Chemistry 434 Fall 2012 Homework Set 3

27-1. In gas-liquid chromatography, the stationary phase is a liquid that is immobilized on a solid. Retention of sample constituents involves equilibria between a gaseous and a liquid phase. In gas-solid chromatography, the stationary phase is a solid surface that retains analytes by physical adsorption. Here separations involve adsorption/desorption equilibria.

27-3. Temperature programming involves increasing the temperature of a GC column as a function of time. This technique is particularly useful for samples that contain constituents whose boiling points differ significantly. Low boiling point constituents are separated initially at temperatures that provide good resolution. As the separation proceeds, the column temperature is increased so that the higher boiling constituents come off the column with good resolution and at reasonable lengths of time.

27-5. A concentration-sensitive detector responds to the concentration of the analyte in the mobile phase, whereas a mass-sensitive detector responds to the number of analyte molecules or ions that come in contact with the detector. Peak areas for a concentration-sensitive detector increase as the flow rate decreases because the analyte is in contact with the detector for a longer period. Peak areas for a mass-sensitive detector are not greatly affected by flow rate. Using CS for concentration sensitive and MS for mass sensitive, we find for each of the detectors listed: (a) *thermal conductivity* (CS), (b) *atomic emission* (MS), (c) *thermionic* (MS), (d) *electron capture* (CS), (e) *flame photometric* (MS), (f) flame ionization (MS).

27-6. (a) The *thermal conductivity detector* is based on the decrease in thermal conductivity of the helium or hydrogen carrier gas brought about by the presence of analyte molecules.

(b) The *atomic emission detector* is based on the intensity of atomic emission lines generated from certain of the elements contained in analyte molecules. Atomization of the analyte and excitation of atomic emission is brought about by passing the eluent through an energetic microwave field.

(c) The *thermionic detector* is based on the ion currents produced when the mobile phase is combusted in a hydrogen flame and then passed overa heated rubidium silicate bead. It is used primarily for analytes that contain phosphorus or nitrogen.

(d) The *electron capture detector* is based on the attenuation by analyte molecules of a standing ion current generated in the effluent by ionization of mobile phase molecules with a β emitter. Electronegative functional groups are particularly effective at capturing electrons and reducing the ion current.

(e) The *flame photometric detector* is based on the radiation emitted by sulfur and phosphorus containing molecules when the eluent is passed into a low-temperature hydrogen/air flame.

(f) The *flame ionization detector* is based on ionization of the analyte in a small air/hydrogen flame. The ions and electrons produced are collected by a pair of biased electrodes giving rise to a current.

27.7 (a) Advantages, thermal conductivity: general applicability, large linear range, simplicity, nondestructive. Disadvatage: low sensitivity.

(b) Advantages, atomic emission: selectivity, large linear range, high sensitivity, general applicability. Disadvantages: destructive, high equipment costs.

(c) Advantages, thermionic: high sensitivity for compounds containing N and P, good linear range. Disadvantages: destructive, not applicable for many analytes.

(d) Advantages, electron capture: high sensitivity, selectivity toward analytes with electronegative functional groups, nondestructive. Disadvantages: nonlinear response under some circumstances, limited response range.

(e) Advantages, flame photometric: selectivity toward S and P containing analytes, good sensitivity. Disadvantages: destructive, limited applicability.

(f) Advantages, flame ionization: general applicability, large linear range, good sensitivity, low noise, low sensitivity toward most carrier gases and water, simplicity, ease of use. Disadvantage: destructive

27-15. Desirable properties of a stationary phase for GC include: low volatility, thermal stability, chemical inertness, and solvent characteristics that provide suitable k and α values for the analytes to be separated.

27-20. The distribution coefficient for a polar compound will be larger on the carbowax 20M column than on the nonpolar SE-30 column.