UNIVERSITI TEKNOLOGI PETRONAS

FINAL EXAMINATION
MAY 2024 SEMESTER

COURSE	:	**YBB1053 - ANALYTICAL INSTRUMENTATION**
DATE	:	**1 AUGUST 2024 (THURSDAY)**
TIME	:	**9:00 AM - 12:00 NOON (3 HOURS)**

INSTRUCTIONS TO CANDIDATES

1. Answer **ALL** questions in the Answer Booklet.
2. Begin **EACH** answer on a new page in the Answer Booklet.
3. Indicate clearly answers that are cancelled, if any.
4. Where applicable, show clearly steps taken in arriving at the solutions and indicate **ALL** assumptions, if any.
5. **DO NOT** open this Question Booklet until instructed.

Note :

i. There are **SEVENTEEN (17)** pages in this Question Booklet including the cover page and Appendices.

ii. **DOUBLE-SIDED** Question Booklet.

iii. Graph paper(s) will be provided

1. a. In spectroscopy, the measurement of spectra depends intimately on both the spectral properties of the sample and the instruments used to make the measurement.

   i. Using electronic energy diagram(s), explain **TWO (2)** modes of measurement in atomic spectroscopy.

   [6 marks]

   ii. List **THREE (3)** analytical instruments in spectroscopy commonly used for quantitative analysis.

   [3 marks]

b. The drug tolbutamide (molecular weight = 270 g mol^{-1}) has a molar absorptivity of 703 M^{-1} cm^{-1} at a lambda maxima (λ_{max}) of 262 nm when a standard cuvette with a path length of 10 mm is used. One tablet of tolbutamide is dissolved in water and diluted to a volume of 3.0 L. If this solution exhibits an absorbance of 0.687 at λ_{max} of 262 nm using the same standard cuvette, calculate the amount of drug tolbutamide (in grams) in the tablet.

[5 marks]

c. Beer's law is an equation that relates the attenuation of light to the properties of a material. This law states that the concentration of a chemical is directly proportional to the absorbance of a solution. Describe **THREE (3)** limitations of Beer's law.

[6 marks]

2. a. Atomic spectroscopy is a technique commonly used to quantize a sample by studying the electromagnetic radiation (EMR) absorbed or emitted by its atoms. This method exploits the fact that each element has a unique set of energy levels, and when atoms transition between these levels, they absorb or emit light at specific wavelengths.

i. Draw a block diagram to illustrate the correct configuration of the basic components of an instrument based on the absorption of EMR by atoms. Identify each basic component.

[5 marks]

ii. Based on your answer in **part (a)(i)**, describe the major difference in the basic components compared to an instrument based on the emission of EMR by atoms

[5 marks]

iii. Microwave plasma (MP) and inductively coupled plasma (ICP) are two common types of plasma used in atomic emission spectroscopy (AES). Rationalize **TWO (2)** advantages of MP over ICP.

[4 marks]

b. Atomization in atomic spectroscopic instruments refers to the process of converting a liquid sample into free atomic gases. Explain how a liquid sample is transformed into free atomic gases in microwave plasma atomic emission spectroscopy (MP-AES). In your explanation, include the roles of the nebulizer, spray chamber, and plasma torch.

[6 marks]

3. a. The external standard solutions of zinc phthalocyanine (ZnPc) were prepared and analysed using ultraviolet-visible (UV-Vis) spectroscopy. The concentration and UV-Vis spectra for the external standard solutions of ZnPc are shown in **TABLE Q3** and **FIGURE Q3**, respectively. ZnPc was dissolved in water and diluted to a volume of 1.50 L. This solution exhibited UV-Vis absorbance of 0.786 at lambda maxima (λ_{max}). The molecular weight of ZnPc is 577.10 g mol^{-1}.

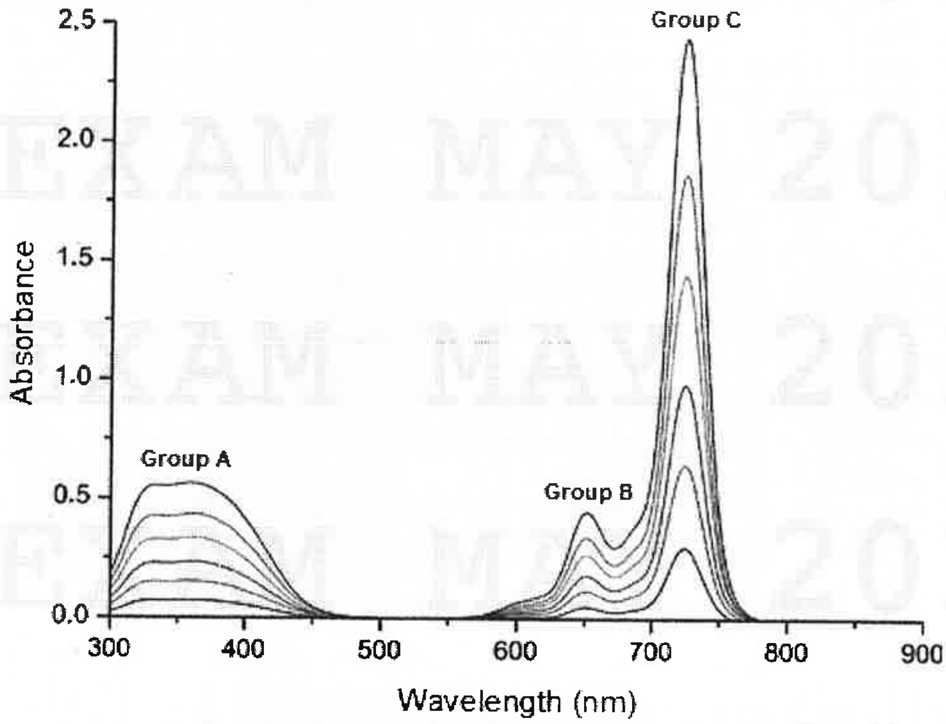


FIGURE Q3: UV-Vis spectra for standard solutions of ZnPc.

TABLE Q3: Absorbance intensity for standard solutions of ZnPc.

Concentration of standard solution (ppm)	Absorbance intensity		
	Group A	Group B	Group C
5.0	0.089	0.075	0.295
10.0	0.191	0.182	0.352
50.0	0.210	0.285	0.925
100.0	0.455	0.399	1.650
150.0	0.510	0.489	2.425

i. There are three groups of peaks in **FIGURE Q3**: group A, group B and group C. Among these groups, suggest which group best corresponds to λ_{max} and justify your answer.

[3 marks]

ii. Based on your answers in **part (a)(i)** and the data in **TABLE Q3**, construct the calibration curve.

[6 marks]

iii. Based on your answers in **part (a)(ii)**, deduce a linear regression equation for the calibration curve and identify all the components in the linear regression equation.

[3 marks]

iv. Using the deduced linear regression equation from **part (a)(iii)**, determine the concentration of ZnPc in molarity.
Note: 1 ppm = 0.001g L^{-1}

[4 marks]

b. Describe **TWO (2)** requirements for a molecular sample to be Fourier-transform infrared spectroscopy (FTIR) active.

[4 marks]

4. a. Sample X, with molecular formula of $C_6H_{14}O$, was analysed using Fourier-transform infrared (FTIR) spectroscopy. The FTIR spectrum of sample X is shown in **FIGURE Q4(a)(i).**

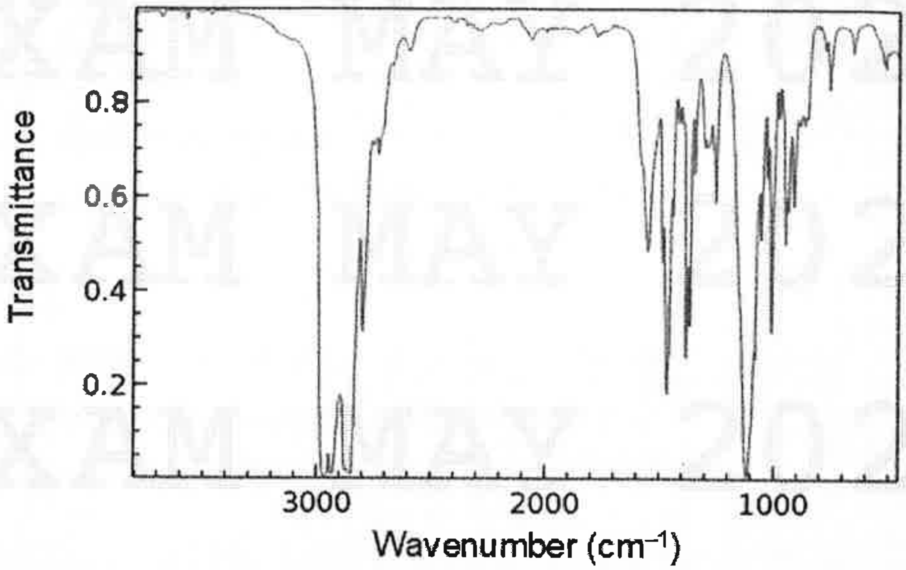
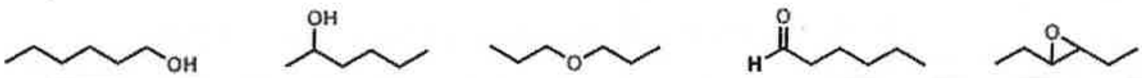


FIGURE Q4(a)(i): FTIR spectrum of $C_6H_{14}O$

Given the compounds in **FIGURE Q4(a)(ii)**, identify **ONE (1)** compound that best corresponds to sample X. Explain your answer (Hint: consider the molecular formula of the given compounds).



Compound I　Compound II　Compound III　Compound IV　Compound V

FIGURE Q4(a)(ii): Compounds I, II, III, IV and V

[5 marks]

b. Nuclear magnetic resonance (NMR) spectroscopy is a widely used and powerful method that exploits the magnetic properties of certain nuclei, such as ^{1}H and ^{13}C. Its most widespread application is in the structural determination of molecules, especially organic compounds.

i. Describe the principles for a sample to be NMR active.

[5 marks]

ii. Using the relevant equation, propose a definition for the chemical shift (δ), which is the frequency of a signal in the NMR spectrum.

[3 marks]

c. **FIGURE Q4(c)** shows the proton nuclear magnetic resonance (^{1}H-NMR) spectrum of iodoethane (CH_3CH_2I).

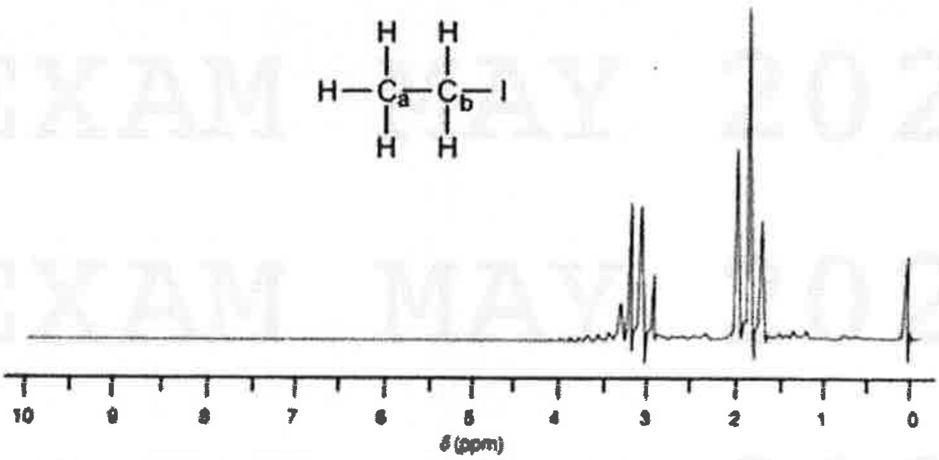


FIGURE Q4(c): ^{1}H-NMR spectrum of CH_3CH_2I

i. Identify protons that are most shielded. Justify your answers.

[3 marks]

ii. Assign the protons to sets of peaks in **FIGURE Q4(c)** based on peak splitting. Provide the rationale for your assignments.

[4 marks]

5. a. Gas chromatography (GC) is a technique used in analytical chemistry to separate and analyze compounds that can be vaporized without decomposition. It is commonly used to determine the composition of a sample and the amount of each component present. One common type of GC used to analyze organic compounds is gas chromatography with a flame ionization detector (GC-FID).

i. Draw the block diagram of GC-FID instrument. Identify all the basic components.

[5 marks]

ii. Provide **TWO (2)** rationales for in using a flame ionization detector (FID) in GC to analyze organic compounds.

[4 marks]

iii. State **TWO (2)** advantages of GC-FID compared to high-performance liquid chromatography (HPLC).

[2 marks]

b. Sketch a typical differential scanning calorimetry (DSC) thermogram and label the followings: melting temperature (T_m) glass transition temperature (T_g), crystallization temperature (T_c).

[4 marks]

c. Consider the following cell without liquid junction.

$$Zn \mid ZnSO_4\ (5.00 \times 10^{-4}\ M),\ PbSO_4(sat'd) \mid Pb$$

The half-reactions and standard electrode potentials are as follows.

$$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq) \qquad E^o_{PbSO_4/Pb} = -0.350\ V$$

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^o_{Zn^{2+}/Zn} = -0.763\ V$$

i. Calculate the ionic strength (μ) of $ZnSO_4$ solution.

[2 marks]

ii. The activity coefficients of Zn^{2+} ($\gamma_{Zn^{2+}}$) and SO_4^{2-} ($\gamma_{SO_4^{2-}}$) are found to be 0.820 and 0.825, respectively. Determine the electrode potentials for Pb electrode ($E_{PbSO_4/Pb}$) and zinc electrode ($E_{Zn^{2+}/Zn}$) by considering the activities.

[3 marks]

- END OF PAPER-

APPENDIX I

List of Atomic Masses

Elements	Symbol	Atomic No.	Atomic Mass	Elements	Symbol	Atomic No.	Atomic Mass
Actinium	Ac	89	[227]	Mercury	Hg	80	200.59
Aluminium	Al	13	26.98	Molybdenum	Mo	42	95.94
Americium	Am	95	[243]	Neodymium	Nd	60	144.24
Antimony	Sb	51	121.76	Neon	Ne	10	20.18
Argon	Ar	18	39.95	Nickel	Ni	28	58.69
Arsenic	As	33	74.92	Niobium	Nb	41	92.91
Astatine	At	85	[210]	Nitrogen	N	7	14.01
Barium	Ba	56	137.33	Osmium	Os	76	190.23
Berkelium	Bk	97	[247]	Oxygen	O	8	15.99
Beryllium	Be	4	9.01	Palladium	Pd	46	106.42
Bismuth	Bi	83	208.98	Phosphorus	P	15	30.97
Bohrium	Bh	107	[264]	Platinum	Pt	78	195.08
Boron	B	5	10.81	Plutonium	Pu	94	[244]
Bromine	Br	35	79.90	Polonium	Po	84	[209]
Cadmium	Cd	48	112.41	Potassium	K	19	39.10
Caesium	Cs	55	132.90	Radium	Ra	88	[226]
Calcium	Ca	20	40.08	Radon	Rn	86	[222]
Californium	Cf	98	[251]	Rhenium	Re	75	186.21
Carbon	C	6	12.01	Rhodium	Rh	45	102.90
Cerium	Ce	58	140.12	Rubidium	Rb	37	85.47
Chlorine	Cl	17	35.45	Ruthenium	Ru	44	101.07
Chromium	Cr	24	51.99	Samarium	Sm	62	150.36
Cobalt	Co	27	58.93	Scandium	Sc	21	44.96
Copper	Cu	29	63.55	Selenium	Se	34	78.96
Fluorine	F	9	18.99	Silicon	Si	14	28.09
Gadolinium	Gd	64	157.25	Silver	Ag	47	107.87
Gallium	Ga	31	69.72	Sodium	Na	11	22.99
Germanium	Ge	32	72.64	Strontium	Sr	38	87.62
Gold	Au	79	196.97	Sulfur	S	16	32.06
Hafnium	Hf	72	178.49	Tellurium	Te	52	127.60
Helium	He	2	4.00	Terbium	Tb	65	158.92
Holmium	Ho	67	164.93	Thallium	Tl	81	204.38
Hydrogen	H	1	1.01	Thorium	Th	90	232.04
Indium	In	49	114.82	Thulium	Tm	69	168.93
Iodine	I	53	126.90	Tin	Sn	50	118.71
Iridium	Ir	77	192.22	Titanium	Ti	22	47.87
Iron	Fe	26	55.84	Tungsten	W	74	183.84
Krypton	Kr	36	83.80	Uranium	U	92	238.03
Lanthanum	La	57	138.91	Vanadium	V	23	50.94
Lead	Pb	82	207.2	Xenon	Xe	54	131.29
Lithium	Li	3	[6.94]	Ytterbium	Yb	70	173.04
Lutetium	Lu	71	174.97	Yttrium	Y	39	88.91
Magnesium	Mg	12	24.31	Zinc	Zn	30	65.41
Manganese	Mn	25	54.94	Zirconium	Zr	40	91.22

APPENDIX II

IR Absorptions of Common Functional Groups

Functional Group	*Absorption Location (cm^{-1})*	*Absorption Intensity*
Alkane (C–H)	2,850–2,975	Medium to strong
Alcohol (O–H)	3,400–3,700	Strong, broad
Alkene (C=C) (C=C–H)	1,640–1,680 3,020–3,100	Weak to medium Medium
Alkyne (C≡C) (C≡C–H)	 2,100–2,250 3,300	 Medium Strong
Nitrile (C≡N)	2,200–2,250	Medium
Aromatics	1,650–2,000	Weak
Amines (N–H)	3,300–3,350	Medium
Carbonyls (C=O) Aldehyde (CHO) Ketone (RCOR) Ester (RCOOR) Acid (RCOOH)	1,720–1,740 1,720–1,740 1,715 1,735–1,750 1,700–1,725	Strong

APPENDIX III

Physical Constants

Atomic mass unit	1 amu	= 1.661×10^{-27} kg
	1 g	= 6.022×10^{23} amu
Avogadro's number	N	= 6.022×10^{23} / mol
Boltzmann's constant	k	= 1.381×10^{-23} J/K
Electron charge	e	= 1.602×10^{-19} C
Faraday's constant	F	= N_e = 9.649×10^{4} C/mol
Gas constant	R	= N_k = 8.314 J/mol.K
		= 0.08206 L-atm/mol.K
Mass of electron	m_e	= 5.486×10^{-4} amu
		= 9.110×10^{-28} g
Mass of neutron	m_n	= 1.009 amu
		= 1.675×10^{-24} g
Mass of proton	m_p	= 1.007 amu
		= 1.673×10^{-24} g
Pi	π	= 3.142
Planck's constant	h	= 6.626×10^{-34} J.s
Speed of light	c	= 2.998×10^{8} m/s
Rydberg constant	R_H	= 1.097×10^{7} m^{-1}
		= 2.179×10^{-18} J

APPENDIX IV

Conversion Factors

Length
SI unit: meter (m)

1 km = 0.62137 mi

1 mi = 5280 ft

= 1.6093 km

1 m = 1.0936 yd

1 in. = 2.54 cm (exactly)

1 cm = 0.39370 in.

Mass

SI unit: kilogram (kg)

1 kg = 2.2046 lb

1 lb = 453.59 g

= 16 oz

= 0.0005 ton

1 amu = 1.66054×10^{-24} g

Temperature
SI unit: Kelvin (K)

0 K = -273.15^0C

= -459.67^0F

Energy (derived)

SI unit: Joule (J)

1 J = 1kg-m^2/s^2

1 J = 0.23901 cal

= 1C X 1V

1 cal = 4.184 J

1 eV = 1.602×10^{-19} J

Pressure (derived)
SI unit: Pascal (Pa)

1 Pa = 1 N/m^2

= 1 kg/m-s^2

1 atm = 101325 Pa

= 760 torr

= 14.70 lb/in^2

1 bar = 10^5 Pa

Volume (derived)

SI unit: cubic meter (m^3)

1 L = 10^{-3} m^3

= 1 dm^3

= 10^3 cm^3

= 1.0567 qt

1 gal = 4 qt

= 3.7854 L

1 cm^3 = 1 mL
1 in^3 = 16.4 cm^3

APPENDIX V

Formulas

Debye-Hückel equation:

$$-\log \gamma_X = \frac{0.5 Z_X^2 \sqrt{\mu}}{1 + 3.3 \alpha_X \sqrt{\mu}}$$

Z_X = charge on species X
μ = ionic strength of the solution
α_X = effective diameter of hydrated ion X in nm (10^{-9}m)

Molecular wavenumber or approximate wavenumber

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

$\bar{\nu}$ = Molecular wavenumber
K = Force constant
μ = Reduced mass
C = Speed of light
π = Pi constant

APPENDIX VI

Standard Reduction Potential at 25°C

Reduction Half–Reaction	Standard Potential, $E^o(V)$
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O(l)$	2.08
$S_2O_8^{2-}(aq) + 2e^- \longrightarrow 2SO_4^{2-}(aq)$	2.01
$Ag^{2+}(aq) + e^- \longrightarrow Ag^+(aq)$	1.98
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	1.81
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O(l)$	1.78
$MnO_4^-(aq) + 4H^+(aq) + 3e^- \longrightarrow MnO_2(s) + 2H_2O(l)$	1.68
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	1.52
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51
$2BrO_3^-(aq) + 12H^+(aq) + 10e^- \longrightarrow Br_2(l) + 6H_2O(l)$	1.48
$PbO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Pb^{2+}(aq) + 2H_2O(l)$	1.46
$ClO_3^-(aq) + 6H^+(aq) + 6e^- \longrightarrow Cl^-(aq) + 3H_2O(l)$	1.45
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	1.44
$Au^{3+}(aq) + 2e^- \longrightarrow Au^+(aq)$	1.36
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l)$	1.22
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	1.23
$2IO_3^-(aq) + 12H^+(aq) + 10e^- \longrightarrow I_2(s) + 6H_2O(l)$	1.20
$NO_2(g) + H^+(aq) + e^- \longrightarrow HNO_2(aq)$	1.07
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	1.07
$NO_2(g) + 2H^+(aq) + 2e^- \longrightarrow NO(g) + H_2O(l)$	1.03
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$	0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	0.90
$Cu^{2+}(aq) + I^-(aq) + e^- \longrightarrow CuI(s)$	0.86
$Hg^{2+}(aq) + 2e^- \longrightarrow Hg(l)$	0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	0.80
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O_2(aq)$	0.70
$2HgCl_2(s) + 2e^- \longrightarrow Hg_2Cl_2(s) + 2Cl^-(aq)$	0.63
$MnO_4^-(aq) + e^- \longrightarrow MnO_4^{2-}(aq)$	0.56
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	0.54
$Cu^+(aq) + e^- \longrightarrow Cu(s)$	0.52
$H_2SO_3(aq) + 4H^+(aq) + 4e^- \longrightarrow S(s) + 3H_2O(l)$	0.45
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	0.34
$2HgCl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-(aq)$	0.27
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O(l)$	0.17
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	0.15
$S(s) + 2H^+(aq) + 2e^- \longrightarrow H_2S(g)$	0.14
$AgBr(s) + e^- \longrightarrow Ag(s) + Br^-(aq)$	0.07
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Fe^{3+}(aq) + 3e^- \longrightarrow Fe(s)$	–0.04

APPENDIX VI (CONT.)

Standard Reduction Potential at 25°C

Reduction Half–Reaction	Standard Potential, E°(V)
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	–0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	–0.14
$AgI(s) + e^- \longrightarrow Ag(s) + I^-(aq)$	–0.15
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	–0.26
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	–0.28
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	–0.40
$Cr^{3+}(aq) + e^- \longrightarrow Cr^{2+}(aq)$	–0.42
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	–0.44
$2CO_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2C_2O_4(aq)$	–0.49
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	–0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	–0.76
$Cr^{2+}(aq) + 2e^- \longrightarrow Cr(s)$	–0.90
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	–1.18
$Ti^{2+}(aq) + 2e^- \longrightarrow Ti(s)$	–1.63
$U^{3+}(aq) + 3e^- \longrightarrow U(s)$	–1.66
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	–1.67
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	–2.36
$Na^+(aq) + e^- \longrightarrow Na(s)$	–2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	–2.84
$K^+(aq) + e^- \longrightarrow K(s)$	–2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	–3.04