UNIVERSITY OF MANITOBA

CHEM 3590 Deferred Final examination Instructor : Dr. Hélène Perreault
Friday January 8, 9-12 am.

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

This picture shows a detection window used in capillary electrophoresis. Which of the following CE detection methods could use such a window? (More than one answer may be possible; you may circle more than one).

a) UV-visible
b) Infrared
c) Raman
d) Amperometric
e) Fluorescence

Question 2

Given the following anions: Cl^-, F^-, SO_4^{2-} and ClO_4^-, predict their migration order in capillary zone electrophoresis (CZE), if the apparatus is operated from - to + at high pH. The order is given from first to last to reach the detector.

a) Cl^-, F^-, SO_4^{2-}, ClO_4^-

b) ClO_4^-, SO_4^{2}, Cl^-, F^-.

c) F^-, Cl^-, SO_4^{2-}, ClO_4^-

d) SO_4^{2-}, Cl^-, F^-, ClO_4^-.

Question 3

Which statement is TRUE about reversed UV-vis detection in CZE?

a) In reversed UV-vis detection, there is no electroosmotic flow and the overall flow is aimed toward the anode (+).
b) This method used a Z-shaped window to reverse the flow direction for a short moment and enhance UV absorptivity due to a longer path.
c) Reversed UV detection in CE involves derivatization of the analyte to make it absorb more light than the buffer.
d) In reversed UV detection, the buffer is highly absorbing and the analytes produce a negative signal relative to the baseline.
e) All statements are true.

Question 4 (NOT COVERED)

What happens if radioactive samples containing atoms such as ^{14}C, ^{19}O and ^{20}F are run in a mass spectrometer? (More than one answer may be possible).

a) During the experiment, the beta decay of these particular atoms produces a mixture of elements.
b) These elements are heavier than their stable counterparts, therefore non-volatile and cannot be analyzed.
c) Care must be taken not to contaminate instruments with radioactive elements.
d) The half-lives of all these elements are shorter than the duration of the experiment.
e) All these answers are correct.

Question 5

Calculate E° for the reaction:

$2Na^+ + ClO_3^- + 2OH^- \rightarrow 2Na(s) + ClO_4^- + H_2O$

a) +2.88 V b) +2.54 V c) -2.54 V d) -5.59 V e) - 2.88 V

Question 6

From the following data, determine which system was used for potentiometric analysis. For SCE E_{ref} = 0.244 V.

Conc M^{n+}	E_{cell}
0.01	-0.0795
0.03	-0.0700
0.05	-0.0657
0.07	-0.0628
0.09	-0.0606
0.11	-0.0589
0.13	-0.0575
0.15	-0.0562

a) SHE||Mg^{2+}|Mg(s)
b) SCE||Al^{3+}|Al(s)
c) SCE|| Cu^{2+}|Cu(s)
d) SHE|| Fe^{3+}|Fe(s)
e) SHE||Ag^{+}|Ag(s)

Question 7 (NOT COVERED)

An unstable nucleus decays by alpha emission, then the product undergoes fission into two identical ^{116}Rh nuclei. The decay constant of the fission process is 3 events/min. Determine the nature of the original isotope and of the intermediate product. What is the half life of the fissible nucleus?

a) ^{120}Ag, ^{116}Rh, 0.046 min b) ^{234}Pu, ^{232}Th, 0.23 min

c) ^{232}Ac, ^{232}Th, 3.08 min d) ^{236}U, ^{232}Th, 0.23 min

Question 8 (NOT COVERED)

A radiochemist does a duplicate analysis of lead in water. He/she takes two 100-mL samples of well water and subjects them to 6 h of neutron irradiation. ^{209}Pb is formed and has a half-life of 3.253 h. A first sample is measured 10 h after irradiation, but the spectrometer breaks down and the second sample can only be analyzed three days after irradiation. What percentage of ^{209}Pb is left in each sample at measurement time?

a) 12% and 2 x 10^{-5} % b) 1.2% and 0.8% c) 1.2% and 0.5% d) 12% and 2 x 10^{-7} %

Question 9 (NOT COVERED)

High performance liquid chromatography may be used with a scintillation detector which is sensitive to the decay of unstable ^{3}H (tritium) atoms. This is useful in biochemical experiments where amino acids labeled with ^{3}H are used for protein biosynthesis. Which of the following statements is FALSE?

a) Tritium decays by radiating β^{-} particles.
b) Tritium labelling does not influence HPLC retention times of proteins significantly.
c) A scintillation detector is a particle counter.
d) Tritium decays by radiating α particles.
e) The exposure to tritium may be hazardous to humans.

Question 10 (NOT COVERED)

In neutron activation analysis (NAA), many experiments require that a destructive route be followed to treat samples after neutron irradiation. Identify the main reason for using this approach.

a) Leaving all radioactive elements together in a sample may burn the sample, especially if it is biological tissue.
b) Short-lived isotopes in general must be removed as they interfere with Na and Br signals.
c) Na and Br must be removed as their decay interferes with that of other elements.
d) Elements must always be isolated from one another and measured in specific compartments.
e) Elements will not capture neutrons if Na and Br are in the sample.

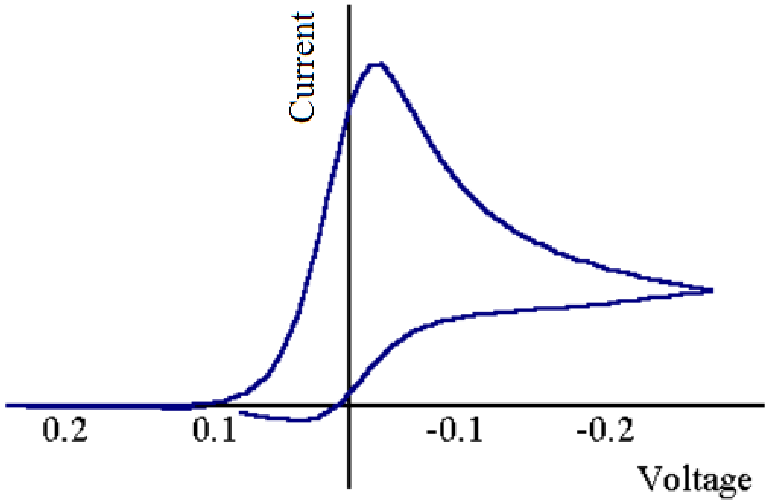
Question 11 (NOT COVERED)

A sample containing 10 g of ^{54}Mn is irradiated and 1 day after cooling, it gives off 20500 decays/h as radiation rate. From an identical sample, all the unstable manganese is extracted and isolated as $MnCO_3$ (100% yield). What will the radiation rate be for 10 g of this compound if measured at the same time as the first sample?

a) 10250 decays/h b) 9804 decays/h c) 330 decays/h d) 2.3×10^{6} decays/h

Question 12

What can be concluded from this voltammogram?



a) The analyte is first reduced, then oxidation is fully reversibley.
b) The analyte is first oxidized, then reduction is fully reversible.
c) The analyte is first reduced, but oxidation is not fully reversible.
d) The analyte is first oxidized, but reduction does not yield the material of origin.

Question 13

In an amperostatic coulometric experiment, a current was fed for 5 minutes to complete the titration of Cl^- using Ag^+ generated from an Ag/Ag(s) electrode. If the original Cl^- concentration was 8 μM and the solution volume 250 mL, what value of current was used? 1 Faraday = 96368 C/mol.

a) 38 μA b) 2.5 mA c) 642 μA d) 193 mA

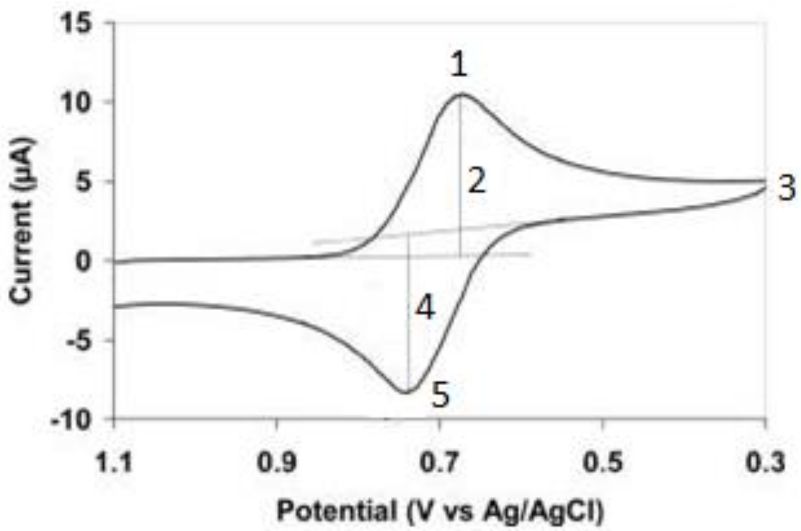
Question 14

Select the INCORRECT statement about the mercury drop electrode:

a) Each drop generates a fresh metallic surface
b) It is often used as a working electrode (µ electrode)
c) The mercury drops serve to form Hg_2Cl_2 as in the SCE reference electrode
d) It can be used in polarography experiments

Question 15

Assign each number correctly on this voltammogram.



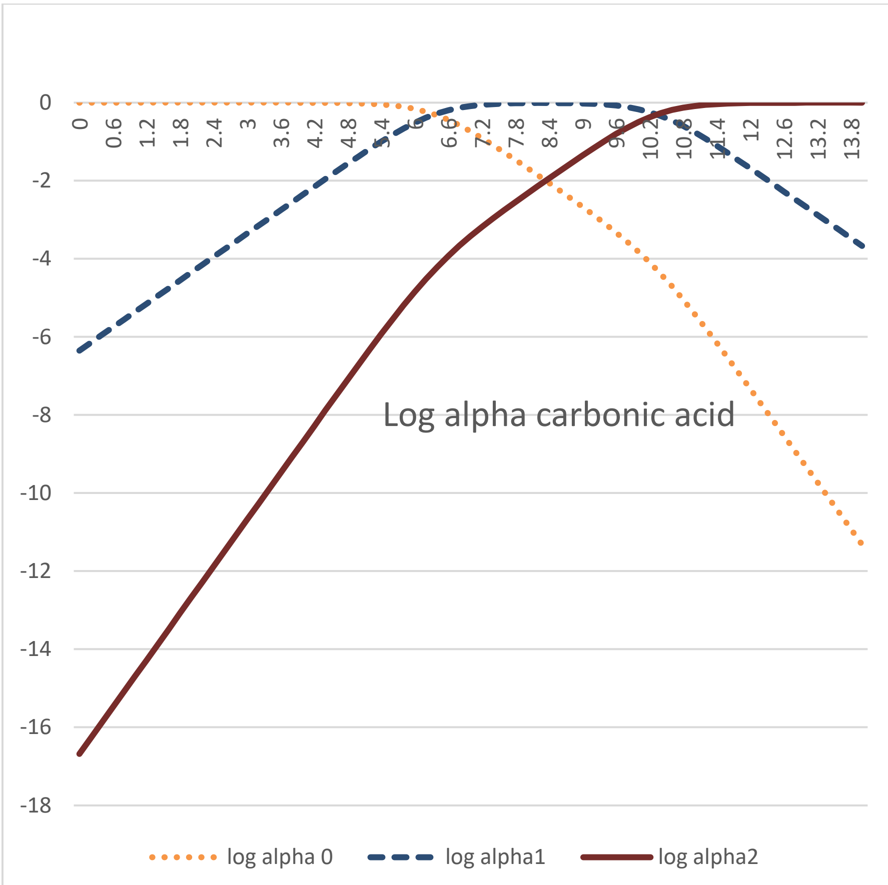
a) 1 peak of cathodic wave; 2 cathodic peak current; 3 potential reversal; 4 anodic peak current; 5 peak of anodic wave.
b) 1 peak of anodic wave; 2 anodic peak current; 3 potential reversal; 4 cathodic peak current; 5 peak of cathodic wave.
c) 1 limiting anodic current; 2 peak anodic current; 3 potential reversal; 4 limiting cathodic current; 5 peak of cathodic wave.
d) 1 start of experiment; 2 anodic peak current; 3 potential reversal; 4 cathodic peak current; 5 end of experiment.

END OF THE MULTIPLE CHOICE SECTION

Question 16

a) What is the concentration of Ca^{2+} ions at pH 3, in a system where the only source of calcium is a solid $CaCO_3$ precipitate (K_{sp} = 5 x 10^{-9})? You may use the graph below.

b) Suggest, by a diagram, a potentiometric electrode system that could be used to measure Ca^{2+} concentration. What would be E^0 for this cell?



Question 17

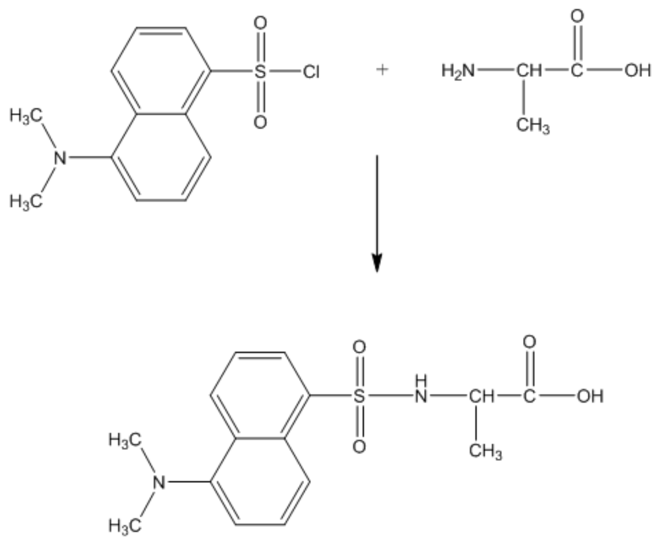
Light is used in different ways to measure concentration in the various spectrophotometric systems in MCAL.

a) Describe how light is used to measure concentration in <u>three</u> different detection systems in MCAL instruments.

b) What is the source of light in each of the three different systems?

Question 18

For the analysis of a mixture of amino acids by capillary zone electrophoresis using fluorescence detection, labelling with dansyl chloride is often used.



a) How in general would this affect the migration order of the amino acids?

b) Using a diagram for a detector, show how fluorescence can be used in combination with CZE.

Question 19 (NOT COVERED)

A 0.20 M solution of radioactive $^{41}CaCO_3$ (100 mL) is measured for its gamma ray radiation intensity and the value obtained is 2.7×10^6 units. This solution is poured into a well of unknown volume and the well water is stirred mechanically. A 100-mL sample of the mixed water is then collected and measured at an intensity of 23 units.

a) Determine the volume of the well.
b) Would it matter if rate measurements were made a few minutes apart?

Question 20 (NOT COVERED)

From the 100 mL sample of mixed water (see question above), all soluble Ca was extracted and weighed as pure metal: 10.05 μg. Determine the concentration of non-radioactive Ca^{2+} in the well.

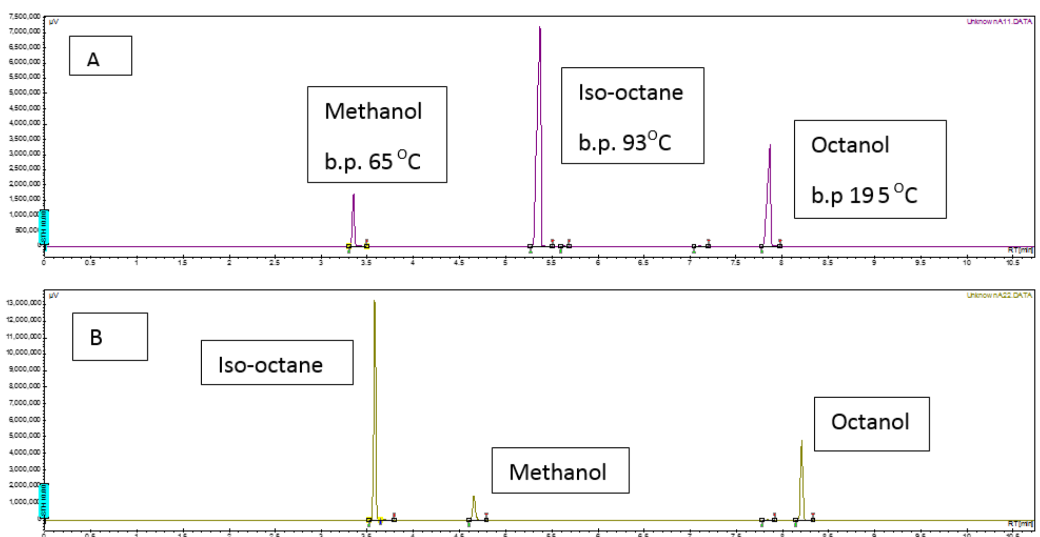
Question 21

Two amino acids, tyrosine (pI 5.66) and lysine (pI 9.74), can be separated by ion exchange chromatography and by capillary zone electrophoresis. Describe the behaviour of these two amino acids (elution order) during separation by:

a) Cation exchange chromatography
b) Anion exchange chromatography
c) Capillary zone electrophoresis (+ to – direction).

Question 22

Two chromatograms A and B (below) are produced by separation of a mixture on two columns. Column A and column B are different types of columns in the same GC, but are identical in size and length and the carrier gas is set the same for both columns. Looking at the two chromatograms, what would you say are the major differences between the two columns? What are the major factors causing separation in the two columns? Explain.



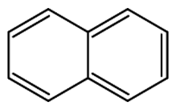
Question 23

The K_{sp} of $Al(OH)_3$ is 1.8×10^{-33}. Determine the E_0 value for the half reaction:

$Al(OH)_3(s) + 3e \rightarrow Al(s) + 3OH^-$

Question 24

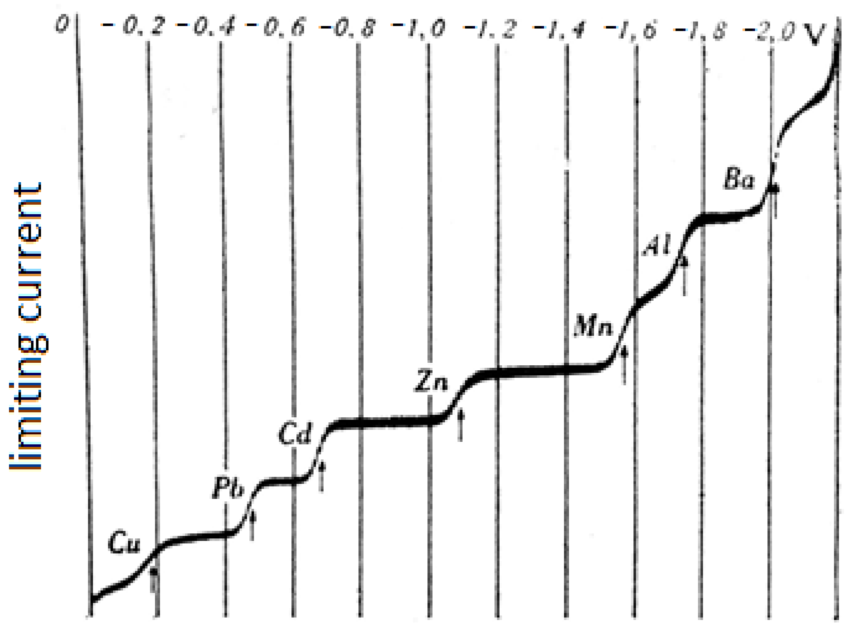
It is possible to synthesize a molecule of naphthalene where all C (^{12}C) atoms have been replaced by the stable isotope ^{13}C. Describe two methods where naphthalene with all ^{13}C would be useful for the quantitative analysis of "normal" naphthalene by mass spectrometry (you may include GC-MS and HPLC-MS in your answer).



Naphthalene

Question 25

The polarogram shown below was obtained using a mercury dropping electrode against a standard hydrogen electrode.



Using this polarogram, classify the metal ions in order from the best oxidizing agent to the best reducing agent.

Standard electrode potentials in aqueous solution at 25°C

Cathode (Reduction) Half-Reaction	Standard Potential E° (volts)
$Li^+(aq) + e^- \to Li(s)$	-3.04
$K^+(aq) + e^- \to K(s)$	-2.92
$Ca^{2+}(aq) + 2e^- \to Ca(s)$	-2.76
$Na^+(aq) + e^- \to Na(s)$	-2.71
$Mg^{2+}(aq) + 2e^- \to Mg(s)$	-2.38
$Al^{3+}(aq) + 3e^- \to Al(s)$	-1.66
$2H_2O(l) + 2e^- \to H_2(g) + 2OH^-(aq)$	-0.83
$Zn^{2+}(aq) + 2e^- \to Zn(s)$	-0.76
$Cr^{3+}(aq) + 3e^- \to Cr(s)$	-0.74
$Fe^{2+}(aq) + 2e^- \to Fe(s)$	-0.41
$Cd^{2+}(aq) + 2e^- \to Cd(s)$	-0.40
$Ni^{2+}(aq) + 2e^- \to Ni(s)$	-0.23
$Sn^{2+}(aq) + 2e^- \to Sn(s)$	-0.14
$Pb^{2+}(aq) + 2e^- \to Pb(s)$	-0.13
$Fe^{3+}(aq) + 3e^- \to Fe(s)$	-0.04
$2H^+(aq) + 2e^- \to H_2(g)$	0.00 (ref)
$Sn^{4+}(aq) + 2e^- \to Sn^{2+}(aq)$	0.15
$Cu^{2+}(aq) + e^- \to Cu^+(aq)$	0.16
$ClO_4^-(aq) + H_2O(l) + 2e^- \to ClO_3^-(aq) + 2OH^-(aq)$	0.17
$AgCl(s) + e^- \to Ag(s) + Cl^-(aq)$	0.199 (ref)
$Cu^{2+}(aq) + 2e^- \to Cu(s)$	0.34
$ClO_3^-(aq) + H_2O(l) + 2e^- \to ClO_2^-(aq) + 2OH^-(aq)$	0.35
$IO^-(aq) + H_2O(l) + 2e^- \to I^-(aq) + 2OH^-(aq)$	0.49
$Cu^+(aq) + e^- \to Cu(s)$	0.52
$I_2(s) + 2e^- \to 2I^-(aq)$	0.54
$ClO_2^-(aq) + H_2O(l) + 2e^- \to ClO^-(aq) + 2OH^-(aq)$	0.59
$Fe^{3+}(aq) + e^- \to Fe^{2+}(aq)$	0.77
$Hg_2^{2+}(aq) + 2e^- \to 2Hg(l)$	0.80
$Ag^+(aq) + e^- \to Ag(s)$	0.80
$Hg^{2+}(aq) + 2e^- \to Hg(l)$	0.85
$ClO^-(aq) + H_2O(l) + 2e^- \to Cl^-(aq) + 2OH^-(aq)$	0.90
$2Hg^{2+}(aq) + 2e^- \to Hg_2^{2+}(aq)$	0.90
$NO_3^-(aq) + 4H^+(aq) + 3e^- \to NO(g) + 2H_2O(l)$	0.96
$Br_2(l) + 2e^- \to 2Br^-(aq)$	1.07
$O_2(g) + 4H^+(aq) + 4e^- \to 2H_2O(l)$	1.23
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \to 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$Cl_2(g) + 2e^- \to 2Cl^-(aq)$	1.36
$Ce^{4+}(aq) + e^- \to Ce^{3+}(aq)$	1.44
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \to Mn^{2+}(aq) + 4H_2O(l)$	1.49
$H_2O_2(aq) + 2H^+(aq) + 2e^- \to 2H_2O(l)$	1.78
$Co^{3+}(aq) + e^- \to Co^{2+}(aq)$	1.82
$S_2O_8^{2-}(aq) + 2e^- \to 2SO_4^{2-}(aq)$	2.01
$O_3(g) + 2H^+(aq) + 2e^- \to O_2(g) + H_2O(l)$	2.07
$F_2(g) + 2e^- \to 2F^-(aq)$	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 VIII 8	9 VIII 8	10 VIII 8	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