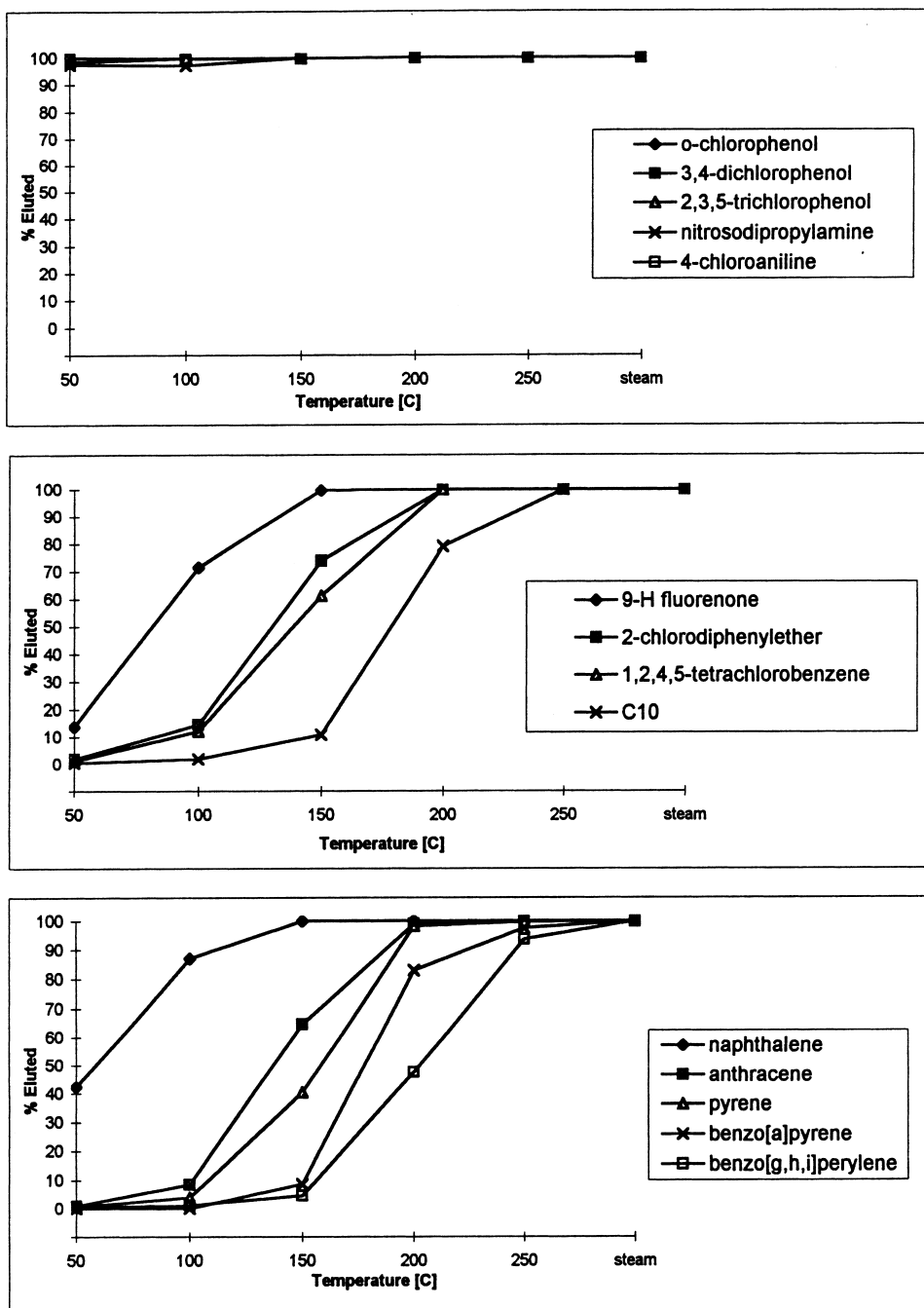


Fig. 4. Elution of organic solutes from alumina using subcritical water at different temperatures. Pressure was held at 50 bar for liquid water at 50 to 250°C, and 5 bar for 250°C steam. The results are similar to those obtained for glass beads and Florisil.

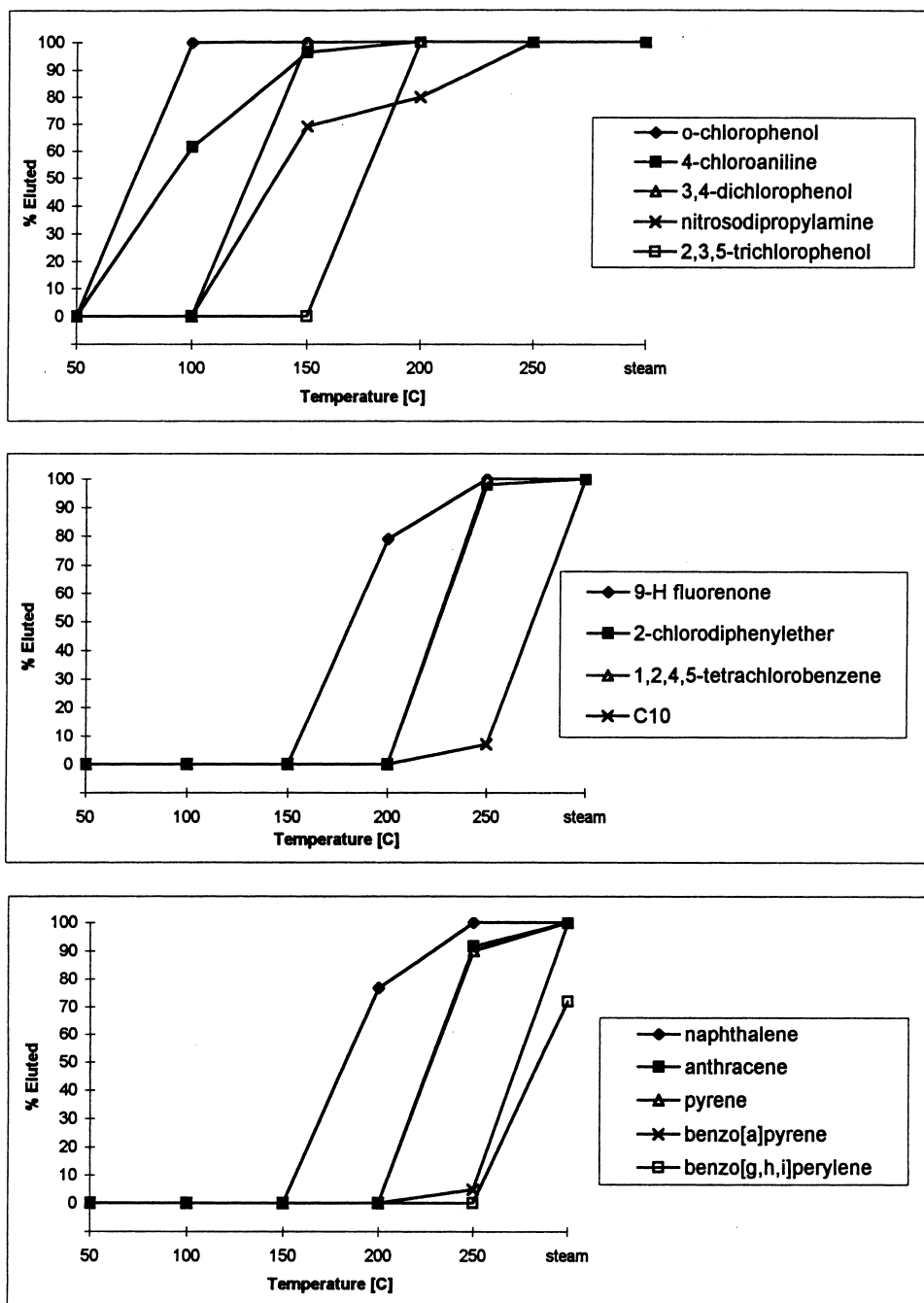


Fig. 5. Elution of organic solutes from silica-bonded  $C_{18}$  using subcritical water at different temperatures. Pressure was held at 50 bar for liquid water at 50 to 250°C, and 5 bar for 250°C steam.

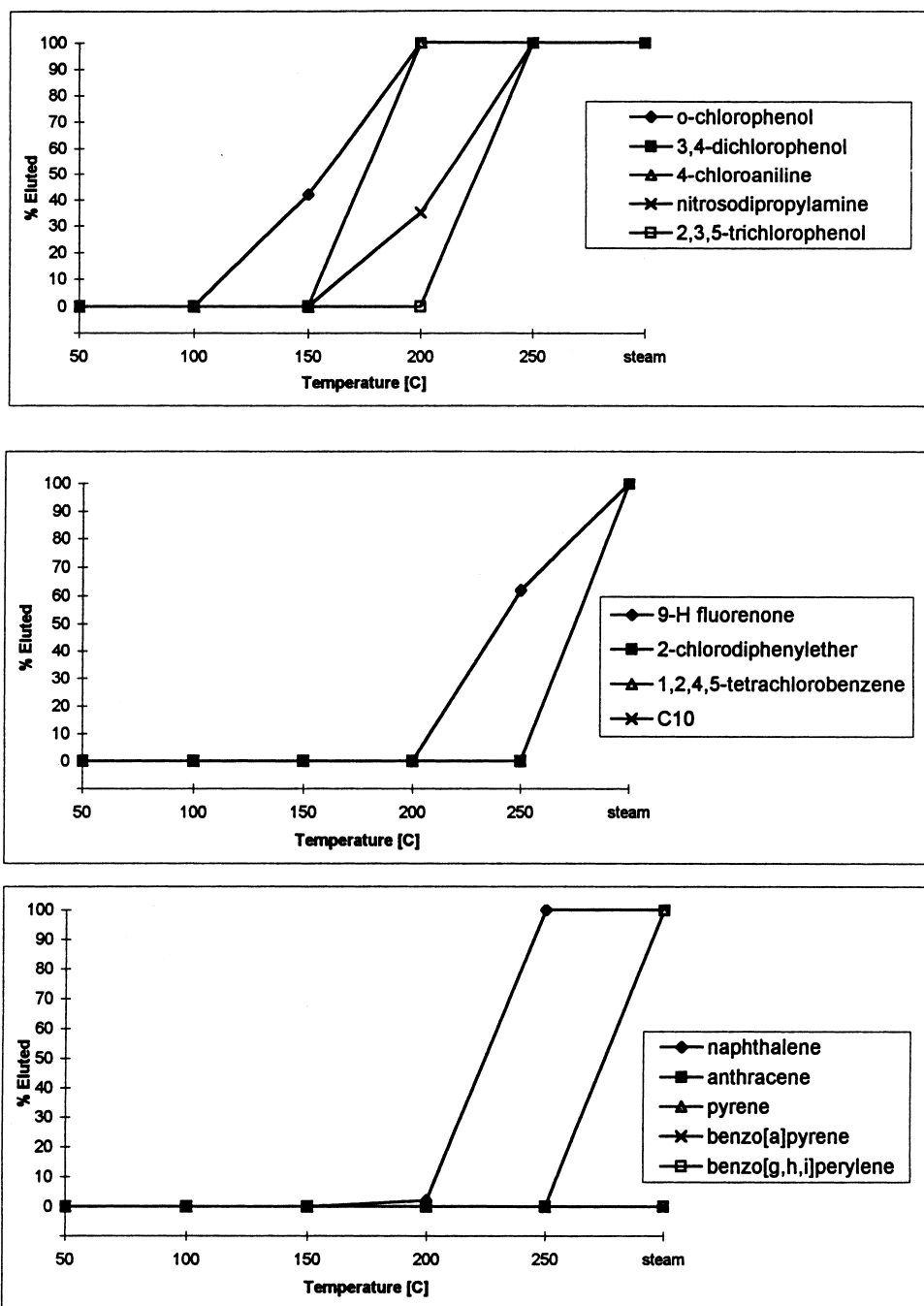


Fig. 6. Elution of organic solutes from XAD-4 using subcritical water at different temperatures. Pressure was held at 50 bar for liquid water at 50 to 250°C, and 5 bar for 250°C steam. Only 9-H-fluorenone and naphthalene elute before exposure to 250°C steam in the middle and bottom graphs, respectively.



fluorenone, and *n*-decane (Fig. 6, middle). For PAHs, only naphthalene was 100% eluted using 250°C liquid water, while anthracene and pyrene required 250°C steam. The high-molecular-mass benzo[*a*]pyrene and benzo[*ghi*]perylene were not eluted under any conditions from XAD-4.

### 3.3. Intermolecular interactions between solute and stationary phase

Comparisons of the ability of water at different temperatures to elute various organics from matrices displaying dipole interactions (Florisil and alumina), van der Waals attractions ( $C_{18}$ ) and  $\pi$ -electron interactions (XAD-4) are shown in Fig. 7. Water effectively disrupts dipole interactions, since all of the polar solutes were quantitatively eluted from alumina and Florisil at 50°C (Fig. 4). However, all of the polar solutes required higher temperatures for elution from  $C_{18}$  and XAD-4. For example, 3,4-dichlorophenol was eluted from  $C_{18}$  until 150°C and from XAD-4 until 200°C (Fig. 7), demonstrating that lower temperature water is not effective at disrupting Van der Waals and  $\pi$ -electron interactions, even when the organics are sufficiently soluble to easily elute from glass beads, alumina, and Florisil.

These results would be expected since alumina and Florisil are polar packings and serve as normal stationary phases, and low-temperature water (at 50°C) has the strongest solvent strength [18] to effectively elute polar solutes. In contrast, silica-bonded  $C_{18}$  and polymeric XAD-4 are nonpolar, reversed-phase packings, and, therefore, low temperature water is the weakest eluent for these reversed-phase packings [18]. Thus, higher water temperature is required to lower the dielectric constant and surface tension (Figs. 1 and 2) so that water becomes an efficient solvent for eluting the solutes from the reversed-phase packings ( $C_{18}$  and XAD-4). In addition, elution of the aromatic acids and bases required an additional 50°C (from  $C_{18}$  to XAD-4), demonstrating that water is less effective at eluting aromatics from sorbents displaying  $\pi$ -electron interactions compared to those having only Van der Waals attractions.

The less polar solutes were also easier to elute from the normal phases than from the reversed

phases. In general, an additional 50–100°C was required to elute all of the less polar solutes from  $C_{18}$  than from the normal phases. For example, 1,2,4,5-tetrachlorobenzene was eluted at 150–200°C from glass beads, alumina, and Florisil, while 250°C was required for elution from  $C_{18}$  (Fig. 7). In addition, all of the aromatic solutes required an additional 50°C for elution from XAD-4 than from  $C_{18}$  (Fig. 7), as would be expected since XAD-4 is capable of  $\pi$ -electron interactions as well as Van der Waals forces presented by  $C_{18}$ .

Although the majority of test solutes were aromatic (and thus would be expected to interact more strongly with XAD-4 than  $C_{18}$ ), the elution of *n*-decane was also studied to include a compound which would have only Van der Waals attractions with XAD-4. Unlike the aromatic solutes, no elution difference was found between  $C_{18}$  and XAD-4 for the *n*-decane (Fig. 7), demonstrating that water is more effective at disrupting Van der Waals attractions than  $\pi$ -electron interactions.

## 4. Conclusions

Subcritical water can efficiently elute both polar and nonpolar solutes from normal and reversed-phase packings based on the lower polarity and surface tension which occurs as water is heated (under enough pressure to maintain the liquid state). More polar solutes (e.g., phenols and amines) generally elute with 50°C water from normal phase packings, but less polar solutes (e.g., PAHs) require higher elution temperatures. As might be expected, elution behavior from normal phase packings can be predicted based on the solute's solubility in ambient water. Regardless of the solute studied, elution from reversed-phase packings ( $C_{18}$  silica and XAD-4) require water which is ~100–150°C hotter than elution from normal phases. In addition, aromatic solutes require ~50°C hotter water for elution from XAD-4 than from  $C_{18}$  packings. This pattern demonstrates that water can most easily disrupt dipole interactions, while higher temperature water is required to interrupt Van der Waals attractions, and even higher temperature water is needed to overcome

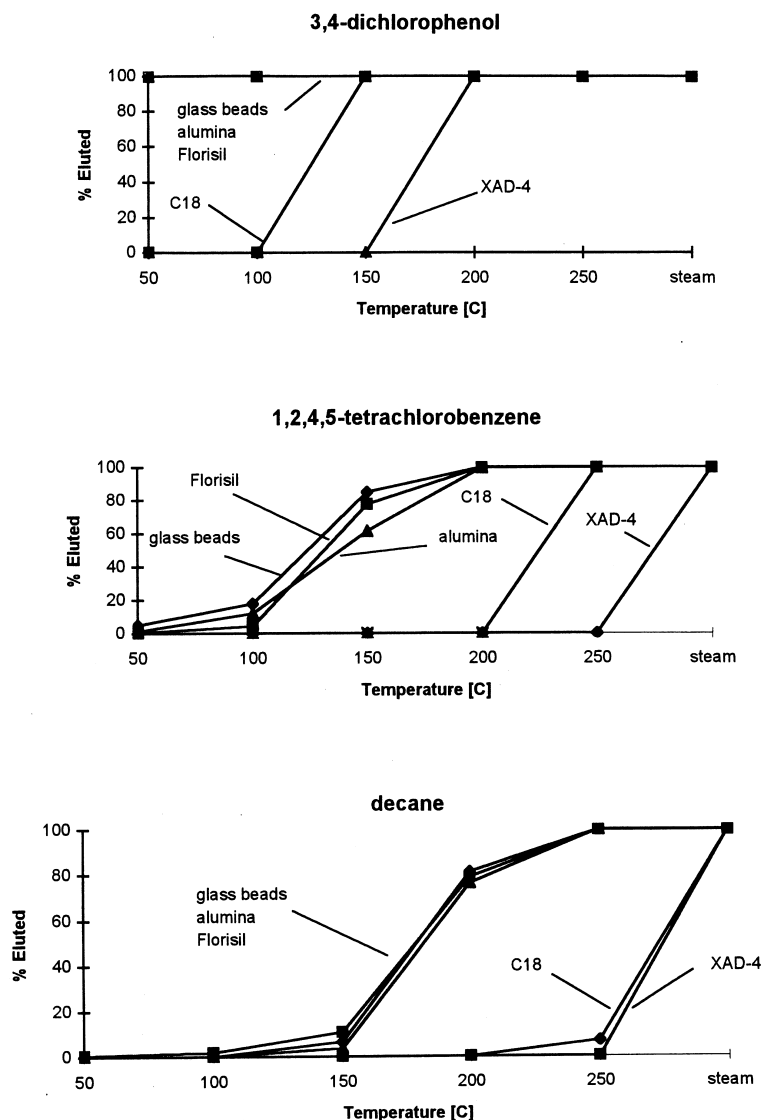


Fig. 7. Elution of 3,4-dichlorophenol, 1,2,4,5-tetrachlorobenzene, and *n*-decane from both normal and reversed-phase packings using subcritical water at different temperatures. Pressure was held at 50 bar for liquid water at 50 to 250°C, and 5 bar for 250°C.

the  $\pi$ -electron interactions between solutes and solid sorbents.

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therefore, does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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