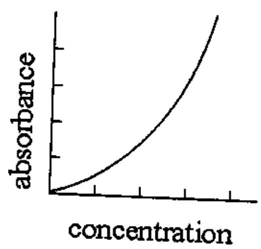
科目：分析化學(2005)　　校系所組：中央大學化學學系　交通大學應用化學系　清華大學化學系

一、選擇題 (30%，單選，每題5分，答錯不倒扣分數)

1. Which is not true about the description of Solid-Phase Microextraction (SPME)?
   (A) It is generally used to analyze samples in solid-phase.
   (B) The apparatus for SPME is commercially available.
   (C) It is quick, highly sensitive, and solvent- free technique.
   (D) It integrates sampling, extraction, concentration, and sample introduction into simple steps.
   (E) Analytes on the fiber coating can be thermally desorbed and quantitatively analyzed by gas chromatography.

2. In order to analyze the trace metals content in a solid sample, the solid sample is decomposed and dissolved into liquid phase through open system wet decomposition method. Which is not true about the main source of error of this method?
   (A) contamination caused by reagents and container material
   (B) losses of elements caused by the formation of precipitate
   (C) losses of elements caused by absorption on the surface of the vessel
   (D) losses of elements caused by reaction with the vessel material
   (E) losses of elements by volatilization

3. An upward-curving calibration (shown in the figure) was found when setting the calibration curve for europium determination by atomic absorption spectrometry. The reason for the depart from linearity of the calibration curve is most probably caused by something related to :



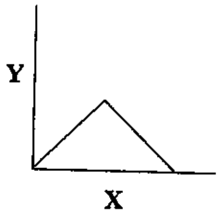
   (A) The calibration curve does not follow Beer's Law at high concentration.
   (B) Spectra interference
   (C) Ionization interference
   (D) Physical interference
   (E) Chemical interference

4. The sample volume of $Al_2(SO_4)_3$, $ZuSO_4$ and Na_2SO_4 solutions are reacted separately with excess $BaCl_2$ solution. If the mole ratio of the $BaSO_4$ precipitate formed is 1:2:3, the mole ratio of the sulfate in these three solutions should be:
   (A) 1: 2: 3
   (B) 1: 6: 9

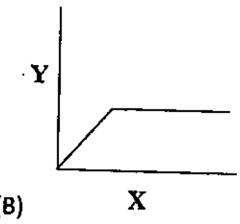
注意：背面有試題

(C) 1: 3: 3
(D) 1: 3: 6
(E) 1: 6: 3

5. A solution of dilute sodium hydroxide is added slowly into a solution containing $Al(NO_3)$ and $Mg(NO_3)_2$. Which of the relationship between the amount of precipitate formed (Y) and the amount of NaOH added (X) is correct?



(A)



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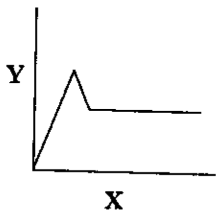
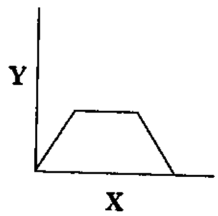
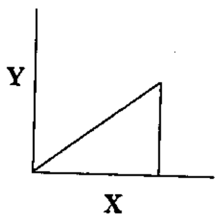


(C)



(D)



(E)

6. Which of the following item or procedure would result is solution with lowest pH at room temperature?
   (A) 0.01M acetic acid solution
   (B) mixing same volume of 0.02 M acetic acid and 0.02M NaOH solution
   (C) mixing same volume of 0.03 M acetic acid and 0.01M NaOH solution
   (D) mixing same volume of HCl solution (pH=2) and NaOH solution (pH=12)
   (E) mixing same volume of 0.03 M sodium acetate and 0.02M NaOH solution

二、簡答題 (70%，請詳列計算過程，並標記答案)

1. (8%) Write three mass-balance equations and a charge balance equation for the system formed when a 0.050 M NH_3 solution is saturated with AgBr.

2. (a) Discuss the factors that determine the particle size of precipitates (4%);
(b) How to control experimental conditions to get larger particle size for precipitation gravimetry (8%).

3. (6%) Using the *Q* test, decide whether the value 0.195 should be rejected from the set of results: 0.217, 0.224, 0.195, 0.221, 0.221, 0.223, at the 95% confidence level?

# observations	3	4	5	6	7
Q_{crit}(90%)	0.941	0.765	0.642	0.560	0.507
Q_{crit}(95%)	0.970	0.829	0.710	0.625	0.568

4. (10%) Karl Fischer titration is a classic titration method that uses coulometric or volumetric titration to determine trace amounts of water in a sample. Karl Fischer reagent contains I_2, SO_2, base and an alcohol (ROH), which may be standardized by titration with H_2O dissolved in methanol. A 25.00-mL aliquot of Karl Fischer reagent reacted with 34.61 mL of methanol to which was added 4.163 mg of H_2O per mL. When pure "dry" methanol was titrated, 25.00 mL of methanol reacted with 3.18 mL of the same Karl Fischer reagent. A suspension of 1.000 g of a hydrated crystalline salt in 25.00 mL of methanol consumed a total of 38.12 mL of Karl Fischer reagent. Please calculate the weight percent of water in the crystal.

5. (8%) Students at Analytical Chemistry Laboratory classes intended to prepare copper(II) carbonate by adding a solution of $CuSO_4 \cdot 5H_2O$ to a solution of Na_2CO_3. [Cu=63.55; Na=22.99; C=12.01; O=16.00; S=32.06]

$$CuSO_4{\cdot}5H_2O_{(aq)} + Na_2CO_{3(aq)} \rightarrow \underset{\text{copper(II) carbonate}}{CuCO_{3(s)}} + Na_2SO_{4(aq)} + 5H_2O_{(l)}$$

After warming the mixture to 60°C, the gelatinous blue precipitate coagulated into an easily filterable pale green solid. The product was filtered, washed, and dried at 70° C. Copper in the product was measured by heating 0.4 g of solid in a stream of methane at high temperature to reduce the solid to pure Cu, which was weighed.

$$4CuCO_{3(s)} + CH_{4(g)} \xrightarrow{\Delta} 4Cu_{(s)} + 5CO_{2(g)} + 2H_2O_{(g)}$$

In 2005, 43 students at class found a mean value of 55.6 wt % Cu with a standard deviation of 2.7 wt %. In 2006, 39 students found 55.9 wt % with a standard deviation of 3.8 wt %. The instructor tried the experiment 9 times and measured 55.8 wt % with a standard deviation of 0.5 wt %. Was the product of the reaction probably CuCO3? Could it have been a hydrate, CuCO3 . *x*H2O or Malachite, $Cu_2(OH)_2(CO_3)$? [Hint: *t*-test can be helpful in this case to predict the product of the reaction]

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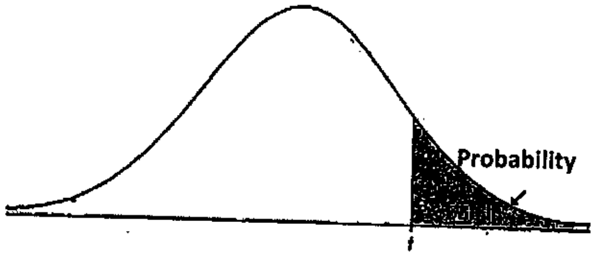


TABLE B: t-DISTRIBUTION CRITICAL VALUES

	Tail probability p											
df	.25	.20	.15	.10	.05	.025	.02	.01	.005	.0025	.001	.0005
1	1.000	1.376	1.963	3.078	6.314	12.71	15.89	31.82	63.66	127.3	318.3	636.6
2	.816	1.061	1.386	1.886	2.920	4.303	4.849	6.965	9.925	14.09	22.33	31.60
3	.765	.978	1.250	1.638	2.353	3.182	3.482	4.541	5.841	7.453	10.21	12.92
4	.741	.941	1.190	1.533	2.132	2.776	2.999	3.747	4.604	5.598	7.173	8.610
5	.727	.920	1.156	1.476	2.015	2.571	2.757	3.365	4.032	4.773	5.893	6.869
6	.718	.906	1.134	1.440	1.943	2.447	2.612	3.143	3.707	4.317	5.208	5.959
7	.711	.896	1.119	1.415	1.895	2.365	2.517	2.998	3.499	4.029	4.785	5.408
8	.706	.889	1.108	1.397	1.860	2.306	2.449	2.896	3.355	3.833	4.501	5.041
9	.703	.883	1.100	1.383	1.833	2.262	2.398	2.821	3.250	3.690	4.297	4.781
10	.700	.879	1.093	1.372	1.812	2.228	2.359	2.764	3.169	3.581	4.144	4.587
11	.697	.876	1.088	1.363	1.796	2.201	2.328	2.718	3.106	3.497	4.025	4.437
12	.695	.873	1.083	1.356	1.782	2.179	2.303	2.681	3.055	3.428	3.930	4.318
13	.694	.870	1.079	1.350	1.771	2.160	2.282	2.650	3.012	3.372	3.852	4.221
14	.692	.868	1.076	1.345	1.761	2.145	2.264	2.624	2.977	3.326	3.787	4.140
15	.691	.866	1.074	1.341	1.753	2.131	2.249	2.602	2.947	3.286	3.733	4.073
16	.690	.865	1.071	1.337	1.746	2.120	2.235	2.583	2.921	3.252	3.686	4.015
17	.689	.863	1.069	1.333	1.740	2.110	2.224	2.567	2.898	3.222	3.646	3.965
18	.688	.862	1.067	1.330	1.734	2.101	2.214	2.552	2.878	3.197	3.611	3.922
19	.688	.861	1.066	1.328	1.729	2.093	2.205	2.539	2.861	3.174	3.579	3.883
20	.687	.860	1.064	1.325	1.725	2.086	2.197	2.528	2.845	3.153	3.552	3.850
21	.686	.859	1.063	1.323	1.721	2.080	2.189	2.518	2.831	3.135	3.527	3.819
22	.686	.858	1.061	1.321	1.717	2.074	2.183	2.508	2.819	3.119	3.505	3.792
23	.685	.858	1.060	1.319	1.714	2.069	2.177	2.500	2.807	3.104	3.485	3.768
24	.685	.857	1.059	1.318	1.711	2.064	2.172	2.492	2.797	3.091	3.467	3.745
25	.684	.856	1.058	1.316	1.708	2.060	2.167	2.485	2.787	3.078	3.450	3.725
26	.684	.856	1.058	1.315	1.706	2.056	2.162	2.479	2.779	3.067	3.435	3.707
27	.684	.855	1.057	1.314	1.703	2.052	2.158	2.473	2.771	3.057	3.421	3.690
28	.683	.855	1.056	1.313	1.701	2.048	2.154	2.467	2.763	3.047	3.408	3.674
29	.683	.854	1.055	1.311	1.699	2.045	2.150	2.462	2.756	3.038	3.396	3.659
30	.683	.854	1.055	1.310	1.697	2.042	2.147	2.457	2.750	3.030	3.385	3.646
40	.681	.851	1.050	1.303	1.684	2.021	2.123	2.423	2.704	2.971	3.307	3.551
50	.679	.849	1.047	1.299	1.676	2.009	2.109	2.403	2.678	2.937	3.261	3.496
60	.679	.848	1.045	1.296	1.671	2.000	2.099	2.390	2.660	2.915	3.232	3.460
80	.678	.846	1.043	1.292	1.664	1.990	2.088	2.374	2.639	2.887	3.195	3.416
100	.677	.845	1.042	1.290	1.660	1.984	2.081	2.364	2.626	2.871	3.174	3.390
1000	.675	.842	1.037	1.282	1.646	1.962	2.056	2.330	2.581	2.813	3.098	3.300
∞	.674	.841	1.036	1.282	1.645	1.960	2.054	2.326	2.576	2.807	3.091	3.291
	50%	60%	70%	80%	90%	95%	96%	98%	99%	99.5%	99.8%	99.9%
	Confidence level C											

6. The electrolysis cell shown below was run at a constant current of 0.02196 A. On one side, 49.22 mL of H_2 were produced (at 303 K and 0.996 bar); on the other side, Cu metal was oxidized to Cu^{2+}

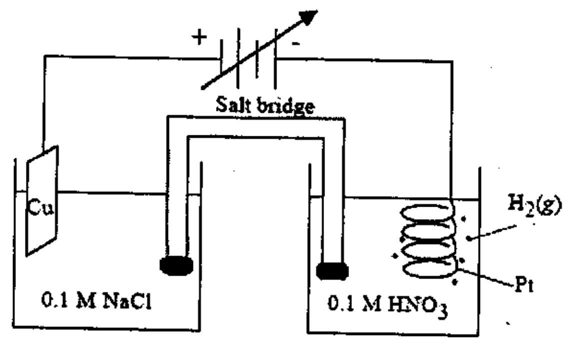
注意：背面有試題

($R = 0.08314$ L bar K^{-1} mol^{-1})

(a) How many moles of H_2 were produced (4%)?

(b) If 47.36 mL of EDTA were required to titrate the Cu^{2+} produced by the electrolysis, what was the molarity of the EDTA (4%)?

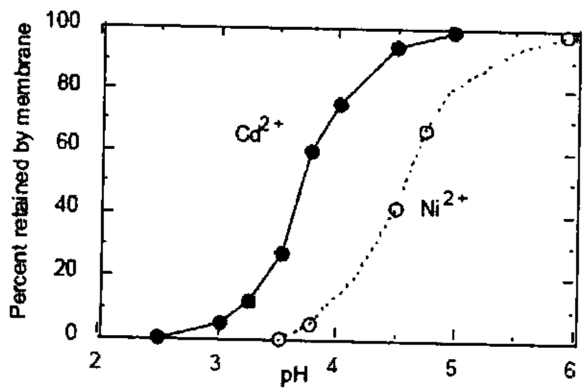
(c) For how many hours was the electrolysis run (4%)?



$Cu_{(s)} \rightarrow Cu^{2+} + 2e^-$ $H_2O + e^- \rightarrow 1/2\, H_{2(g)} + OH^-$

7. (a) A method involving "ultrafiltration" has been commonly used for removing metal cations from industrial waste. To sequester metal ions, a water-soluble polymer containing many carboxyl (–COOH) groups can be used by adding into the waste. The carboxyl groups are found to be capable of binding cations. When the waste liquid is concentrated by ultrafiltration, small molecules and solvent are separated from the polymer containing undesirable cations. Please describe the principle of ultrafiltration, and draw a sketch of this process and explain how it can be used to concentrate metals from a waste stream (7%).

(b) The effect of pH on the ultrafiltration of Cd^{2+} and Ni^{2+} is shown as below. Please explain the shapes of these curves and predict which metal has a higher formation constant for binding to the polymer and why (7%)? [Cd=112.41; Ni=58.69]



Effect of pH on retention of metal ion during ultrafiltration of waste stream containing added metal-binding polymer.