



UNIVERSITY OF SWAZILAND

FACULTY OF HEALTH SCIENCES

Department of Environmental Health Sciences

Main examination 2014/15

Title : Instrumental methods for environmental analysis

Code : EHM 204

Time : 2 hours

Marks : 100

Instructions:

1. Answer any 4 questions,
2. Each question weighs 25 marks,
3. Start each question on a fresh page,
4. Diagrams and graphs should be large and clearly well labeled,
5. Non-programmable scientific calculators may be used.

Additional material;

- Graph papers (3),
- Periodic table,

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CHIEF INVIGILATOR**

QUESTION 1

It is suspected that soils in the KSSC plantations are high in the non-essential and toxic element Cr (VI). You are working in the analytical laboratory of the company and tasked with determining the amount of the metal in the soil.

- a) List the important factors that you would consider in choosing an appropriate analytical technique for the task. [4]
- b) With respect to sampling:
 - i. Define the term 'sampling'. [2]
 - ii. Name and explain the 3 main types of sampling. [6]
- c) List and explain 3 sample pre-treatment steps required prior to instrumental analysis of the soil samples. [6]
- d) With respect to data quality assurance:
 - i. What does the acronym 'CRM' stand for? [1]
 - ii. Briefly explain how commercial CRMs are determined? [4]
 - iii. List 2 other steps that you can use to ensure that the data generated from your analysis is reliable. [2]

QUESTION 2

Caffeine and aspirin are both found in many commercial analgesic preparations. Both compounds absorb in the UV-vis region and the spectra overlap to some extent. An experiment to determine the concentrations of these compounds in a tablet is performed. Using a 1 cm quartz cuvette, absorbance spectra of these 2 compounds were obtained from standard solutions of 1 mmol/L and 5 mmol/L of caffeine and aspirin, respectively and the UV-vis data are presented in Table 1;

Table 1: UV-vis data for caffeine and aspirin at different wavelengths

Caffeine		Aspirin	
Wavelength (nm)	Absorbance (au)	Wavelength (nm)	Absorbance (au)
150	0.3	150	0.4
200	0.5	200	0.5
250	0.3	250	0.6
300	0.2	300	0.3
350	0.3	350	0.4

- a) Graphically show the relationship between the wavelength and absorbance, hence determine/clearly show the analytical wavelength for each compound. [6]

- b) Convert the absorbance at the analytical wavelength to percentage transmittance, for each compound. [4]

The absorbances of the 2 compounds were then determined using a UV-vis spectrophotometer using a 1 cm quartz cuvette. This was done by preparing standards of known concentrations and running them at the analytical wavelengths determined in (a) above. The results are shown in Table 2 for caffeine and aspirin, respectively;

Table 2: Absorbance values for caffeine at the analytical wavelengths

Concentration of standards(nM)	Absorbances for caffeine (au)		Absorbances for Aspirin (au)	
	$\lambda_{\max} 1$ (nm)	$\lambda_{\max} 2$ (nm)	$\lambda_{\max} 1$ (nm)	$\lambda_{\max} 2$ (nm)
0	0.00	0.00	0.00	0.00
0.05	0.45	0.10	0.30	0.35
0.1	0.90	0.20	0.60	0.70

- c) Assuming Beers law holds for this system, **graphically** determine the extinction coefficients for caffeine and aspirin at both analytical wavelengths. [8]

To determine the total absorbances of the compounds at the analytical wavelengths, the tablet was ground and dissolved in appropriate solvents and then diluted to a 200 cm³ volumetric flask. An aliquot of 10 cm³ was then transferred into a 1000 cm³ volumetric flask and diluted to the mark with distilled water. This was then run using a UV-vis spectrophotometer, and the results are presented in Table 3;

Table 3: Absorbance values for the tablet at the analytical wavelengths.

Compound	Absorbance	
	$\lambda_{\max} 1$ (nm)	$\lambda_{\max} 2$ (nm)
Mixture	1.11	1.03

- d) Determine the concentration (M) of caffeine, [4]

- e) Determine the concentration (M) of aspirin. [3]

QUESTION 3

- a) Define the following terms as applied in analytical chemistry:
- Instrument calibration
 - Sample pre-treatment
 - Standard solution
 - Aliquot
 - Chromophore [5]
- b) Explain the term 'deviations from Beer's law. Using a graphical illustration distinguish between positive and negative deviations from this law. [5]
- c) Give any five (5) assumptions made during the derivation of Beer-Lambert's law. [5]
- d) A 0.11 M copper solution contained in a 1.00 cm cell had a percentage transmittance of 31.4 at 324.7 nm wavelength. Calculate:
- Absorbance of the solution. [2]
 - Molar absorptivity of the solution. [2]
 - The cell path that will give a percentage transmittance of 20.0. [2]
 - The energy of one photon of the radiation at the specified wavelength. [2]
 - The frequency of the copper emission line at 324.7 nm. [2]

QUESTION 4

It is suspected that a mining operation is disposing a toxic metal (lead) into a stream in trace amounts (in the ppb range). You are working in the analytical laboratory of the Department of Water Affairs and tasked with determining the amount of the metal in the water.

- a) **Which** of the following would you prefer to use and **why**?
- Wet chemistry techniques or instrumental techniques. [2]
 - An AAS or an ICP-MS [2]

An atomic absorption spectrophotometric technique was used to determine the concentration of the lead in the water sample. Prepared working standards were determined together with the unknown sample and the results are shown below.

Concentration of standard (mg/L)	Signal output
0.8	0.9
0.6	0.45

0.4	0.22
0.2	0.11
0	0
Water sample	0.34

b) Determine the concentration (mg/L) of the unknown sample using the **graphical method**. [8]

c) For the ICP-OES,

i. Draw a fully labeled schematic diagram of the plasma, clearly indicating the different temperature regions. [5]

ii. Hence explain the processes involved during ignition of the plasma. [8]

QUESTION 5

For the FAAS, a mixture of combustible gases is ignited at temperature ranges from 2100 to 2800 °C.

a) Give an example of a gas mixture that can achieve these temperatures, clearly showing the oxidant and fuel. [2]

b) Explain, using a fully labeled schematic diagram, the working principle of a PMT detector commonly used in FAAS. [9]

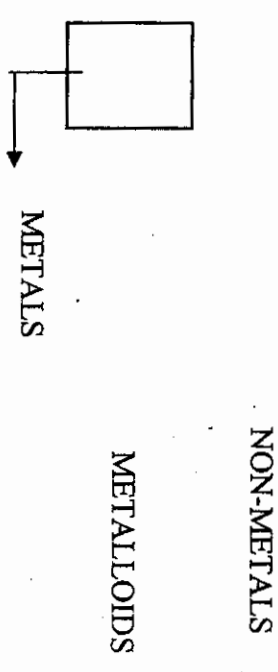
c) **State** the most significant difference between FAAS and ETAAS, hence **explain** the important processes that take place during atomization in ETAAS [7]

The production of ground state gaseous atoms in flame spectroscopy can be largely inhibited by chemical interferences.

d) Define the term 'chemical interferences' [1]

e) List some of the most common chemical interferences and describe how they can be overcome. [6]

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIB	IVB	VB	VIB	VIIIB		VIIIB		IB	IIIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
Period 1	1 H 1.008																	2 He 4.003
2	3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.9	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.01	25 Mn 54.9	26 Fe 55.85	27 Co 58.71	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.7	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.91	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 91.22	42 Mo 95.94	43 Tc 98.9	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	71 Lu 174.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 196.9	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 208.9	84 Po 210	85 At 210	86 Rn 222
7	87 Fr 223	88 Ra 226.0	103 Lr 257	104 Uuq	105 Uup	106 Uuh	107 Uus	108 Uuo	109 Uue									



Lanthanides									
57	58	59	60	61	62	63	64	65	66
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy
138.9	140.1	140.9	144.2	146.9	150.9	151.3	157.3	158.9	162.5
67	68	69	70	71	72	73	74	75	76
Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os
164.9	167.3	168.9	173.0	174.9	178.5	180.9	183.8	186.2	190.2

Actinides	
89	90
Ac	Th
227.0	232.0