Chapter 2: End-of-Chapter Solutions

1.
a) methane: gas, nonpolar
b) octane: liquid, nonpolar
c) water: liquid, polar
d) beeswax: solid, nonpolar
e) acetic acid: liquid, polar
f) sodium acetate: solid, ionic, soluble in water
g) K_2CrO_4: solid, ionic, soluble in water
h) methyl tert-butyl ether (MTBE): liquid, moderate polararity
i) ethanol: liquid, moderate polararity
j) perchloric acid: liquid, polar (ionic in water)
k) NaOH: solid, ionic, soluble in water
l) KCl: solid, ionic, soluble in water
m) $CaCO_3$: solid, ionic, insoluble in water

2.
a) dissolve aspirin tablets in water; filter through coffee filter; dry and weigh insoluble
starch
b) filter gravel from mixture with window screen, weigh either gravel or sand
c) weigh water sample; allow water to evaporate; weigh remaining salt
d) extract caffeine with organic solvent; allow solvent to evaporate and weigh remaining caffeine
(repeat with SPE cleanup after extraction; drying down and weigh each fraction to determine if
any other extractable components are present)

3.
a) acetic acid - predominantly in water ($\alpha_{S(aq)} = 0.6$)
b) hexane - predominantly in octanol
c) 1-hexanol - predominantly in octanol
d) methanol - predominantly in octanol
e) oleic acid - predominantly in octanol

4. For K_D of 1200 and equal volumes of water and octanol, $\alpha_{S(aq)} = 8.3\times10^{-4}$. For 100 mL of each
solution this becomes 0.083 mL octanol in 100 mL of water. Using the density of octanol (0.8
g/mL) the solubility is approximately 0.06 g/100 mL solution. (Note that this approach is an
approximate prediction since the $\alpha_{S(aq)}$ calculation is dependent on relative volumes.)

Brian M. Tissue, *Basics of Analytical Chemistry and Chemical Equilibria*, (J. Wiley, New York, 2013).

5. The general expression is:

$$\alpha_{S(aq)} = \left[\cfrac{1}{1 + K_D' \cfrac{V_{org}}{V_{aq}}} \right]^n$$

a)

$$0.10 = \left[\cfrac{1}{1 + K_D' \cfrac{30 \text{ mL}}{100 \text{ mL}}} \right]^1$$

$K_D' = 30$

(b)

$$\alpha_{S(aq)} = \left[\cfrac{1}{1 + 30 \cfrac{7.5 \text{ mL}}{100 \text{ mL}}} \right]^4$$

$\alpha_{S(aq)} = 0.0090$ (or 0.9 %)

(c)

$$\alpha_{S(aq)} = \left[\cfrac{1}{1 + 30 \cfrac{10 \text{ mL}}{100 \text{ mL}}} \right]^n$$

The easiest way to solve this question is to calculate $\alpha_{S(aq)}$ as a function of n:

n	$\alpha_{S(aq)}$
1	0.25
2	0.062
3	0.016
4	0.0039
5	0.00098

Doing 5 extractions leaves slightly less than 0.1 % of the solute in the aqueous phase and meets the state criterion.

6.
For $K_D' = 66$ and two sequential extractions ($n = 2$):

$$0.001 = \left[\cfrac{1}{1 + 66 \cfrac{V_{org}}{100 \text{ mL}}} \right]^2$$

$V_{org} = 46.4$ mL
The total volume of organic phase will be twice this amount or 92.8 mL.

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7.
Adding acid to lower the pH below the pK_a of phenol will protonate the phenol so that it is a neutral molecule and will be soluble in organic solvents. To avoid extracting acetic acid, the pH should not be lowered to within two pH units of 4.76. Acidifying to a pH near 8 should work well.

8.
- A field blank to check for contamination during sample collection
- A lab blank to check for cross-contamination or instrument carryover.
- A field spike to check for analyte loss.
- Addition of an internal standard before sample preparation for calibration.

9.
A strong anion-exchange stationary phase consist of a quaternary ammonium species that cannot lose it's positive charge. Anions attracted to the stationary phase can be eluted by lowering the pH so that the anions are protonated and become neutral.

A weak anion-exchange stationary phase consist of an ammonium species that can lose it's positive charge at high pH. Anions attracted to the stationary phase can be eluted by raising the pH so that the stationary phase is neutralized.

The carbonate buffer system is a convient eluant for anion-exchange SPE. Adjusting the pH of the buffer can increase the mobile phase concentration of CO_3^{2-}, which can displace monovalent anions from the stationary phase.

10.
a) A buffer solution at an acidic pH will keep the amino acids present as cations. Lowering the pH with time will elute the more strongly retained components faster.
b) normal-phase chromatography uses a nonpolar solvent, e.g., hexane or a mixture, e.g., hexane-isopropanol (99:1)
c) reverse-phase chromatography uses a polar solvent, e.g., water:acetonitrile mixture (mixtures are common because they allow fine tuning of the mobile phase to optimize separations)
d) a buffer solution at a basic pH to prevent the anions from becoming protonated. Raising the pH with time will elute the more strongly retained components faster.

11.
(a) Normal-phase partition chromatography usually uses a non-polar mobile phase such as hexane. For these alcohol solutes, methanol will have low solubility in hexane and an alternate mobile phase is needed. A possible choice is acetonitrile. The solutes will elute in the order from least polar to most polar: butanol, propanol, ethanol, methanol.

(b) Short chain alcohols are soluble in water, so a suitable mobile phase will be a water:acetonitrile mixture. The elution orde will be from most polar to least polar: methanol, ethanol, propanol, butanol.

12.
Find the answer to this question by searching manufacturer literature.

13.
The solution concentration of each analyte can be predicted from:
        (SRM concentration)×(SRM amount)/(volume)
which gives µg/mL or ppm in the test solution. The results are:

	SRM (µg/g)	SRM amount (g)	volume (mL)	solution (ppm)
Cd	2.48	0.3	25	0.02976
Cu	71.6	0.3	25	0.8592
Fe	205.8	0.3	25	2.4696
Pb	0.038	0.3	25	0.000456
Zn	1424	0.3	25	17.088

Comparing these calculations to the method measurement ranges, we find:
        Cd: measurable with no dilution
        Cu: dilute by 5 or more
        Fe: measurable with no dilution
        Pb: detectable with no dilution (below LOQ, detectable but cannot be quantitated)
        Zn: measurable with no dilution

14. A polar bear of course – smile, it's a joke.

15.
(a)
The online literature gives a psilocin pK_a near 8.5, so it is a cation at pH = 6.

(b)
The measurement will be erroneously low if the sample is heated too high. The method must be validated by running through the procedure with certified reference materials or spiked samples of known psilocin content.

(c)
The concentration of psilocin in the test solution is:
$$\frac{psilocin}{4130} = \frac{500 \ \mu g}{82110}$$
$$psilocin = 25.1 \ \mu g$$

Brian M. Tissue, *Basics of Analytical Chemistry and Chemical Equilibria*, (J. Wiley, New York, 2013).

For a sample weight of 200 mg, the concentration in ppm is:

$$\frac{25.1\ \mu g\ psilocin}{0.200\ g\ sample} = 126\ ppm\ psilocin$$

(d)
The internal standard will correct for any inefficiency in the SPE cleanup step. The internal standard will not correct for systematic errors due to incomplete conversion of psilocybin to psilocin or loss of psilocin due to degradation.

16.
(a) hexane (non-polar organic) – may be retained to some extent
(b) sodium acetate (mostly an anion at pH = 6) – not retained
(c) sodium benzoate (mostly an anion at pH = 6) – not retained
(d) phosphoric acid (mostly an anion at pH = 6) – not retained
(e) acetone (moderate polarity organic) – should be retained

17.
The limit of detection (LOD) and the lower limit on a control chart are two completely different things. What they have in common is that they are each a measurement from a given instrument or procedure. The LOD is the concentration that gives a measurement that is just detectable, usually three times the noise level. The limits on a control chart are usually three times the standard deviation of measurements of a standard. The standard will usually be at a concentration that is similar to samples being measured and usually much higher than the LOD.

18.
A large number of sampling sites should be selected at random to provide the highest confidence in the results.

Given obvious evidence of a soda spill, judgmental sampling is appropriate. You sample around the soda bottle to determine the extent of the spill.

19.
Since the ore has been mixed to some extent, a systematic sampling plan is reasonable. Two samples should be taken from each rail car. The sampling sites within each car should be far apart to catch heterogeneity. Depending how the cars are loaded, samples might be taken from the front and rear of a car of from the top and bottom of the ore load. The systematic approach is useful to try to determine the degree of heterogeneity in a sample batch.