UNIVERSITY OF MANITOBA

CHEM 3590 Final examination 2017 Instructor : Dr. Hélène Perreault
Monday December 11, 1:30-4:30 pm, Frank Kennedy Gold Gym seats 310-343

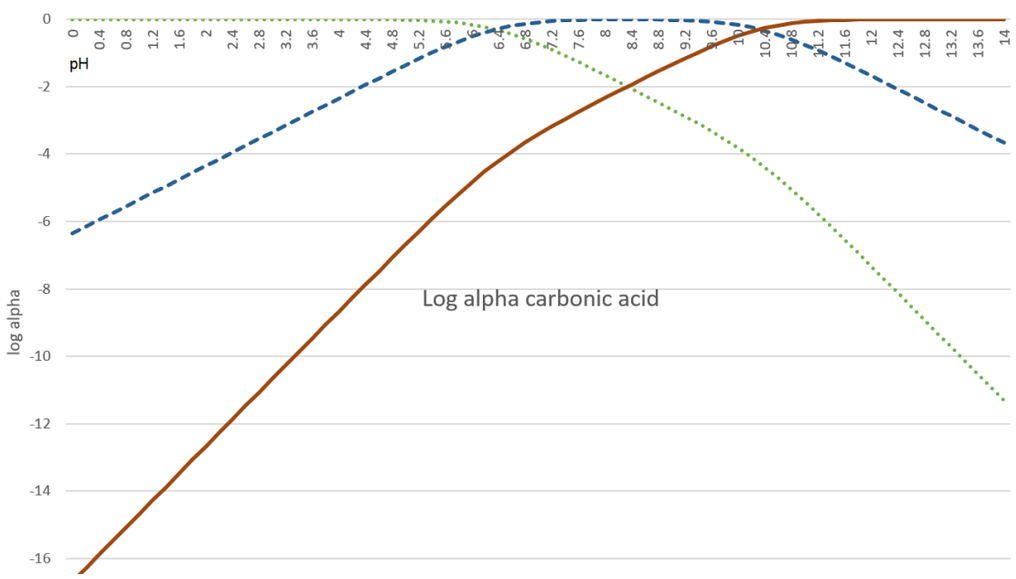
Questions 1-15 have multiple choices (50 pts). Please answer on the bubble sheet.
Questions 16-25 must be answered in the examination booklet (50 pts).

Question 1:

Given the following K_{sp} values:

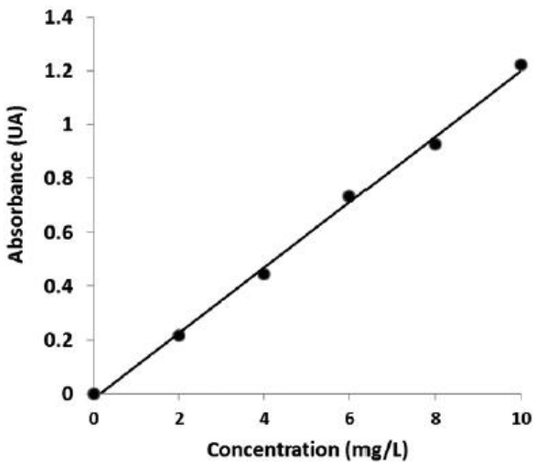
a) $CdCO_3$: 1.8×10^{-14}
b) $CoCO_3$: 1.0×10^{-10}
c) $FeCO_3$: 2.1×10^{-11}
d) $NiCO_3$: 1.3×10^{-7}

Which of these carbonate salts has a solubility of 0.005 M at pH 8?



Question 2

The following calibration curve was obtained by UV-vis absorbance. Determine the concentration of a solution whose transmittance is 30%.



a) 2.50 mg/L
b) 4.25 mg/L
c) above 10 mg/L
d) 8.75 mg/L

Question 3

In ICP-OES, sensitivity may be improved if:

a) Argon of higher rather than lower quality is used
b) Ca and Ar are present at the same time in the torch
c) The radial rather than axial viewing mode is used
d) Larger droplets are directed to the plasma torch

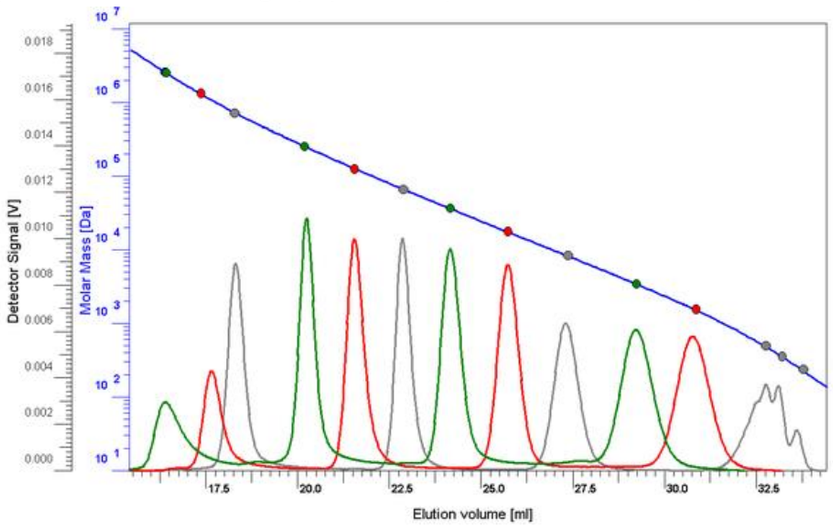
Question 4

In GC/MS, most often an electron impact ionization source is used. What is the role of the magnet component inside the source?

a) It repels the ions formed toward the mass analyzer
b) It gives the electrons a spiral-like trajectory
c) It ionizes the analyte molecules
d) It pulls the electrons away from the tungsten filament

Question 5

Only one statement is true about this superimposition of figures obtained by gel permeation chromatography with amperometric detection, which one?



a) The peak heights are proportional to molecular weights measured.
b) High MW species are more concentrated in this sample than low MW ones.
c) A molecule of MW 75 would likely not come out of the column in 33 min.
d) A molecule of MW 10^7 would saturate the detector.

Question 6

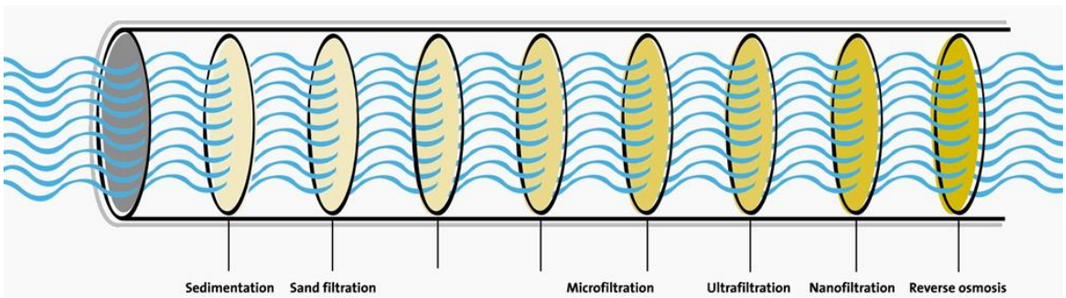
You decide to use cation exchange chromatography at pH 7 to separate the following compounds: Aniline (aromatic amine, pKa = 9.4)
Phenylalanine (an amino acid, pI = 5.9)
Acetyl salicylic acid (weak organic acid, pKa = 2.7)
Acetone (no pKa)

Predict the order of elution (1st eluting to last eluting):

a) Acetone and ASA together; phenylalanine; alanine.
b) Acetone; phenylalanine; aniline; ASA.
c) Alanine; acetone; phenylalanine and ASA together.
d) Phenylalanine; acetone, ASA, aniline.

Question 7 (NOT COVERED)

The diagram below represents a typical membrane water filtration system.



What is the direction of flow in this diagram, and why is sand used?

a) Flow: right to left. Sand helps to trap heavy metal cations.
b) Flow: right to left. Sand captures polar molecules and large solid particles.
c) Flow: left to right. Sand captures polar molecules and large solid particles.
d) Flow: left to right. Sand helps to trap heavy metal cations.

Question 8

What phenomenon causes the electroosmotic flow (EOF) in capillary zone electrophoresis?

a) When a pressure is applied to one end of the capillary, the EOF is the counter pressure created.
b) Deprotonated silanol walls are covered by a layer of mobile cations that are attracted to the cathode, this causes the EOF.
c) When one end of the capillary is placed higher than the other, the pressure created is called the EOF.
d) The Joule effect (heating) of the capillary due to resistance causes an increase of the solvent's dissociation and diffusion along the capillary walls, thus EOF.

Question 9 (NOT COVERED)

At the scene of a fire (arson):

a) Investigators carry a portable GC-FID device to detect the presence of trace volatile fuel components.
b) Investigators carry a portable photoionization device to detect the presence of trace volatile fuel components.
c) Investigators carry a portable UV-vis detection device to detect any organic component.
d) All samples are brought to the lab before any type of analysis is performed.

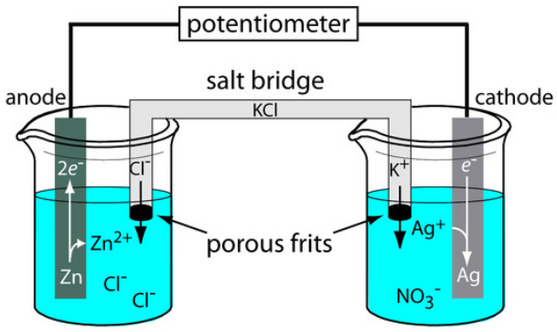
Question 10 (NOT COVERED)

A sample of a pure element is irradiated with neutrons, then left to cool for the appropriate time and measured for gamma ray emission at a specific wavelength. Ten hours after irradiation, the rate is 7250 counts, and a week after irradiation, the rate is 6815. Which one of these elements is being considered?

a) ^{137}Ba, $t_{½}$=2.55 min
b) ^{60}Co, $t_{½}$=5.27 years
c) ^{192}Ir, $t_{½}$=73.83 days
d) ^{24}Na, $t_{½}$ = 14.9 hours

Question 11

The electrochemical cell illustrated below corresponds to:



a) Zn(s)|[Zn^{2+}]=xM||[Ag^{+}]=yM|Ag(s),
E_0 = 1.560 V

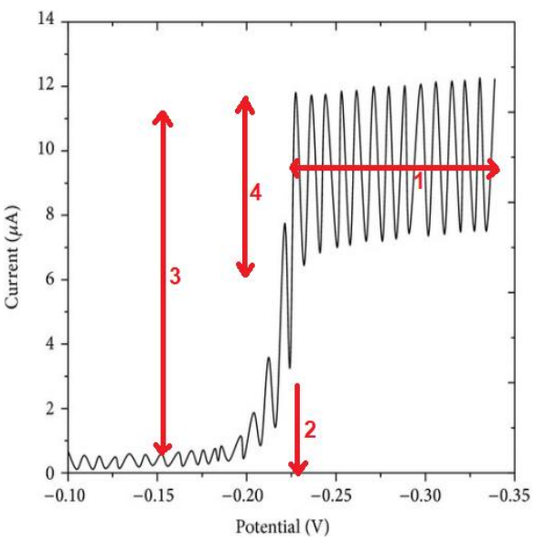
b) Zn(s)|[Zn^{2+}]=xM||[Ag^{+}]=yM|Ag(s),
E_0 = 0.036 V

c) Zn(s)| | [Zn^{2+}]=xM|[Ag^{+}]=yM||Ag(s),
E_0 = 0.564 V

d) Zn(s)| | [Zn^{2+}]=xM|[Ag^{+}]=yM||Ag(s),
E_0 = 0.763 V

Question 12

Identify each of the numbered arrows on this polarogram.



a) 1 diffusion current; 2 diffusion potential; 3 hydrolysis current; 4 Ilkovic current.

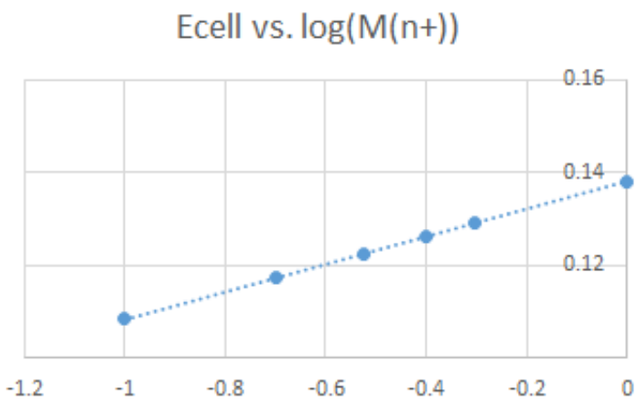
b) 1 post-reduction measurements; 2 reduction potential; 3 maximum diffusion current; 4 current fluctuations of dropping Hg electrode.

c) 1 post-oxidation measurements; 2 oxidation potential; 3 diffusion current; 4 alternate current (AC) portion of the polarogram.

d) 1 average diffusion current; 2 standard electrode potential; 3 oxidation potential; 4 E_0 of Hg dropping electrode.

Question 13

A potentiometric cell uses the Ag/AgCl (E_{ref} = + 0.199 V) to produce the graph below. Which working electrode is used?



a) Fe^{3+}/Fe(s)
b) Fe^{2+}/Fe(s)
c) Ca^{2+}/Ca(s)
d) Cu^{2+}/Cu(s)

Question 14

In ICP-MS coupled with OES, ions corresponding to metal oxides often interfere **in mass** with other elements. An example is the formation of MgO ions at m/z 60, which can interfere with an isotope of neodymium at the same mass. How could you address this problem?

a) By observing the emission wavelengths that would be different
b) By using a standard additions-like method
c) By using high resolution mass spectrometry
d) By distinguishing the isotopic patterns of each element
e) All of the above

Question 15

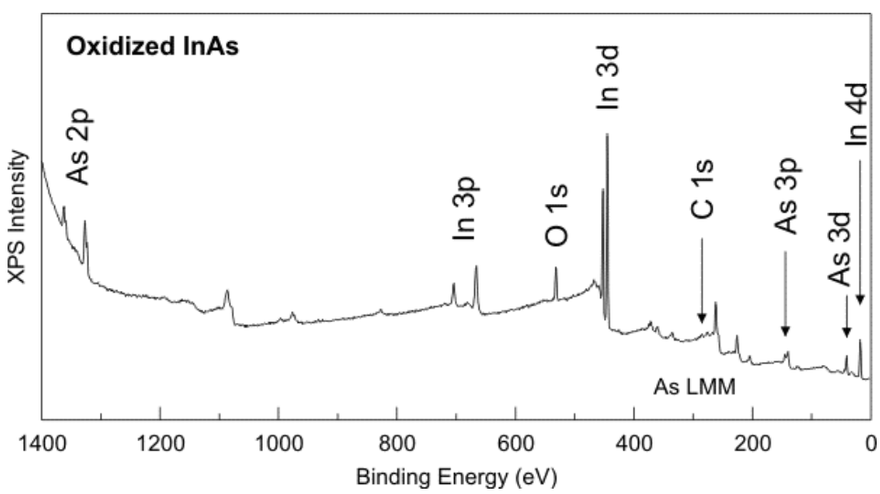
Electrospray ionization is a technique which allows:

a) Direct interfacing of HPLC and MS; formation of multiply charged ions.
b) Direct interfacing of GC and MS; formation of $M^{+\cdot}$ ions for small molecules.
c) Direct interfacing of ICP and MS; formation of hydrated elemental ions.
d) Direct interfacing of both GC and LC to MS; formation of all types of ions.

END OF THE MULTIPLE CHOICE SECTION

Question 16

The spectrum below was obtained by photoelectron spectroscopy (XPS).



Comment on the positions of the lines in the spectrum based on the atomic number and orbitals considered.

Question 17

You are to make up a water solution containing three compounds: A, B, and C. The final concentrations should be 20 µg/mL for A, 10 µg/mL for B and 5 µg/mL for C. The three stock solutions contain 1 mg/mL of either A, B or C. The final volume needed is at least 2 mL, and enough solution should be made so automatic pipettes can be used for dilutions.

a) Describe the preparation of this solution.
b) If you inject 10 µL of this solution in an instrument, how much of A, B, C do you inject?

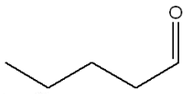
Question 18 (NOT COVERED)

A 0.25 M solution of radioactive $^{41}CaC_2O_4$ (50 mL) is measured for its gamma ray radiation intensity and the value obtained is 6500 counts. This solution is poured into a large container of unknown volume and the well water is stirred mechanically. A 50-mL sample of the mixed water is then collected and measured for radiation at an intensity of 72 counts.

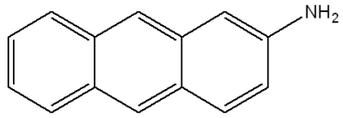
a) Determine the volume of the container.
b) What is the concentration of the mixed water sample?
c) How much ^{41}Ca (in µg) is in the mixed 50 mL sample?

Question 19

A series of aliphatic aldehydes (pentanal, hexanal and heptanal) are to be separated by normal phase HPLC and detected by fluorescence after labelling with amino-anthracene.



e.g. pentanal



2-aminoanthracene

a) Write the chemical reaction for labelling, for one of the aldehydes.
b) How would labelling influence the retention times of these aldehydes. Justify.
c) What is the advantage of using the same label for all aldehydes in this experiment?

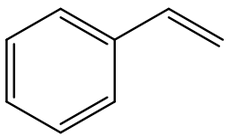
Question 20

Write the two balanced half reactions that make up this redox reaction. Indicate which one is an oxidation and which one is a reduction, and determine the E_o value.

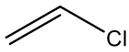
$2NO_3^- + 3ClO_3^- + 2H^+ \rightarrow 2NO + 3ClO_4^- + H_2O$

Question 21

A polymer chemist wants to analyze three types of monomers by GC before performing a polymerization reaction. However, polymerization happens in the GC injector due to high temperature, which plugs the injector and the top of the column. Here are the three building block monomers:



Styrene



Vinyl chloride

Ethylene

a) What types of polymers will clog up the injector and top of column?
b) What should be done to the GC to get it in working order again?
c) Suggest an alternative chromatographic technique to analyze these monomers; predict their elution order.

Question 22 (NOT COVERED)

Plutonium-239 decays by loss of an alpha particle. The product in turn also decays by loss of an alpha particle. At last, this second decay product undergoes fission into two nuclei, one of which being zirconium-107.

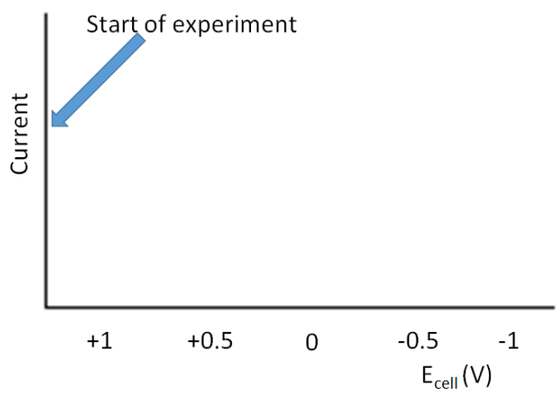
a) Write these statements as nuclear reactions.
b) What is the other nucleus produced besides ^{107}Zr?

Question 23

Name and describe three different modes of sample injection for capillary electrophoresis.

Question 24

In a solution containing iron, you are interested in determining the concentrations of Fe^{2+} and Fe^{3+} species. Draw a cyclic voltammogram for this solution, if the reference is the standard hydrogen electrode. Use the blank graph below as a model. Do you believe this process to be reversible and why?



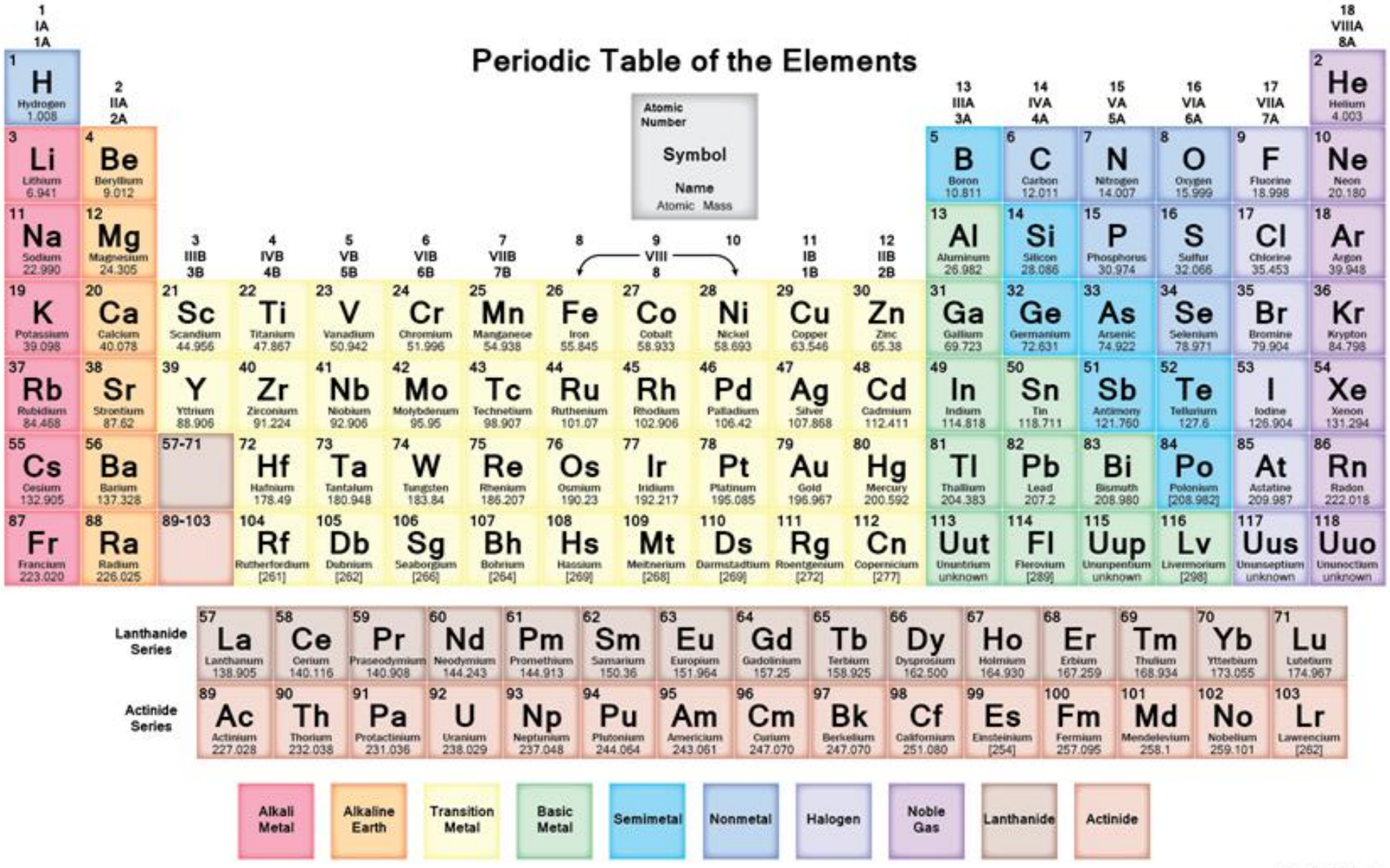
Question 25 (NOT COVERED)

If you had to set up your own laboratory for arson forensics (fires), which three instruments would you purchase and what would their use(s) be?

Standard electrode potentials in aqueous solution at 25°C

Cathode (Reduction) Half-Reaction	Standard Potential E° (volts)
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.04
$K^+(aq) + e^- \rightarrow K(s)$	-2.92
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	-2.76
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	-2.38
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	-1.66
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	-0.74
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.41
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	-0.40
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	-0.23
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	-0.14
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	-0.13
$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$	-0.04
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00 (ref)
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	0.15
$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$	0.16
$ClO_4^-(aq) + H_2O(l) + 2e^- \rightarrow ClO_3^-(aq) + 2OH^-(aq)$	0.17
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	0.199 (ref)
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$ClO_3^-(aq) + H_2O(l) + 2e^- \rightarrow ClO_2^-(aq) + 2OH^-(aq)$	0.35

Cathode (Reduction) Half-Reaction	Standard Potential E° (volts)
$IO^-(aq) + H_2O(l) + 2e^- \rightarrow I^-(aq) + 2OH^-(aq)$	0.49
$Cu^+(aq) + e^- \rightarrow Cu(s)$	0.52
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	0.54
$ClO_2^-(aq) + H_2O(l) + 2e^- \rightarrow ClO^-(aq) + 2OH^-(aq)$	0.59
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.77
$Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(l)$	0.80
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.80
$Hg^{2+}(aq) + 2e^- \rightarrow Hg(l)$	0.85
$ClO^-(aq) + H_2O(l) + 2e^- \rightarrow Cl^-(aq) + 2OH^-(aq)$	0.90
$2Hg^{2+}(aq) + 2e^- \rightarrow Hg_2^{2+}(aq)$	0.90
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$	0.96
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	1.07
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	1.23
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	1.36
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	1.44
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.49
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$	1.78
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	1.82
$S_2O_8^{2-}(aq) + 2e^- \rightarrow 2SO_4^{2-}(aq)$	2.01
$O_3(g) + 2H^+(aq) + 2e^- \rightarrow O_2(g) + H_2O(l)$	2.07
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	2.87


Periodic Table of the Elements
Atomic Number
Symbol
Name
Atomic Mass
1 IA 1A
2 IIA 2A
3 IIIB 3B
4 IVB 4B
5 VB 5B
6 VIB 6B
7 VIIB 7B
8
9 VIII 8
10
11 IB 1B
12 IIB 2B
13 IIIA 3A
14 IVA 4A
15 VA 5A
16 VIA 6A
17 VIIA 7A
18 VIIIA 8A
1 H Hydrogen 1.008
2 He Helium 4.003
3 Li Lithium 6.941
4 Be Beryllium 9.012
5 B Boron 10.811
6 C Carbon 12.011
7 N Nitrogen 14.007
8 O Oxygen 15.999
9 F Fluorine 18.998
10 Ne Neon 20.180
11 Na Sodium 22.990
12 Mg Magnesium 24.305
13 Al Aluminum 26.982
14 Si Silicon 28.086
15 P Phosphorus 30.974
16 S Sulfur 32.066
17 Cl Chlorine 35.453
18 Ar Argon 39.948
19 K Potassium 39.098
20 Ca Calcium 40.078
21 Sc Scandium 44.956
22 Ti Titanium 47.867
23 V Vanadium 50.942
24 Cr Chromium 51.996
25 Mn Manganese 54.938
26 Fe Iron 55.845
27 Co Cobalt 58.933
28 Ni Nickel 58.693
29 Cu Copper 63.546
30 Zn Zinc 65.38
31 Ga Gallium 69.723
32 Ge Germanium 72.631
33 As Arsenic 74.922
34 Se Selenium 78.971
35 Br Bromine 79.904
36 Kr Krypton 84.798
37 Rb Rubidium 84.468
38 Sr Strontium 87.62
39 Y Yttrium 88.906
40 Zr Zirconium 91.224
41 Nb Niobium 92.906
42 Mo Molybdenum 95.95
43 Tc Technetium 98.907
44 Ru Ruthenium 101.07
45 Rh Rhodium 102.906
46 Pd Palladium 106.42
47 Ag Silver 107.868
48 Cd Cadmium 112.411
49 In Indium 114.818
50 Sn Tin 118.711
51 Sb Antimony 121.760
52 Te Tellurium 127.6
53 I Iodine 126.904
54 Xe Xenon 131.294
55 Cs Cesium 132.905
56 Ba Barium 137.328
57-71
72 Hf Hafnium 178.49
73 Ta Tantalum 180.948
74 W Tungsten 183.84
75 Re Rhenium 186.207
76 Os Osmium 190.23
77 Ir Iridium 192.217
78 Pt Platinum 195.085
79 Au Gold 196.967
80 Hg Mercury 200.592
81 Tl Thallium 204.383
82 Pb Lead 207.2
83 Bi Bismuth 208.980
84 Po Polonium [208.982]
85 At Astatine 209.987
86 Rn Radon 222.018
87 Fr Francium 223.020
88 Ra Radium 226.025
89-103
104 Rf Rutherfordium [261]
105 Db Dubnium [262]
106 Sg Seaborgium [266]
107 Bh Bohrium [264]
108 Hs Hassium [269]
109 Mt Meitnerium [268]
110 Ds Darmstadtium [269]
111 Rg Roentgenium [272]
112 Cn Copernicium [277]
113 Uut Ununtrium unknown
114 Fl Flerovium [289]
115 Uup Ununpentium unknown
116 Lv Livermorium [298]
117 Uus Ununseptium unknown
118 Uuo Ununoctium unknown
Lanthanide Series
57 La Lanthanum 138.905
58 Ce Cerium 140.116
59 Pr Praseodymium 140.908
60 Nd Neodymium 144.243
61 Pm Promethium 144.913
62 Sm Samarium 150.36
63 Eu Europium 151.964
64 Gd Gadolinium 157.25
65 Tb Terbium 158.925
66 Dy Dysprosium 162.500
67 Ho Holmium 164.930
68 Er Erbium 167.259
69 Tm Thulium 168.934
70 Yb Ytterbium 173.055
71 Lu Lutetium 174.967
Actinide Series
89 Ac Actinium 227.028
90 Th Thorium 232.038
91 Pa Protactinium 231.036
92 U Uranium 238.029
93 Np Neptunium 237.048
94 Pu Plutonium 244.064
95 Am Americium 243.061
96 Cm Curium 247.070
97 Bk Berkelium 247.070
98 Cf Californium 251.080
99 Es Einsteinium [254]
100 Fm Fermium 257.095
101 Md Mendelevium 258.1
102 No Nobelium 259.101
103 Lr Lawrencium [262]
Alkali Metal
Alkaline Earth
Transition Metal
Basic Metal
Semimetal
Nonmetal
Halogen
Noble Gas
Lanthanide
Actinide
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