

作业20081218 (MAC) 参考答案

A类

18. In a particular analysis the selectivity coefficient, $K_{A,I}$, is 0.816. When a standard sample known to contain an analyte to interferent ratio of 5:1 is carried through the analysis, the error in determining the analyte is +6.3%.

- (a) Determine the apparent recovery for the analyte if $R_I = 0$.
 (b) Determine the apparent recovery for the interferent if $R_A = 1$.

Solution:

The error in determining the analyte is

$$E = (R_A - 1) + \frac{K_{A,I}c_I^0}{c_A^0} R_I$$

Thus,

- (a) the apparent recovery for the analyte if $R_I = 0$ is

$$R_A = E + 1 - \frac{K_{A,I}c_I^0}{c_A^0} R_I = 0.063 + 1 = 1.063 = 106.3\%$$

- (b) the apparent recovery for the interferent if $R_A = 1$ is

$$R_I = E - (R_A - 1) \frac{c_A^0}{K_{A,I}c_I^0} = 0.063 \times \frac{5}{1 \times 0.816} = 0.386 = 38.6\%$$

19. The amount of Co in an ore sample is to be determined using a procedure for which Fe is an interferent. To evaluate the procedure's accuracy, a standard sample of ore known to have a Co/Fe ratio of 10.2:1 is analyzed. When pure samples of Co and Fe are taken through the procedure, the following calibration relationships are obtained

$$S_{Co} = 0.786 \times \text{number of grams Co}$$

$$S_{Fe} = 0.699 \times \text{number of grams Fe}$$

When 278.3 mg of Co is taken through the separation step, 275.9 mg is recovered.

Only 3.6 mg of Fe is recovered when a 184.9-mg sample of Fe is carried through the separation step. Calculate

- (a) the recoveries for Co and Fe;
 (b) the separation factor;
 (c) the error if no attempt is made to separate the Co and Fe before the analysis;
 (d) the error if the separation step is carried out;
 (e) the maximum recovery for Fe if all the Co is recovered and the maximum allowed error is 0.05%.

Solution:

- (a)

$$R_{Co} = \left(\frac{m_r}{m_0}\right)_{Co} = \frac{275.9}{278.3} = 0.991 = 99.1\%$$

$$R_{Fe} = \left(\frac{m_r}{m_0}\right)_{Fe} = \frac{3.6}{184.9} = 0.019 = 1.9\%$$

(b)

$$S_{I,A} = \frac{R_{Fe}}{R_{Co}} = \frac{1.9}{99.1} = 0.019$$

(c)

$$E = (R_{Co} - 1) + \frac{\frac{k_{Fe}}{k_{Co}} c_{Fe}^0}{c_{Fe}^0} R_{Fe} = (1 - 1) + \frac{0.699}{0.786} \times 1 = 0.0872 = 8.72\%$$

(d)

$$E = (R_{Co} - 1) + \frac{\frac{k_{Fe}}{k_{Co}} c_{Fe}^0}{c_{Fe}^0} R_{Fe} = (0.991 - 1) + \frac{0.699}{0.786} \times 0.019 = -0.0073 = -0.73\%$$

(e)

$$R_{Fe,max} = [E - (R_{Co} - 1)] \frac{c_{Co}^0}{\frac{k_{Fe}}{k_{Co}} c_{Fe}^0} = [0.05\% - (1 - 1)] \times \frac{10.2}{\frac{0.699}{0.786} \times 1} = 0.57\%$$

20. The amount of calcium in a sample of urine was determined by a method for which magnesium is an interferent. The selectivity coefficient, $K_{Ca,Mg}$, for the method is 0.843. When a sample with a Mg/Ca ratio of 0.50 was carried through the procedure, an error of -3.7% was obtained. The error was $+5.5\%$ when a sample with a Mg/Ca ratio of 2.0 was used.

(a) Determine the recoveries for Ca and Mg.

(b) What is the expected error for a urine sample in which the Mg/Ca ratio is 10.0?

Solution:

Since

$$E = (R_{Ca} - 1) + \frac{K_{Ca,Mg} c_{Mg}^0}{c_{Ca}^0} R_{Mg}$$

We get

$$E_1 = (R_{Ca} - 1) + 0.843 \times 0.50 R_{Mg} = (R_{Ca} - 1) + 0.42 R_{Mg} = -3.7\%$$

$$E_2 = (R_{Ca} - 1) + 0.843 \times 2 R_{Mg} = (R_{Ca} - 1) + 1.68 R_{Mg} = 5.5\%$$

Solve the equations, the recoveries for Ca and Mg are given as

$$R_{Ca} = 0.93\%, \quad R_{Mg} = 0.073\%$$

参考文献

MAC pp.201-205

B类

27. A weak acid, HA, with a K_a of 1.0×10^{-5} , has a partition coefficient, K_D , between water and an organic solvent of 1200. What restrictions on the sample's pH are necessary to ensure that a minimum of 99.9% of the weak acid is extracted in a single step from 50.0 mL of water using 50.0 mL of the organic solvent?

Solution:

$$D = \frac{[HA]_o}{[HA]_o + [HA]_w} = \frac{K_D[H^+]}{[H^+] + K_a}$$

$$E = \frac{D}{D + \frac{V_w}{V_o}} = \frac{D}{D+1}$$

Thus

$$E = \frac{D}{D + \frac{V_w}{V_o}} = \frac{D}{D+1} = \frac{K_D[H^+]}{K_D[H^+] + [H^+] + K_a}$$

Solve the equation, give

$$[H^+] = \frac{K_a E}{K_D - E + K_D E} = 5.0 \times 10^{-5}$$

$$pH < 4.3$$

30. A sample contains a weak acid analyte, HA, and a weak acid interferent, HB. The acid dissociation constants and partition coefficients for the weak acids are as follows:

$$K_{a,HA} = 1.0 \times 10^{-3}, K_{a,HB} = 1.0 \times 10^{-7}, K_{D,HA} = K_{D,HB} = 500.$$

(a) Calculate the extraction efficiency for HA and HB when 50.0 mL of sample, buffered to a pH of 7.0, is extracted with 50.0 mL of the organic solvent.

(b) Which phase is enriched in the analyte?

(c) What are the recoveries for the analyte and interferent in this phase?

(d) What is the separation factor?

(e) A quantitative analysis is conducted on the contents of the phase enriched in analyte. What is the expected relative error if the selectivity coefficient, $K_{HA,HB}$, is 0.500 and the initial ratio of HB/HA was 10.0?

Solution:

(a) Since

$$E = \frac{D}{D + \frac{V_w}{V_o}} = \frac{D}{D+1} = \frac{K_D[H^+]}{K_D[H^+] + [H^+] + K_a}$$

Thus, the extraction efficiency for HA is

$$\begin{aligned} E &= \frac{D}{D + \frac{V_w}{V_o}} = \frac{D}{D+1} = \frac{K_D[H^+]}{K_D[H^+] + [H^+] + K_a} \\ &= \frac{500 \times 10^{-7}}{500 \times 10^{-7} + 1 \times 10^{-7} + 1 \times 10^{-3}} = 4.8\% \end{aligned}$$

the extraction efficiency for HB is

$$\begin{aligned} E &= \frac{D}{D + \frac{V_w}{V_o}} = \frac{D}{D+1} = \frac{K_D[H^+]}{K_D[H^+] + [H^+] + K_a} \\ &= \frac{500 \times 10^{-7}}{500 \times 10^{-7} + 1 \times 10^{-7} + 1 \times 10^{-7}} = 99.6\% \end{aligned}$$

(b) According to the calculated extraction efficiency for HA and HB, we can easily tell that aqueous phase is enriched in the analyte.

(c)

$$\begin{aligned} R_{HA} &= \frac{m_r}{m_0} = \frac{m_0(1-E)}{m_0} = 1 - 0.048 = 0.952 = 95.2\% \\ R_{HB} &= \frac{m_r}{m_0} = \frac{m_0(1-E)}{m_0} = 1 - 0.996 = 0.004 = 0.4\% \end{aligned}$$

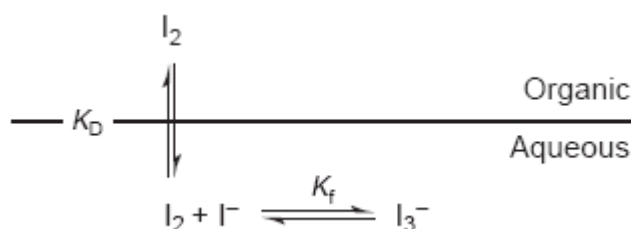
(d)

$$S_{HB,HA} = \frac{R_{HB}}{R_{HA}} = \frac{0.004}{0.952} = 4.2 \times 10^{-3}$$

(e)

$$E = (R_{HA} - 1) + \frac{K_{HA,HB} c_{HB}^0}{c_{HA}^0} R_{HB} = (0.952 - 1) + 0.5 \times 10 \times 0.004 = -0.028 = -2.8\%$$

31. The relevant equilibria for the extraction of I_2 from an aqueous solution of KI into an organic phase are shown in the following diagram.



- (a) Will the extraction efficiency for I_2 be greater for higher or lower concentrations of I^- ?
- (b) Derive an expression for the distribution ratio for this extraction.

Solution:

(a) Since I^- reacts with the I_2 in aqueous phase and decreases the concentrations of I_2 and, therefore, decreases the extraction efficiency, thus, lower concentrations of I^- increase the partition ratio and, therefore, the extraction efficiency.

(b)

$$D = \frac{K_D}{\alpha_{I_2(I^-)}} = \frac{K_D}{1 + K_f [I^-]_{aq}}$$

参考文献

MAC pp. 211-223