CHUKA UNIVERSITY

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY

CHEM 342: ATOMIC SPECTROSCOPY

STREAMS: BSc CHEM **TIME: 2 HOURS**

DAY/DATE: WEDNESDAY 20/12/2023 **8.30 A.M. – 10.30 A.M.**

INSTRUCTIONS

- **Answer question one and any other two questions**

General data and fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	c	2.997 925 58*	10^{8}	m s^{-1}
Elementary charge	e	1.602 176	10^{-19}	C
Faraday's constant	$F = N_A e$	9.648 53	10^{4}	C mol^{-1}
Boltzmann's constant	k	1.380 65	10^{-23}	J K^{-1}
Gas constant	$R = N_A k$	8.314 47		J K^{-1} mol^{-1}
		8.314 47	10^{-2}	dm^{3} bar K^{-1} mol^{-1}
		8.205 74	10^{-2}	dm^{3} atm K^{-1} mol^{-1}
		6.236 37	10	dm^{3} Torr K^{-1} mol^{-1}
Planck's constant	h	6.626 08	10^{-34}	J s
	$\hbar = h/2\pi$	1.054 57	10^{-34}	J s
Avogadro's constant	N_A	6.022 14	10^{23}	mol^{-1}
Atomic mass constant	m_u	1.660 54	10^{-27}	kg
Mass				
electron	m_e	9.109 38	10^{-31}	kg
proton	m_p	1.672 62	10^{-27}	kg
neutron	m_n	1.674 93	10^{-27}	kg
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	8.854 19	10^{-12}	J^{-1} C^{2} m^{-1}
	$4\pi\varepsilon_0$	1.112 65	10^{-10}	J^{-1} C^{2} m^{-1}
Vacuum permeability	μ_0	4π	10^{-7}	J s^{2} C^{-2} m^{-1} (= T^{2} J^{-1} m^{3})
Magneton				
Bohr	$\mu_B = e\hbar/2m_e$	9.274 01	10^{-24}	J T^{-1}
nuclear	$\mu_N = e\hbar/2m_p$	5.050 78	10^{-27}	J T^{-1}
g value	g_e	2.002 32		
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	5.291 77	10^{-11}	m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	7.297 35	10^{-3}	
	α^{-1}	1.370 36	10^{2}	
Second radiation constant	$c_2 = hc/k$	1.438 78	10^{-2}	m K
Stefan–Boltzmann constant	$\sigma = 2\pi^5 k^4/15h^3c^2$	5.670 51	10^{-8}	W m^{-2} K^{-4}
Rydberg constant	$R = m_e e^4/8h^3 c\varepsilon_0^2$	1.097 37	10^{5}	cm^{-1}
Standard acceleration of free fall	g	9.806 65*		m s^{-2}
Gravitational constant	G	6.673	10^{-11}	N m^{2} kg^{-2}

**Exact value*

QUESTION ONE (30 MARKS)

1.a Discuss the principal applications of the following instrumental methods:

i) X-ray diffraction (XRD) [2 marks]

ii) X-ray absorption spectroscopy [1 mark]

iii) Atomic emission spectrometry (AES), Optical emission spectrometry (OES) [1.5marks]

iv) X-ray Fluorescence (XRF) [1 mark]

v) Inorganic mass spectrometry (MS) [1.5 mark]

b i) Write short notes on the photoelectric effect [3 marks]

ii) Calculate the percentage loss of intensity due to the reflection of a perpendicular beam of yellow light as it passes through a glass cell that contains water. Assume that for yellow radiation the refractive index of glass is 1.50, of water is 1.33, and of air is 1.00. [2 marks]

iii) Cesium is used extensively in photocells and in television cameras because it has the lowest ionization energy of all the stable elements.

(a) What is the maximum kinetic energy of a photoelectron ejected from cesium by 520 nm light? Note that if the wavelength of the light used to irradiate the cesium surface becomes longer than 660 nm, no photoelectrons are emitted. [1 mark]

(b) Use the rest mass of the electron to calculate the velocity of the photoelectron in (a). [1 mark]

iv) Why must the slit width of a prism monochromator be varied to provide constant effective bandwidths but a nearly constant slit width provides constant bandwidth with a grating monochromator? [2 marks]

c i) In high-temperature sources, sodium atoms emit a doublet with an average wavelength of 1139 nm. The transition responsible is from the 4*s* to the 3*p* state. Set up a spreadsheet to calculate the ratio of the number of excited atoms in the 4*s* state to the number in the ground 3*s* state over the temperature range from an acetylene-oxygen flame (3000°C) to the hottest part of an inductively coupled plasma source (8750°C). [3.5 marks]

ii) In the concentration range of 500 to 2000 ppm of U, there is a linear relationship between absorbance at 351.5 nm and concentration. At lower concentrations, the relationship is nonlinear unless about 2000 ppm of an alkali metal salt is introduced into the sample. Explain. [2 marks]

iii) An analyst attempts to determine strontium with an atomic absorption instrument equipped with nitrous oxide–acetylene burner, but the sensitivity associated with the 460.7- nm atomic resonance line is not satisfactory. Suggest at least three things that might be tried to increase sensitivity. [1.5marks]

iv) Use the Equation for the resolving power of a grating monochromator to estimate the theoretical minimum size of a diffraction grating that would provide a profile of an atomic absorption line at 500 nm having a line width of 0.002 nm. Assume that the grating is to be used in the first order and that it has been ruled at 2400 grooves/mm. [2 marks]

d i) Describe how the isotope dilution technique is used in atomic mass spectrometry [1.5mark]

ii) Calculate the goniometer setting, in terms of 2u, required to observe the Ka1 lines for Fe (1.76 Å), Se (0.992 Å), and Ag (0.497 Å) and Ag (0.497 Å) when the diffracting crystal is (a) topaz, (b) LiF, and (c) NaCl. [4.5 marks]

QUESTION TWO (20 MARKS)

2 a With the aid of Figures 7-2 and 7-3, suggest instrument components and materials for constructing an instrument that would be well suited for [7 marks]

I) The investigation of the fine structure of absorption bands in the region of 450 to 750 nm.

II) Obtaining absorption spectra in the far IR (20 to 50 μm).

III)A portable device for determining the iron content of natural water based on the absorption of Radiation by the red $Fe(SCN)^{2+}$ complex.

IV) The routine determination of nitrobenzene in air samples based on its absorption peak at 11.8 μm.

V) Determining the wavelengths of flame emission lines for metallic elements in the region from 200 to 780 nm.

VI) Spectroscopic studies in the vacuum UV region.

VII) Spectroscopic studies in the near IR.

b. A simultaneous determination for cobalt and nickel can be based on absorption by their respective 8-hydroxyquinolinol complexes. Molar absorptivities corresponding to their absorption maxima are as follows: [4 marks]

	Molar Absorptivity, ε	
	365 nm	700 nm
Co	3529	428.9
Ni	3228	10.2

Calculate the molar concentration of nickel and cobalt in each of the following solutions using the following data:

	Absorbance, *A* (1.00-cm cells)	
Solution	365 nm	700 nm
(a)	0.349	0.022
(b)	0.792	0.081

c) Palladium (II) forms an intensely colored complex at pH 3.5 with arsenazo III at 660 nm.33 A meteorite was pulverized in a ball mill, and the resulting powder was digested with various strong mineral acids. The resulting solution was evaporated to dryness, dissolved in dilute hydrochloric acid, and separated from interferents by ion-exchange chromatography. The resulting solution containing an unknown amount of Pd (II) was then diluted to 50.00 mL with pH 3.5 buffer. Ten milliliter aliquots of this analyte solution were then transferred to six 50-mL volumetric flasks. A standard solution was then prepared that was 1.0×10^{-5} M in Pd (II). Volumes of the standard solution shown in the table were then pipetted into the volumetric flasks along with 10.00 mL of 0.01 M arsenazo III. Each solution was then diluted to 50.00 mL, and the absorbance of each solution was measured at 660 nm in 1.00 cm cells.

Volume Standard Solution, mL	A_{660}
0.00	0.216
5.00	0.338
10.00	0.471
15.00	0.596
20.00	0.764
25.00	0.850

i) Determine the slope and y-intercept of the line using regression equation

[4 marks]

ii) Determine the standard deviation of the slope and of the intercept [2 marks]

iii) Calculate the concentration of Pd (II) in the analyte solution [1 mark]

iv) Find the standard deviation of the measured concentration [1 mark]

d) Distinguish between pressure broadening and Doppler broadening [1 mark]

QUESTION THREE (20 MARKS)

3 .a i) What is an internal standard and why is it used? [1 mark]

ii) Why do ion lines predominate in spark spectra and atom lines in arc spectra?[1.5marks]

iii) What are the relative advantages and disadvantages of ICP plasmas compared to microwave plasmas? [1.5 marks]

iv) What are some of the advantages of plasma sources compared with flame sources for emission spectrometry? [2 marks]

b. i) What types of mass spectrometers are used in ICPMS? How do they differ from one another? [7 marks]

ii) Why is an internal standard often used in quantitative analysis by ICPMS? [2 marks]

iii) A 5.00-mL sample of blood was treated with trichloroacetic acid to precipitate proteins. After centrifugation, the resulting solution was brought to a pH of 3 and was extracted with two 5-mL portions of methyl isobutyl ketone containing the organic lead complexing agent APCD. The extract was aspirated directly into an air-acetylene flame yielding an absorbance of 0.454 at 283.3 nm. Five milliliter aliquots of standard solutions containing 0.240 and 0.475 ppm Pb were treated in the same way and yielded absorbances of 0.412 and 0.642. Calculate the concentration Pb (ppm) in the sample assuming that Beer’s law is followed. [2.5 marks]

iv In a hydrogen-oxygen flame, the atomic absorption signal for iron decreases in the presence of large concentrations of sulfate ion.

a) Suggest an explanation for this observation. [1 mark]

b) Suggest three possible methods for overcoming the potential interference of sulfate in a quantitative determination of iron. [1.5marks]

QUESTION FOUR (20 MARKS)

a) The sodium in a series of cement samples was determined by flame emission spectroscopy. The flame photometer was calibrated with a series of NaCl standards that contained sodium equivalent to 0, 20.0, 40.0, 60.0, and 80.0 µg Na_2O per mL. The instrument readings *R* for these solutions were 3.1, 21.5, 40.9, 57.1, and 77.3.

   i. Obtain a least-squares equation for the data. [3.5 marks]

   ii. Calculate the statistics for the line in (i). [1.5marks]

   iii. The following data were obtained for replicating 1.000-g samples of cement that were dissolved in HCl and diluted to 100.0 mL after neutralization

		Emission Reading		
	Blank	**Sample A**	**Sample B**	**Sample C**
Replicate 1	5.1	28.6	40.7	73.1
Replicate 2	4.8	28.2	41.2	72.1
Replicate 3	4.9	28.9	40.2	Spilled

Calculate the percentage of Na_2O in each sample and also determine the absolute and relative standard deviations for the average of each determination. [4.5 marks]

b) Discuss quantitative instrument performance criteria that can be used to decide whether a given instrumental method is suitable for attacking an analytical problem. [3 marks]

c) Write short notes on the application of the following in Atomic Emission spectroscopy.

   1. Arc and spark emission [1.5 marks]
   2. plasma sources [2 marks]

d) The drug tolbutamine (fw=270) has a molar absorptivity of 703 at 262nm. One tablet is dissolved in water and diluted to a volume of 2L. If the solution exhibits an absorbance in the UV region at 262nm equal to 0.687 in a 1-cm cell, determine the amount of tolbutamine contained in the tablet. [2 marks]

e) Amines (weak base) form salts with picric acid (trinitrophenol), and all amine picrates exhibit an absorption maximum at 359nm with a molar absorptivity of 1.25×10^4. A 0.200g sample of aniline, $C_6H_5NH_2$, is dissolved in 500 mL of water. A 25.0 mL aliquot is reacted with picric acid in a 250 mL, volumetric flask and diluted to volume. A 10.0 mL, aliquot of this is diluted to 100mL and the absorbance read at 359nm in a 1-cm. If the absorbance is 0.425, determine the percent purity of the aniline. [2 marks]

Figures 7.2 and 7.3

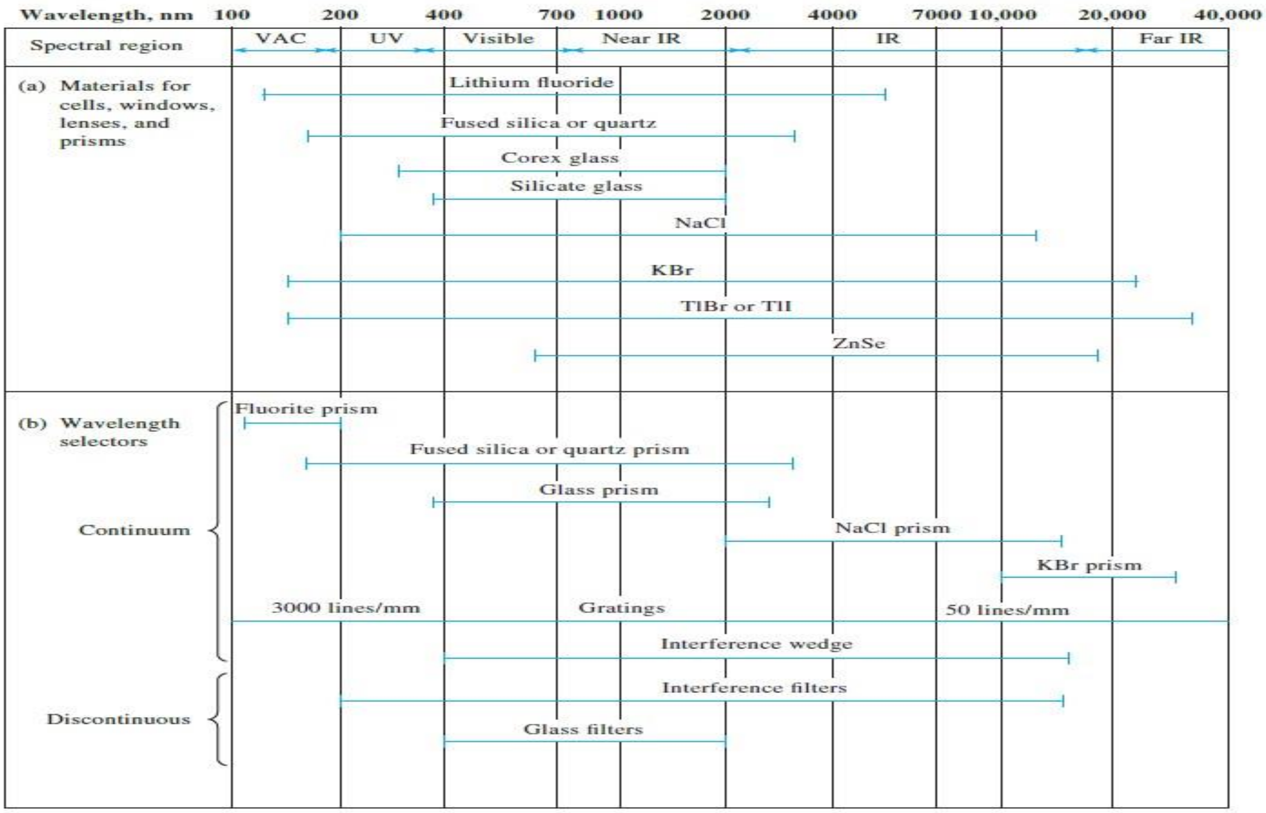


FIGURE 7-2 (a) Construction materials and (b) wavelength selectors for spectroscopic instruments.

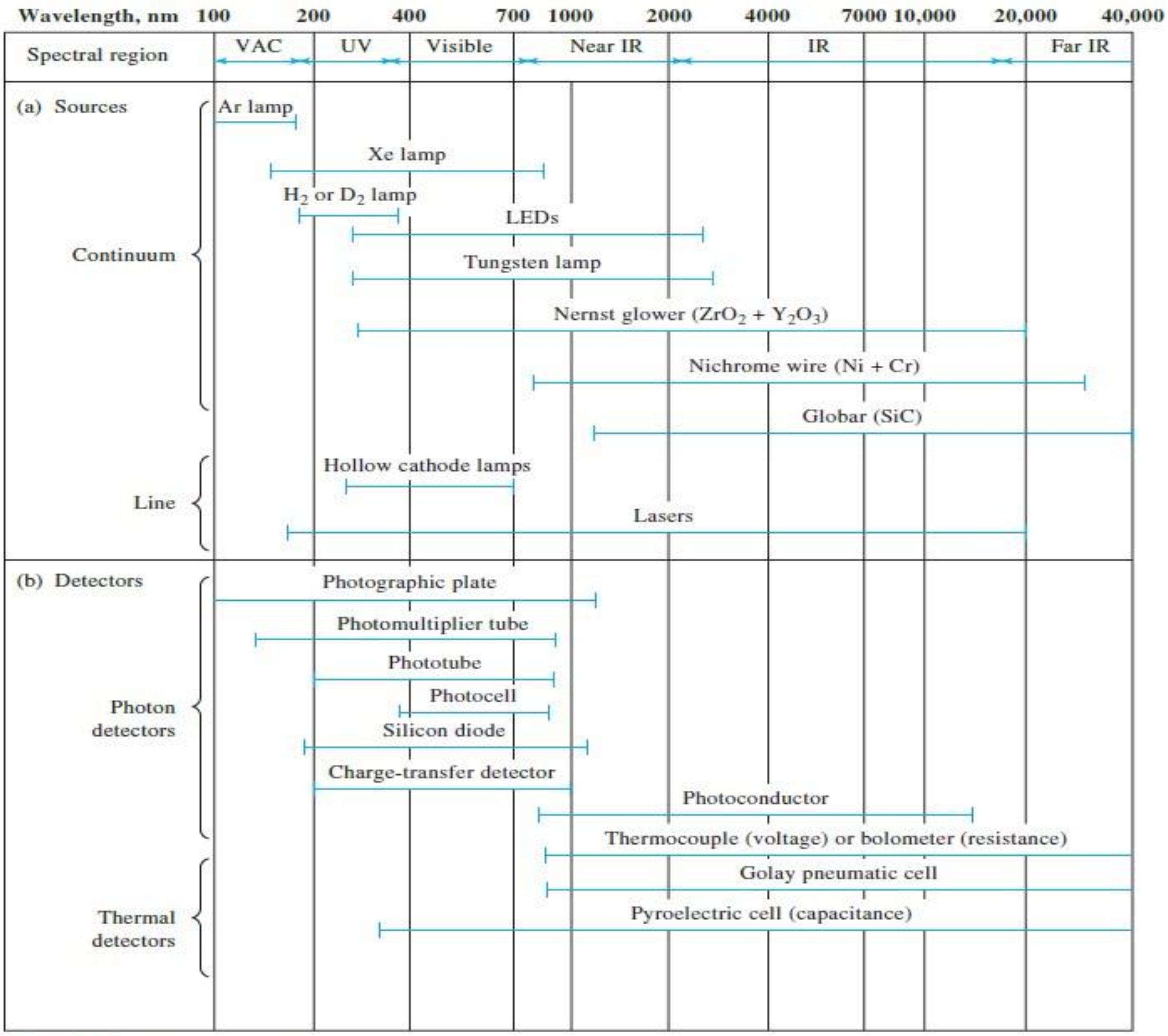


FIGURE 7-3 (a) Sources and (b) detectors for spectroscopic instruments.

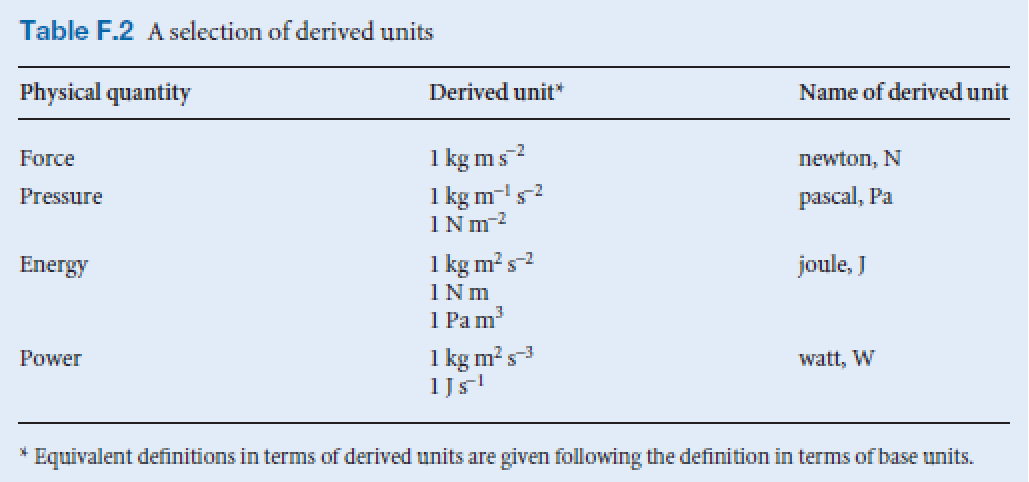


Table F.2 A selection of derived units

Physical quantity	Derived unit*	Name of derived unit
Force	1 kg m s^{-2}	newton, N
Pressure	1 kg m^{-1} s^{-2} 1 N m^{-2}	pascal, Pa
Energy	1 kg m^2 s^{-2} 1 N m 1 Pa m^3	joule, J
Power	1 kg m^2 s^{-3} 1 J s^{-1}	watt, W

* Equivalent definitions in terms of derived units are given following the definition in terms of base units.

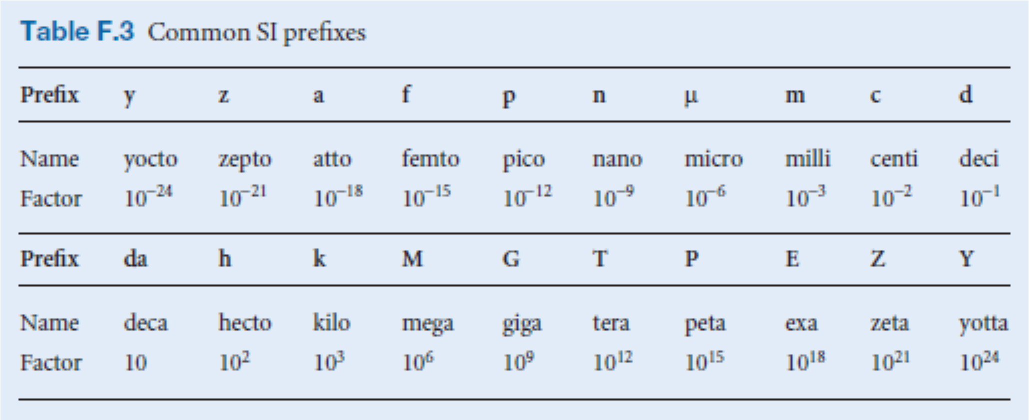
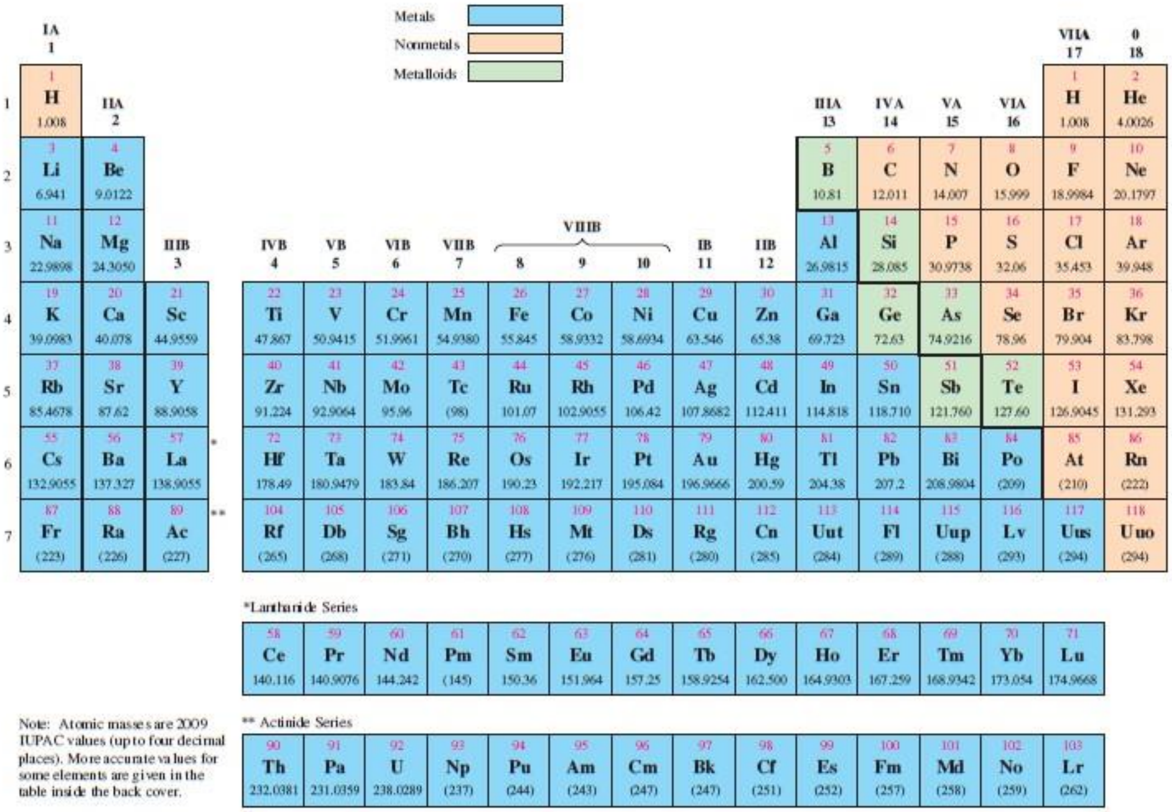


Table F.3 Common SI prefixes

Prefix	y	z	a	f	p	n	μ	m	c	d
Name	yocto	zepto	atto	femto	pico	nano	micro	milli	centi	deci
Factor	10^{-24}	10^{-21}	10^{-18}	10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}

Prefix	da	h	k	M	G	T	P	E	Z	Y
Name	deca	hecto	kilo	mega	giga	tera	peta	exa	zeta	yotta
Factor	10	10^2	10^3	10^6	10^9	10^{12}	10^{15}	10^{18}	10^{21}	10^{24}

PERIODIC TABLE OF THE ELEMENTS



Metals	🟦
Nonmetals	🟧
Metalloids	🟩

	IA 1	IIA 2	IIIB 3	IVB 4	VB 5	VIB 6	VIIB 7	VIIIB 8	9	10	IB 11	IIB 12	IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	0 18
1	1 **H** 1.008																1 **H** 1.008	2 **He** 4.0026
2	3 **Li** 6.941	4 **Be** 9.0122											5 **B** 10.81	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.9984	10 **Ne** 20.1797
3	11 **Na** 22.9898	12 **Mg** 24.3050											13 **Al** 26.9815	14 **Si** 28.085	15 **P** 30.9738	16 **S** 32.06	17 **Cl** 35.453	18 **Ar** 39.948
4	19 **K** 39.0983	20 **Ca** 40.078	21 **Sc** 44.9559	22 **Ti** 47.867	23 **V** 50.9415	24 **Cr** 51.9961	25 **Mn** 54.9380	26 **Fe** 55.845	27 **Co** 58.9332	28 **Ni** 58.6934	29 **Cu** 63.546	30 **Zn** 65.38	31 **Ga** 69.723	32 **Ge** 72.63	33 **As** 74.9216	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.798
5	37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.9058	40 **Zr** 91.224	41 **Nb** 92.9064	42 **Mo** 95.96	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.9055	46 **Pd** 106.42	47 **Ag** 107.8682	48 **Cd** 112.411	49 **In** 114.818	50 **Sn** 118.710	51 **Sb** 121.760	52 **Te** 127.60	53 **I** 126.9045	54 **Xe** 131.293
6	55 **Cs** 132.9055	56 **Ba** 137.327	57 **La** 138.9055 *	72 **Hf** 178.49	73 **Ta** 180.9479	74 **W** 183.84	75 **Re** 186.207	76 **Os** 190.23	77 **Ir** 192.217	78 **Pt** 195.084	79 **Au** 196.9666	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.9804	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
7	87 **Fr** (223)	88 **Ra** (226)	89 **Ac** (227) **	104 **Rf** (265)	105 **Db** (268)	106 **Sg** (271)	107 **Bh** (270)	108 **Hs** (277)	109 **Mt** (276)	110 **Ds** (281)	111 **Rg** (280)	112 **Cn** (285)	113 **Uut** (284)	114 **Fl** (289)	115 **Uup** (288)	116 **Lv** (293)	117 **Uus** (294)	118 **Uuo** (294)

*Lanthanide Series

58 **Ce** 140.116	59 **Pr** 140.9076	60 **Nd** 144.242	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.964	64 **Gd** 157.25	65 **Tb** 158.9254	66 **Dy** 162.500	67 **Ho** 164.9303	68 **Er** 167.259	69 **Tm** 168.9342	70 **Yb** 173.054	71 **Lu** 174.9668

Note: Atomic masses are 2009 IUPAC values (up to four decimal places). More accurate values for some elements are given in the table inside the back cover.

** Actinide Series

90 **Th** 232.0381	91 **Pa** 231.0359	92 **U** 238.0289	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)