Chemistry 447-- Answers to Exam #2 -- Fall 2001

1. a) **False**; Furnace AA will generally have much lower detection limits compared to flame AA because of the greater atomization efficiency that exists within the furnace. This is due to the confined environment in which the sample is placed, and the longer residence time of the sample in the furnace so that more complete desolvation, ashing and atomization of the sample can take place.

b) **False**; The lower detection limits for ICP vs. flame AE is due primarily to the much higher temperature of the plasma vs. a flame. The higher temperature greatly enhances the population of atoms in a given excited state, which thereby increases the intensity of emission for the transition from the excited to ground state.

c) **True**: Nebulizers are almost always used for liquid samples in atomic spectroscopy to create tiny droplets of the solution phase. These small droplets can be efficiently desolvated and further atomized within the flame or plasma portion of the instrument.

d) **False**: Potentiometric carbon dioxide electrodes are usually prepared by incorporating a glass membrane H^+-selective electrode (pH), not a bicarbonate selective membrane electrode, behind a gas permeable membrane, and using an internal filling solution that contains a constant level of bicarbonate ions.

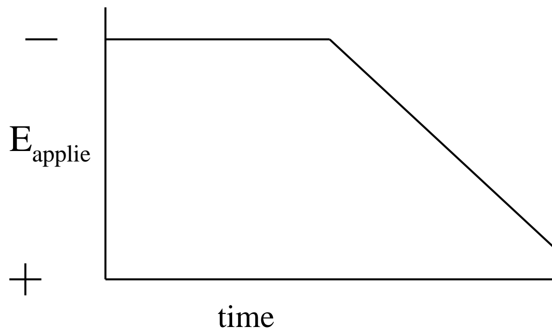
e) **True**; A three electrode potentiostat should always be used when the working electrode area approaches and/or surpasses the surface area of the reference electrode. This prevents current from flowing through the reference electrode, and therefore eliminates concentration polarization of the reference electrode (which changes the potential of the electrode), a problem that can occur when only two electrodes are employed to do voltammetry.

f) **False;** The waveforms used in differential pulse voltammetry or differential pulse polarography increase i_f / i_c ratios by decreasing the contribution from the non-faradaic charging current (i_c), and thus yield an electrochemical method with lower detection limits.

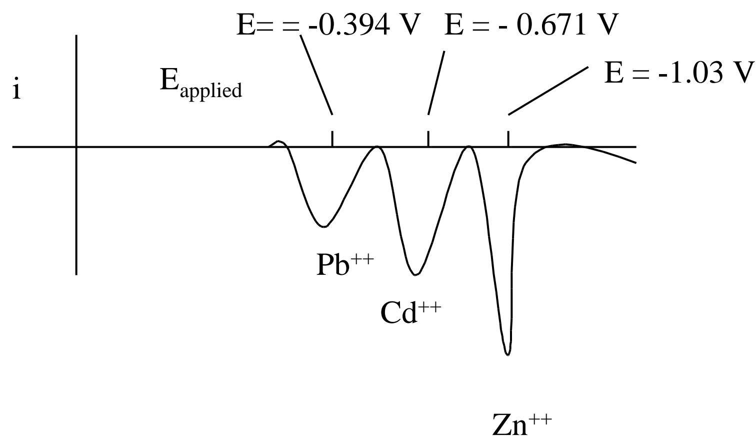
g) **True**; Slow electron transfer kinetics at solution/electrode interfaces mandate the use of more potential than predicted by the Nernst equation to adjust the surface concentrations of a given REDOX couple to a desired ratio of [OX] and [RED] via an oxidation or reduction reaction at the electrode surface.

2. ASV achieves very low detection limits for various metal ions because the ions are first preconcentrated from the sample solution into a hanging mercury drop or mercury film electrode. This is accomplished by initially applying a very negative potential to the Hg working electrode, a voltage negative enough to reduce all the metal ions to elemental species dissolved in the mercury. This preconcentration step is carrying out for a set period of time while vigorously stirring the solution. Then there is a short rest period, following by a ramping (scan) of the voltage applied to the working electrode in a positive potential direction. When the potential of the electrode reaches a value where the elemental metal will oxidize back to the ionic form, the metal is "stripped" from the electrode, and current flows until all of the metal is removed from

from the working electrode. This yields a negative current (anodic current) peak at approx. the E^o value (corrected for the given reference electrode used) for each of the metal ions that were present in the original sample. Usually, a three electrode potentiostat would be used as the instrument; especially if a thin film large surface area mercury electrode is employed as the working electrode. The $E_{applied}$ vs. time waveform would look as follows:



The resulting ASV for the three component mixture indicated in this problem would look as follows:



The potential values for the anodic peak currents are the E^o values minus the potential of a calomel reference electrode Vs. an NHE (+ 0.268 V).

3. The most common glucose electrode configuration used for blood measurements is an amperometric sensor n which a layer of glucose oxidase enzyme is sandwiched behind an outer glucose and oxygen permeable membrane and an inner low molecular weight cut-off cellulose or other membrane material (prevents interferences from reaching electrode surface).
This, enzyme/membrane sandwich is held at the tip of a platinum workinggelectrode that is poised at +0.6-+0.7 V vs. a Ag/AgCl reference electrode. Diffusion of glucose from the sample into the enzyme layer generates the products of the enzymatic reaction, gluconic acid and hydrogen peroxide (H_2O_2). The amount of hydrogen peroxide formed is proportional to the concentration of glucose in the sample. The peroxide is detected by oxidation to $2\ H^+ + O_2 + 2\ e^-$ at the inner platinum electrode. Hence, the measured anodic current is directly proportional to the concentration of glucose present. (see figure below)

A schematic of such a glucose sensor is as follows: