

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF SWAZILAND

C304

INSTRUMENTAL ANALYSIS

JULY 2007 SUPPLEMENTARY EXAMINATION

Time Allowed :

Three (3) Hours

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**Instructions:**

1. This examination has six (6) questions and one data sheet. The total number of pages is five (5) including this page.
2. Answer any four (4) questions fully; diagrams should be clear, large and properly labeled. Marks will be deducted for improper units and lack of procedural steps in calculations.
3. Each question is worth 25 marks.

**Special Requirements**

1. Data sheet.

**YOU ARE NOT SUPPOSED TO OPEN THIS PAPER UNTIL PERMISSION TO DO SO HAS BEEN GIVEN BY THE CHIEF INVIGILATOR.**

**QUESTION 1 [25]**

- a) Spectroscopy is an analytical technique based on the interaction between “emr” and atoms/molecules.
- What does the acronym “emr” stand for? [1]
  - Draw and label the different components of an emr wave. [2]
- b) i) Describe the two main practical emr sources in IR. [2]
- ii) Use the chromate/dichromate equilibrium system to illustrate what is known in spectroscopic terms as a “hypsochromic shift”. [2]
- c) Use diagrams to explain what a “double beam” instrument is in IR, and explain its role in this technique [3]
- d) The “monochromator” in a spectrometer is a critical component.
- What role does a “monochromator “ play in a spectrometer? [1]
  - State Snell’s Law of refraction, and use it to explain how a prism acts as a monochromator. [ 3 ]
  - Write down the Bragg equation for diffraction, and explain how a grating acts as a monochromator.[ 3 ]
- e) In spectroscopy, several types of detectors are used.
- Draw and label a vacuum phototube and explain how it works. [ 4 ]
  - Draw and label a photovoltaic cell and explain how it works. [ 4 ]

**QUESTION 2 [25]**

- a. For a spectroscopic band occurring at  $1685\text{cm}^{-1}$ ,
- Convert this wave number to energy in joules [1]
  - state in which region of the electromagnetic spectrum the band falls [1]
  - state the kind of transition taking place [1]
- b. Explain using diagrams, why atomic spectra appears as lines, whereas molecular spectra appear as bands [4]
- c. The cheapest (affordable) uv-visible instruments (typically the *Bosch and Laumb Spectronic 20* series) rely on the use of a “Bunsen” arrangement of the optical components.
- By means of a diagram, explain what is meant by this arrangement. [3]
  - Explain how this arrangement enables light from the source to be split into individual wavelengths. [3]

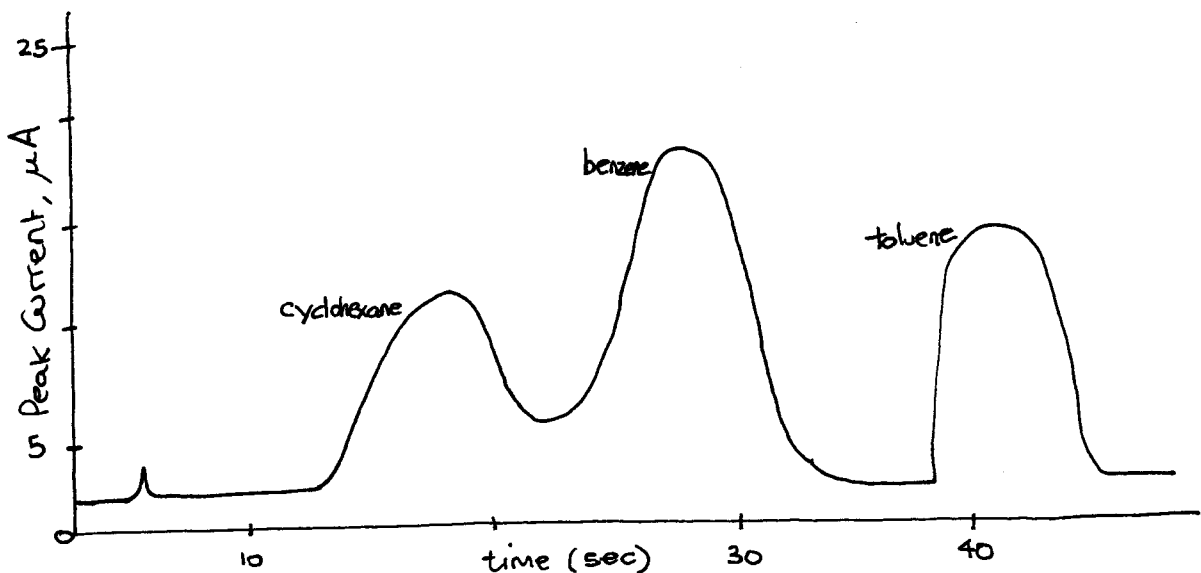
- d. The cheapest (affordable) infrared instruments rely on the use of a “Czerny-Turner” arrangement of the optical components.
- By means of a diagram, explain what is meant by this arrangement. [3]
  - Explain how this arrangement enables light from the source to be split into individual wavelengths. [3]
- e. In the *Jasco* instrument used by researchers at the University of Swaziland for functional group identification of molluscicidal compounds in traditional herbs, a bolometer is used for detection. With the aid of a diagram explain how this detector works. [4]
- f. State two (2) reasons why in the *Jasco* instrument the sample is placed before the monochromator, whereas in the *Spectronic 20* instrument the sample is placed after it. [2]

**QUESTION 3 [25]**

- (a) Atomic Absorption Spectroscopy (AAS) is one of the most versatile analytical techniques available.
- Draw a cross section of an air-acetylene flame and label the main regions that make up the flame. [ 2 ]
  - What chemical processes occur in each region of the flame? [ 3 ]
  - Indicate the region where atomization efficiency is at the maximum. [ 1 ]
- (b) One of the problems associated with AA analysis of several elements is the susceptibility to interferences. Not forgetting to quote specific examples in each of the cases below,
- Describe ionization interference, and explain how it is eliminated in AA. [ 2 ]
  - Describe chemical interference, and explain how it is eliminated in AA. [ 2 ]
  - Describe “matrix effects” and outline one procedure used to combat these effects in AA.[ 2 ]
- a) A major breakthrough in atomic absorption spectrophotometry since the invention of the hollow cathode lamp is graphite furnace AA.
- What is the major structural difference between flame AA and graphite furnace AA? Use diagrams to support your answer. [3]
  - Outline three (3) advantages of graphite furnace AA over flame AA. [3]
- b) Perhaps the most sensitive technique in analytical atomic spectrometry in the 1990’s is the ICP.
- What does the acronym “ICP” stand for? [1]
  - In ICP-OES, solutions are normally introduced by the “Venturi Effect”. Describe this effect. [3]
  - Optics in an ICP are mounted in a “Rowland Circle”. Draw this optical arrangement, and show how it enhances the multielement capability of ICP. [3]

**QUESTION 4 [25]**

- a) A typical GC instrument has several standard components, each of which is listed below. In each case give a brief description of the component, followed by its function.
- Nitrogen Gas Cylinder [2]
  - Filter Cartridge [2]
  - Soap Bubble Flow meter [2]
  - Syringe [2]
  - Oven [2]
- b) One of the applications of GC is the separation of benzene from its mixture with cyclohexane, followed by quantification of the benzene. A typical output from the instrument is shown below:



- In the experiment, explain the role of toluene (explain how it serves this role) [3]
- Calculate the capacity factor of cyclohexane [3]
- Are the cyclohexane and benzene peaks properly resolved? Why or why not? [3]
- Use the benzene peak in the sample chromatogram to calculate  $N$ ; show how this value was obtained. [4]
- Given that the column used was 10m, calculate HETP in mm. [3]

**QUESTION 5 [25]**

- Use diagrams to describe the process of "elution" in chromatography. [3]
- Describe each of the two ways by which elution is performed in Gas Chromatography (GC). [2]
- Sketch the Van Deemter plot for GC, and indicate the region where mobile phase velocity is optimum for analysis. [3]

- d) i) What is meant by Eddy Diffusion in GC? [2]
  - ii) State the HETP equation for Eddy Diffusion in a packed bed [2]
- e) i) What is meant by Longitudinal Diffusion in GC? [2]
  - ii) State the HETP equation for Longitudinal Diffusion in a packed bed [2]
- f) i) What is meant by resistance to mass transfer in the mobile phase in GC? [3]
  - iii) State the HETP equation for resistance to mass transfer in the mobile phase in GC. [3]
  - iv) State the HETP equation for resistance to mass transfer in stationary phase in GC. [3]

### **QUESTION 6**

- a) What is meant by the “race track” effect in chromatography, and how is it eliminated? [2]
- b) Sketch the Van Deemter plot for liquid Chromatography (LC) and explain how it is different from that of GC. [3]
- c) Use equations to describe the process of “silanization” in LC. [3]
- d) A typical LC instrument has several standard components, each of which is listed below. In each case give a brief description of the component, followed by its function.
  - i) Column [3]
  - ii) Sample loop and injector [3]
- e) Describe each of the two ways by which elution is performed in LC. [2]
- f) i) With the aid of a diagram, explain how a thermal conductivity detector works. [3]
  - ii) With the aid of a diagram, explain how a flame ionization detector works. [3]
  - iii) With the aid of a diagram, explain how an electron capture detector works. [3]

1. PERIODIC CHART OF THE ELEMENTS

1A		2A												3A	4A	5A	6A	7A	18
3		4												5	6	7	8	9	10
Li		Be												B	C	N	O	F	Ne
11		12		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Na		Mg		3B	4B	5B	6B	7B	8	9	10	11	12	13	14	15	16	17	18
19		20		21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K		Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37		38		39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb		Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55		56		57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs		Ba		La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87		88		89	104	105	106	107	108	109									
Fr		Ra		Ac	Unq	Unp	Unh	Uns	Uno	Uue									

A value in brackets denotes the mass number of the longest lived or best known isotope.

★ Lanthanide series  
▲ Actinide series

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.12	140.9077	144.24	(145)	150.36	151.96	157.25	158.9254	162.50	164.9304	167.26	168.9342	173.04	174.967
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
231.0361	231.0359	238.0289	237.0482	(244)	(243)	(247)	(247)	(285)	(252)	(257)	(288)	(259)	(260)

4. NET STABILITY CONSTANTS

Ag(CN) <sub>2</sub> <sup>-</sup>	5 × 10 <sup>21</sup>
Ag(NH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	1.6 × 10 <sup>7</sup>
Ag(S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> <sup>-3</sup>	4.7 × 10 <sup>13</sup>
Al(OH) <sub>4</sub> <sup>-</sup>	1.0 × 10 <sup>16</sup>
Ca(EDTA)	1.0 × 10 <sup>10</sup>
Cd(CN) <sub>4</sub>	8.3 × 10 <sup>16</sup>
Cd(NH <sub>3</sub> ) <sub>4</sub> <sup>++</sup>	5.5 × 10 <sup>10</sup>
Co(NH <sub>3</sub> ) <sub>6</sub> <sup>+3</sup>	2 × 10 <sup>10</sup>
Cr(OH) <sub>4</sub> <sup>-</sup>	4 × 10 <sup>10</sup>
Cu(CN) <sub>4</sub> <sup>-3</sup>	1 × 10 <sup>16</sup>
Cu(NH <sub>3</sub> ) <sub>4</sub> <sup>++</sup>	1.2 × 10 <sup>10</sup>
Fe(CN) <sub>6</sub> <sup>-3</sup>	4.0 × 10 <sup>10</sup>
Fe(CN) <sub>6</sub> <sup>-4</sup>	2.5 × 10 <sup>10</sup>
Fe(SCN) <sup>+</sup>	1.0 × 10 <sup>10</sup>
HgCl <sub>4</sub>	1.3 × 10 <sup>10</sup>
Hg(CN) <sub>4</sub>	8.3 × 10 <sup>16</sup>
Hg(SCN) <sub>4</sub>	5.0 × 10 <sup>10</sup>
HgI <sub>4</sub>	6.3 × 10 <sup>10</sup>
Mg(EDTA)	1.3 × 10 <sup>10</sup>
Ni(NH <sub>3</sub> ) <sub>4</sub> <sup>++</sup>	4.7 × 10 <sup>10</sup>
Pb(OH) <sub>3</sub> <sup>-</sup>	7.9 × 10 <sup>10</sup>
Zn(CN) <sub>4</sub>	4.2 × 10 <sup>10</sup>
Zn(NH <sub>3</sub> ) <sub>4</sub> <sup>++</sup>	7.8 × 10 <sup>10</sup>
Zn(OH) <sub>4</sub>	6.3 × 10 <sup>10</sup>

2. IONIZATION CONSTANTS (K<sub>a</sub>) FOR WEAK ACIDS

Acetic	1.9 × 10 <sup>-5</sup>	Hypochlorous	3.7 × 10 <sup>-8</sup>
2-Amino-pyridinium Ion	2 × 10 <sup>-7</sup>	H <sub>2</sub> S	K <sub>1</sub> 9 × 10 <sup>-8</sup> K <sub>2</sub> 1 × 10 <sup>-15</sup>
Ammonium Ion	5.6 × 10 <sup>-10</sup>	Imidazolium Ion	1.1 × 10 <sup>-7</sup>
Anilinium Ion	2.3 × 10 <sup>-5</sup>	Lactic	1.4 × 10 <sup>-4</sup>
Arsenic	K <sub>1</sub> 5.6 × 10 <sup>-3</sup>	Methylammonium Ion	2.7 × 10 <sup>-11</sup>
Benzoic	6.7 × 10 <sup>-5</sup>	Monoethanol-ammonium Ion	3 × 10 <sup>-10</sup>
Boric	K <sub>1</sub> 5 × 10 <sup>-10</sup>	Nicotinium Ion	9.6 × 10 <sup>-9</sup>
Carbonic	K <sub>1</sub> 4.3 × 10 <sup>-7</sup> K <sub>2</sub> 5.6 × 10 <sup>-11</sup>	Oxalic	K <sub>1</sub> 6 × 10 <sup>-2</sup> K <sub>2</sub> 6 × 10 <sup>-5</sup>
Chloroacetic	1.5 × 10 <sup>-3</sup>	Phenol	1.3 × 10 <sup>-10</sup>
Chromic	K <sub>2</sub> 3.2 × 10 <sup>-7</sup>	Phthalic	K <sub>1</sub> 4 × 10 <sup>-6</sup> K <sub>2</sub> 4 × 10 <sup>-8</sup>
Citric	K <sub>1</sub> 8.7 × 10 <sup>-4</sup> K <sub>2</sub> 1.8 × 10 <sup>-5</sup> K <sub>3</sub> 4 × 10 <sup>-6</sup>	Phosphoric	K <sub>1</sub> 7.5 × 10 <sup>-3</sup> K <sub>2</sub> 6.2 × 10 <sup>-8</sup> K <sub>3</sub> 4.7 × 10 <sup>-13</sup>
Dichloroacetic	5 × 10 <sup>-2</sup>	Phosphorous	K <sub>1</sub> 1.0 × 10 <sup>-2</sup> K <sub>2</sub> 2.6 × 10 <sup>-7</sup>
EDTA	K <sub>1</sub> 7 × 10 <sup>-3</sup> K <sub>2</sub> 2 × 10 <sup>-3</sup> K <sub>3</sub> 7 × 10 <sup>-7</sup> K <sub>4</sub> 6 × 10 <sup>-11</sup>	Pyridinium Ion	1 × 10 <sup>-5</sup>
Formic	2 × 10 <sup>-4</sup>	Succinic	K <sub>1</sub> 7 × 10 <sup>-5</sup> K <sub>2</sub> 2.5 × 10 <sup>-6</sup>
α-D(+)-Glucose	5.2 × 10 <sup>-13</sup>	Sulfuric	K <sub>1</sub> 1.2 × 10 <sup>-2</sup> K <sub>2</sub> 2 × 10 <sup>-2</sup>
Glycinium Ion	K <sub>1</sub> 4.6 × 10 <sup>-3</sup> K <sub>2</sub> 2.5 × 10 <sup>-10</sup>	Sulfurous	K <sub>1</sub> 2 × 10 <sup>-2</sup> K <sub>2</sub> 6 × 10 <sup>-8</sup>
Hydrazinium Ion	5.9 × 10 <sup>-9</sup>	Trimethyl-ammonium Ion	1.6 × 10 <sup>-10</sup>
Hydrocyanic	7 × 10 <sup>-10</sup>	Uric	1.3 × 10 <sup>-4</sup>
Hydrofluoric	7 × 10 <sup>-4</sup>	Water, K <sub>w</sub> , 24°C	1.0 × 10 <sup>-14</sup>
Hydroxyl-ammonium Ion	9.1 × 10 <sup>-7</sup>		

3. SOLUBILITY PRODUCT CONSTANTS

AgBr	4 × 10 <sup>-13</sup>	BaC <sub>2</sub> O <sub>4</sub>	2 × 10 <sup>-8</sup>	KClO <sub>4</sub>	2 × 10 <sup>-2</sup>
Ag <sub>2</sub> CO <sub>3</sub>	6 × 10 <sup>-12</sup>	BaSO <sub>4</sub>	1 × 10 <sup>-10</sup>	MgCO <sub>3</sub>	1 × 10 <sup>-5</sup>
AgCl	1 × 10 <sup>-10</sup>	CaCO <sub>3</sub>	5 × 10 <sup>-9</sup>	MgC <sub>2</sub> O <sub>4</sub>	9 × 10 <sup>-5</sup>
Ag <sub>2</sub> CrO <sub>4</sub>	2 × 10 <sup>-12</sup>	CaF <sub>2</sub>	4 × 10 <sup>-11</sup>	MgNH <sub>4</sub> PO <sub>4</sub>	2 × 10 <sup>-13</sup>
Ag[Ag(CN) <sub>2</sub> ] <sub>4</sub>	4 × 10 <sup>-12</sup>	CaC <sub>2</sub> O <sub>4</sub>	2 × 10 <sup>-9</sup>	Mg(OH) <sub>2</sub>	1 × 10 <sup>-11</sup>
AgI	1 × 10 <sup>-16</sup>	CdS	1 × 10 <sup>-28</sup>	MnS	1 × 10 <sup>-15</sup>
Ag <sub>3</sub> PO <sub>4</sub>	1 × 10 <sup>-19</sup>	Cu(OH) <sub>2</sub>	2 × 10 <sup>-20</sup>	PbCrO <sub>4</sub>	2 × 10 <sup>-14</sup>
Ag <sub>2</sub> S	1 × 10 <sup>-50</sup>	CuS	1 × 10 <sup>-36</sup>	PbS	1 × 10 <sup>-28</sup>
AgCNS	1 × 10 <sup>-12</sup>	Fe(OH) <sub>3</sub>	1 × 10 <sup>-36</sup>	PbSO <sub>4</sub>	2 × 10 <sup>-8</sup>
Al(OH) <sub>3</sub>	2 × 10 <sup>-32</sup>	Hg <sub>2</sub> Br <sub>2</sub>	3 × 10 <sup>-23</sup>	SrCrO <sub>4</sub>	4 × 10 <sup>-5</sup>
BaCO <sub>3</sub>	5 × 10 <sup>-9</sup>	Hg <sub>2</sub> Cl <sub>2</sub>	6 × 10 <sup>-19</sup>	Zn(OH) <sub>2</sub>	3.6 × 10 <sup>-16</sup>
BaCrO <sub>4</sub>	1 × 10 <sup>-10</sup>	HgS	1 × 10 <sup>-52</sup>	ZnS	1 × 10 <sup>-24</sup>

5. FIRST IONIZATION ENERGIES, e.v.

1A		2A												14	3A	4A	5A	6A	7A
5.4	9.3											8.3	11	15	14	17			
5.1	7.6	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	6.0	8.1	11	10	13			
4.3	6.1	6.6	6.8	6.7	6.8	7.4	7.9	7.9	7.6	7.7	9.4	6.0	8.1	10	9.8	12			
4.2	5.7	6.6	7.0	6.8	7.2		7.5	7.7	8.3	7.6	9.0	5.8	7.3	8.6	9.0	10			
3.9	5.2	5.0	5.5	6	8.0	7.9	8.7	9.2	9.0	9.2	10	6.1	7.4	8					

6. ELECTRONEGATIVITIES, Pauling

1A		2A												21	3A	4A	5A	6A	7A
1.0	1.5											2.0	2.5	3.0	3.5	4.0			
0.9	1.2	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	1.5	1.8	2.1	2.5	3.0			
0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6	1.8	1.8	2.0	2.4	2.8			
0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5			
0.7	0.9	1.1	1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.8	1.9	2.0	2.2			

7. ATOMIC RADII picometers

1A		2A												37	3A	4A	5A	6A	7A
155	112											143	132	128	127	99			
190	160	3B	4B	5B	6B	7B	8B	9B	10B	11B	12B	143	132	128	127	99			
235	197	162	147	134	130	135	126	125	124	128	138	141	137	139	140	114			
248	215	178	160	146	139	136	134	134	137	144	154	166	162	159	160	133			
287	222	187	167	149	141	137	135	136	139	146	157	171	175	170	176				

8. IONIC RADII pm

Li <sup>+</sup>	60	Sr <sup>+2</sup>	113	S <sup>-2</sup>	184
Na <sup>+</sup>	95	Ba <sup>+2</sup>	135	Se <sup>-2</sup>	198
K <sup>+</sup>	133	B <sup>+3</sup>	20	Te <sup>-2</sup>	221
Rb <sup>+</sup>	148	Al <sup>+3</sup>	50	F <sup>-</sup>	136
Be <sup>+2</sup>	31	N <sup>+3</sup>	171	Cl <sup>-</sup>	181
Mg <sup>+2</sup>	65	P <sup>+3</sup>	212	Br <sup>-</sup>	195
Ca <sup>+2</sup>	99	O <sup>-2</sup>	140	I <sup>-</sup>	216

9. LATTICE ENERGIES

(All negative) kJ/n

F	Cl	Br	
Li	1030	840	781
Na	914	770	728
K	812	701	671
Rb	780	682	654
Cs	744	630	613

10. HALF LIVES

H <sup>3</sup>	12.3 years	K <sup>40</sup>	1.28 × 10 <sup>8</sup> y	I <sup>131</sup>	8.1 day
F <sup>20</sup>	11.4 secs	Ca <sup>45</sup>	165 days	Cs <sup>137</sup>	30 yea
C <sup>14</sup>	5730 years	Fe <sup>59</sup>	45 days	Au <sup>198</sup>	2.69 da
Na <sup>24</sup>	15.0 hours	Co <sup>60</sup>	5.26 y	Ra <sup>226</sup>	1620 y
P <sup>32</sup>	14.3 days	Br <sup>82</sup>	35.5 hours	U <sup>235</sup>	7.1 × 10 <sup>8</sup>
S <sup>35</sup>	88 days	Sr <sup>90</sup>	28 years	U <sup>238</sup>	4.51 × 10 <sup>9</sup>
Cl <sup>36</sup>	3.1 × 10 <sup>5</sup> y	I <sup>129</sup>	1.7 × 10 <sup>7</sup> y	Pu <sup>239</sup>	24,400

