The Chemistry of Extraction and Preparation

Extraction

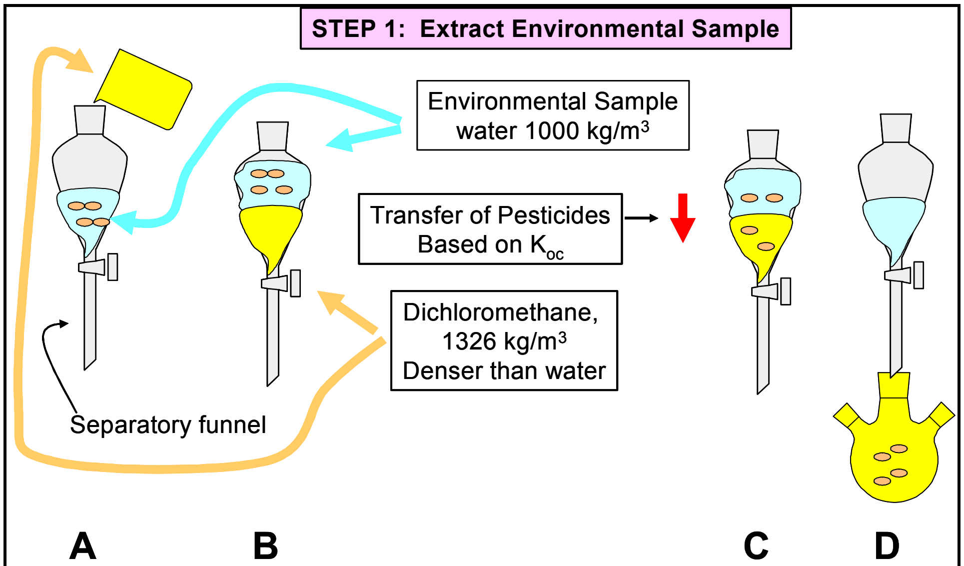
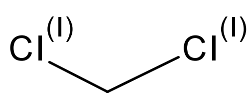
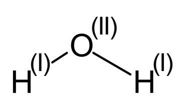


Figure 1 The extraction of an organochlorine pesticide from an aqueous environmental sample with dichloromethane depends upon a difference in solubility of the pesticide and a difference in density between water and dichloromethane.

The aqueous environmental sample suspected of containing pesticides is placed in a separatory funnel and dichloromethane (yellow) added (A). The dichloromethane is denser (heavier) than water so it sinks to the bottom of the funnel (B).



Dichloromethane



Water

Because pesticides high partition coefficients from water to octanol, K_{OW}, we predict that they will also move from water to dichloromethane (C).

$$X_{aq} \rightleftarrows X_{octanol}$$

$$K_{OW} = \frac{[X]_{acqueous}}{[X]_{octanol}}$$

After shaking to help move the pesticides into the dichloromethane fraction we pull off the dichloromethane containing the pesticides (D).

Removal of Water

The sample is next concentrated. If the sample is concentrated while containing trace amounts of water the rate of hydrolysis of the pesticide may increase (due to increasing concentration of water). (See “Environmental Chemistry” module). Therefore we must remove any trace amount of water within the sample prior to reducing the volume. This is accomplished by passing the dichloromethane containing the pesticides through a filter which contains anhydrous sodium sulfate. The reactive ingredient is the sulfate which strongly binds water. The reason for the strong binding of water is related, in part, to the charge of the sulfate anion (2-) to the volume of the anion (as measured by the ionic radius). The larger the charge per volume the more likely the anion is to electrostatically attract water close enough to bind.

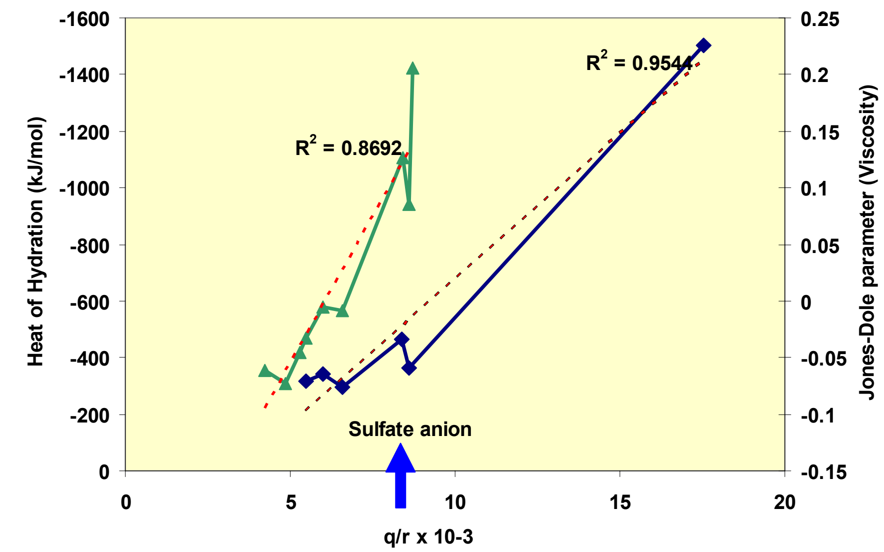


Figure 2: The heat of hydration (left) and the Jones-Dole parameter (measure of ordering of water) (right) as a function of the charge to radius ratio of several ions.

Figure 2 shows the heat of hydration and the Jones-Dole parameter (a measure of water organization) for a variety of anions with q/r (charge to radius) along the x axis. Sulfate causes a high degree of ordering of water molecules around it do to the number of oxygen and their arrangement which allows a cage of water to be formed. Figure 3 shows an image of the high degree of order of water around a sulfate anion.

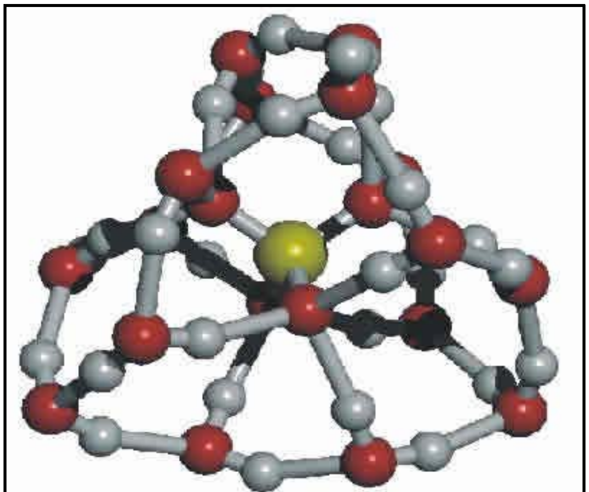


Figure 3: source of this picture is : http://www.lsbu.ac.uk/water/hofmeist.html This image shows a dodecahedron of water molecules surrounding a sulfate anion.

Concentration and Change of Solvent

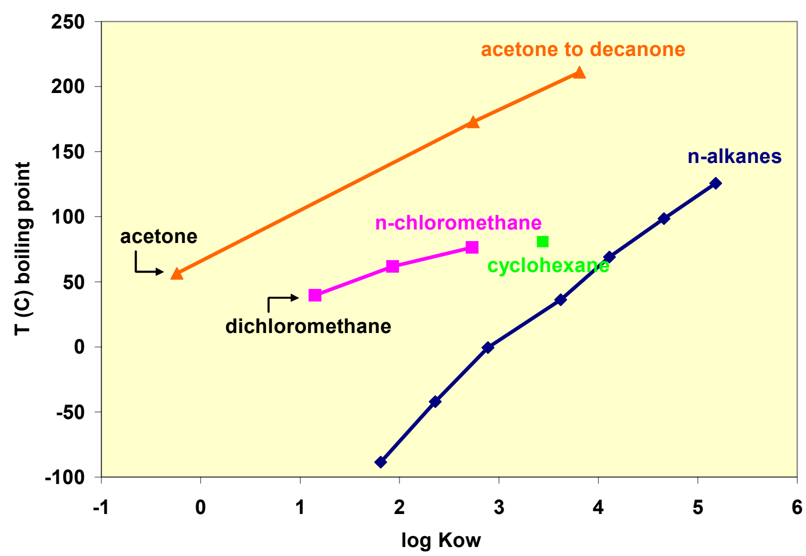


Figure 4 data source http://homepages.uc.edu:8000/~maynarjb/482/refer/propert.htm
Plot of the boiling point of a variety of solvents vs the octanol water partition coefficients.

In order to remove chloride, Cl^-, which is a contaminate in the GCMS analysis for the pesticides, and to avoid extensive use of hexachloromethane (itself an organochlorine compound) we change the solvent. The dichloromethane solvent containing the pesticide is evaporated down.. The ease of evaporation is another reason that the dichloromethane was chosen for the extraction. Dichloromethane boils at 39.7 °C, a temperature too low to be stable for storage of the sample. Furthermore, the temperature is low enough that injection of the solvent into the GC would require a cold injection in order to stabilize the sample and prevent rapid boiling off with loss of the sample at the injection port to the GCMS. As a result we would have difficulty in making a measurement of the sample in via GCMS using dichloromethane. Cyclohexane boils 40 °C higher at 80.7 °C. Acetone boils at 56.5 °C.

The mix of cyclohexane and acetone is optimized to adjust the polarity of the solvent and its ability to separate compounds eluting on the GC column. The total solvent strength of a binary solvent is the arithmetic average of the solvent polarity parameter, P', of each solvent. The solvent polarity parameter, P', for acetone is 5.1 and for cyclohexane is 0.0. Thus elution of the column with cyclohexane would have a total solvent strength of 0, a 50% mixture of cyclohexane and acetone of 2.55, and 100% acetone of 5.1.