八十五學年度 原子科學 系（所） 乙 組碩士班研究生入學考試

科目 分析化學 科號 4102 共 4 頁第 1 頁 *請在試卷【答案卷】內作答

1. A solution whose volume is 100 mL is about 0.1 *M* in both Ag^+ an Cu^{2+}. It is desired to determine the exact quantity of silver by electrodepostition on a weighed platinum cathode; the result will be high if copper also plates onto the cathode. Can this separation of silver from copper be done ? If so, what range of cathode potentials can be used ? (At. wt. of Ag is 108 g)

$$Cu^{2+} + 2e^- \rightleftharpoons Cu(s) \qquad E^\circ = +0.34\ V$$

$$Ag^+ + e^- \rightleftharpoons Ag(s) \qquad E^\circ = +0.80\ V \qquad (12\%)$$

2. A 0.4058-g sample containing lead, magnesium, and zinc was dissolved and treated with cyanide to complex and mask the zinc:

$$Zn^{2+} + 4CN^- \longrightarrow Zn(CN)_4^{2-}$$

Titration of the lead and magnesium required 42.22 mL of 0.02064 *M* EDTA. The lead was next masked with BAL (2,3-dimercaptopropanol) and the released EDTA was titrated with 19.35 mL of a 0.007657 *M* magnesium solution. Finally, formaldehyde was introduced to demask the zinc:

$$Zn(CN)_4^{2-} + 4HCHO + 4H_2O \longrightarrow Zn^{2+} + 4HOCH_2CN + 4OH^-$$

which was titrated with 28.63 mL of 0.02064 *M* EDTA. Calculate the percentages of the three metals in the sample.

(At. wt. for Pb=207.2 g, Mg=24.3 g and Zn=65.4 g) (12%)

3. A person with average eyesight can see the red color that $Fe(SCN)^{2+}$ imparts to an aqueous solution when the concentration of the complex is 6.4×10^{-6} *M* or greater. What minimum concentration

of KSCN is required to make it possible to detect 1 ppm of iron(III) in water from a spring if the formation constant for the complex is 1.4×10^2 ? (At. wt. for Fe=55.8 g)

$$Fe^{3+} + SCN^- \rightleftharpoons Fe(SCN)^{2+} \qquad K_f = 1.4 \times 10^2$$

(12%)

4. A certain chlorinated hydrocarbon, 1,1,1-trichloroethane, is run through a gas chromatograph. The apex of its peak appears 137 seconds after the apex of the air peak. The trichloroethane peak is 10 seconds wide. What is the value of HEPT (Height equivalent of a theoretical plate) in cm, for this species on this column under these conditions, if the column is five feet long ? (Note: 1 feet = 12 inches, 1 inch = 2.54 cm). (12%)

5. $^{14}CO_2$ may be used as a radioactive tracer to study metabolism in plants. Suppose that a compound isolated from a plant exhibited 28, 32, 27, 39, and 40 radioactive dacays per minute. A blank sample used to measure the background of the radiation counter (due to electrical noise and background radiation) gave 28, 21, 28, and 20 counts per minute. It appear that the isolated compound gives more counts than background. Can we be 95% confident that the compound is indeed radioactive ?

Hint: to determine whether the two sets of data, $\bar{x}_1$ and $\bar{x}_2$, are identical, the following equation can be used

$$t = \frac{\bar{x}_1 - x_2}{s} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

where i) s is pooled standard deviation and expressed as

$$s = \sqrt{\frac{\sum_{set\,1}(x_i - \bar{x}_1)^2 + \sum_{set\,2}(x_j - \bar{x}_2)^2}{n_1 + n_2 - 2}}$$

ii) n_1 and n_2 are the number of replicate measurements for each set of data.

iii) t is student's test (for the seven degrees of freedom and 95% confident, the t value is 2.365). (12%)

6. Phosphoric acid is a typical polyfunctional acid. In aqueous solution it undergoes the following three dissociation reactions:

$$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_2O^+ \qquad K_1 = 7.11 \times 10^{-3}$$

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+ \qquad K_2 = 6.34 \times 10^{-8}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^- \qquad K_3 = 4.2 \times 10^{-13}$$

Explain the possible reason why the dissociation constants of this acid are in the order of $K_1 > K_2 > K_3$. (6%)

7. Describe and compare the differences between the following terms:

a). Atomic absorption spectrometry / Atomic emission spectrometry

b). Reverse-phase chromatography / Normal-phase chromatography

c). Equivalent point / End point (of titration)

d) Determinate error / Indeterminate error

e) Size-exclusion chromatography / Supercritical-fluid chromatography

(20%)

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8. Potentiomentry, electrogravimetry, coulometry and voltammetry are the four important methods in electroanalytical techniques.

a). Explain briefly the basic principle of the respective analytical techniques.

b). Compare the following techniques from the points of view such as analytical principle, end point detection, accuracy or precision.

i). Conventional titration vs potentiometric titration.

ii). Conventional gravimetric method vs electrogravimetric method.

(14%)