S21-1. The Doppler linewidth is given by $\Delta\lambda = \lambda (7 \times 10^{-7}) \sqrt{T/M}$

$= 0.0013$ nm for Fe at 3 000 K (with $\lambda = 248$ nm and M = 56)

$= 0.0018$ nm for Fe at 6 000 K (with $\lambda = 248$ nm and M = 56)

$= 0.000\ 7$ nm for Hg at 3 000 K (with $\lambda = 254$ nm and M = 201)

$= 0.0010$ nm for Hg at 6 000 K (with $\lambda = 254$ nm and M = 201)

S21-2. (a) $\Delta E = h\nu = \dfrac{hc}{\lambda} = \dfrac{(6.626\ 1 \times 10^{-34}\ \text{J·s})(2.997\ 9 \times 10^{8}\ \text{m/s})}{327 \times 10^{-9}\ \text{m}}$

$= 6.07 \times 10^{-19}$ J/molecule $= 366$ kJ/mol

(b) $\dfrac{N^{*}}{N_{0}} = \dfrac{g^{*}}{g_{0}}\ e^{-\Delta E/kT} = 3e^{-(6.07\ \times\ 10^{-19}\ \text{J})/(1.381\ \times\ 10^{-23}\ \text{J/K})(2\ 400\text{K})} = 3.29 \times 10^{-8}$

(c) At 2 415 K, $N^{*}/N_{0} = 3.69 \times 10^{-8} \Rightarrow$ 12% increase from 2 400 to 2 415 K

(d) At 6 000 K, $N^{*}/N_{0} = 0.002\ 0$

S21-3. Sensitivity $=$ concentration of Mo giving $A = 0.004\ 36$ $(= 99\%\ T)$

$\dfrac{[\text{Mo}]\ \text{giving}\ A = 0.004\ 36}{[\text{Mo}]\ \text{giving}\ A = 0.025} = \dfrac{0.004\ 36}{0.025}$

$\dfrac{x}{23.6\ \mu\text{g/mL}} = \dfrac{0.004\ 36}{0.025} \Rightarrow x = 4.1\ \mu\text{g/mL}$

S21-4. (a)

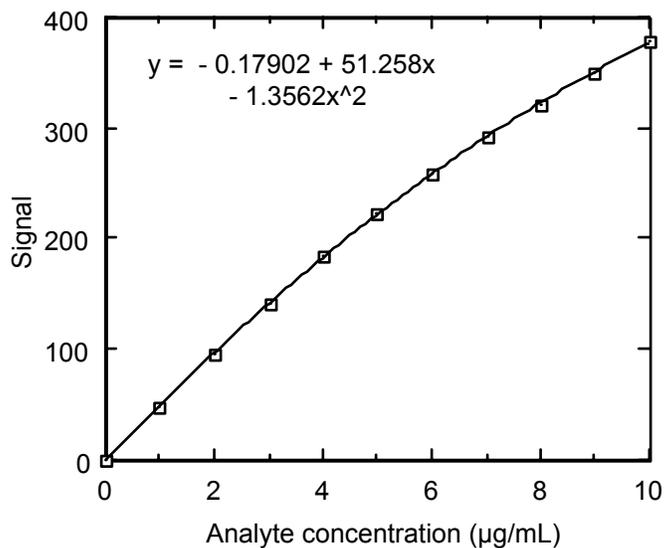| µg/mL	$A_{422.7}/A_{324.7}$	
1.00	0.6056	
2.00	0.6062	average $= 0.6019$
3.00	0.5913	
4.00	0.6045	

(b) Standard mixture has equal concentrations of Ca and Cu:

$\dfrac{A_{\text{Ca}}}{[\text{Ca}]} = F\left(\dfrac{A_{\text{Cu}}}{[\text{Cu}]}\right) \Rightarrow \dfrac{0.6019}{[\text{Ca}]} = F\left(\dfrac{1.000}{[\text{Cu}]}\right) \Rightarrow F = 0.6019$

Unknown mixture:

$\dfrac{A_{\text{Ca}}}{[\text{Ca}]} = F\left(\dfrac{A_{\text{Cu}}}{[\text{Cu}]}\right) \Rightarrow \dfrac{0.218}{[\text{Ca}]} = 0.6019\left(\dfrac{0.269}{[2.47\ \mu\text{g/mL}]}\right) \Rightarrow [\text{Ca}] = 3.33\ \mu\text{g/mL}$

S21-5. (a) The graph below shows the quadratic fit to the calibration data.

(b) $344.0 = -0.179\,02 + 51.258x - 1.356\,2x^2 \Rightarrow x = 8.73$ µg/mL

(by solving quadratic equation and using the root that lies on this graph)

$346.2 = -0.179\,02 + 51.258x - 1.356\,2x^2 \Rightarrow x = 8.81$ µg/mL

$341.8 = -0.179\,02 + 51.258x - 1.356\,2x^2 \Rightarrow x = 8.65$ µg/mL

Concentration of unknown $= 8.73 \pm 0.08$ µg/mL

S21-6. Emission is observed only if the narrow laser excitation frequency overlaps the even narrower atomic absorption line. The laser bandwidth is narrow enough to excite Mn without exciting Ga.

S22-1. (a) The peak at m/z 71 is $C_4H_7O^+$. Its contribution to m/z 72 should be

$$\text{Intensity} \ = \ 4 \times 1.08\% + 7 \times 0.012\% + 1 \times 0.038\% \ = \ 4.4\% \text{ of } m/z \text{ 71}$$

$$\underbrace{\qquad\qquad}_{^{13}C} \quad \underbrace{\qquad\qquad}_{^{2}H} \quad \underbrace{\qquad\qquad}_{^{17}O}$$

The observed intensity of 4.9% in spectrum (*a*) is reasonable, but the 10.7% intensity in spectrum (*b*) is too great. There is probably another contribution to the m/z 72 peak in spectrum (*b*).

(b) The extra intensity in the peak at m/z 72 in represents loss of a neutral molecule with a mass of 28 Da from the molecular ion. The McLafferty rearrangement can split C_2H_4 from 3-hexanone, but not from 2-methyl-3-pentanone, which lacks a γ-CH group.

3-Hexanone	Ethylene 28 Da	$m/z = 72$
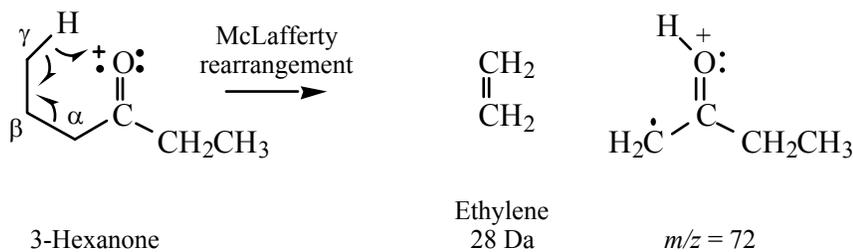
S22-2. ^{12}C abundance + a = 0.989 3 ^{13}C abundance + b = 0.010 7
Abundance of $^{12}C_3H_6 = a^3 = 0.968\ 2$
Abundance of $^{12}C_2{}^{13}CH_6 = 3a^2b = 0.031\ 4_2$
Abundance of $^{12}C^{13}C_2H_6 = 3ab^2 = 0.000\ 339_8$
Abundance of $^{13}C_3H_6 = b^3 = 0.000\ 001\ 22_5$
Relative abundances: $M^+ : M+1 : M+2 : M+3 = 1 : 0.032\ 4 : 0.000\ 351 : 0.000\ 001\ 27$

S22-3. (a) Relative abundances of isotopic labels are obtained by subtracting the natural abundance column of the table from the experimental abundance column:

$$^{144}Nd = 160.53 - 87.97 = 72.56 \quad\quad ^{148}Nd = 38.73 \quad\quad ^{150}Nd = 59.37$$

The relative number of atoms of each isotope reaching the detector are

$$^{144}Nd : {}^{148}Nd : {}^{150}Nd \ = \ 72.56 : 38.73 : 59.37$$

The 1.00-g dust sample contained 0.100 µg of ^{144}Nd, which is $6.94_9 \times 10^{-10}$ mol with an atomic mass of $143.909\ 9 = 4.18_5 \times 10^{14}$ atoms of ^{144}Nd. Therefore the number of atoms of ^{148}Nd is $(38.73/72.56)(4.18_5 \times 10^{14}) = 2.23_4 \times 10^{14}$ atoms. The number of atoms of ^{150}Nd is $(59.37/72.56)(4.18_5 \times 10^{14}) = 3.42_4 \times 10^{14}$ atoms. Converting each number of

atoms to the number of moles and multiplying by the atomic mass of that isotope tells us that the masses are 0.054 87 µg of ^{148}Nd and 0.085 24 µg of ^{150}Nd.

(b) We know that ash emerging from smokestack A contained 10.2 ppm (10.2 µg/g) of ^{148}Nd and ash from smokestack B had 11.4 ppm of ^{150}Nd. The experimental 1.00-g sample contained 0.054 87 µg of ^{148}Nd. To find the mass of ash from smokestack A in the 1.00-g sample, we can write

$$\frac{0.054\ 87\ \mu\text{g of }^{148}\text{Nd}}{x\ \text{g ash}} = \frac{10.2\ \mu\text{g of }^{148}\text{Nd}}{1\ \text{g ash}} \Rightarrow x = 5.38 \text{ mg ash from stack A}$$

For smokestack B, we can say

$$\frac{0.085\ 24\ \mu\text{g of }^{150}\text{Nd}}{x\ \text{g ash}} = \frac{11.4\ \mu\text{g of }^{150}\text{Nd}}{1\ \text{g ash}} \Rightarrow x = 7.48 \text{ mg ash from stack B}$$

(c) The first step separates lanthanide ions from other cations in the digested dust sample. It does not separate the lanthanides from one another. The second separation, done under milder conditions on the same ion-exchange resin, separates individual lanthanides from each other. In the second separation, elution is conducted with a much weaker acid (0.225 M 2-methyl lactic acid versus 6 M HCl in the first separation), so a finer separation of similar cations can occur. It is also possible that 2-methyl lactic acid coordinates to lanthanide ions to form complexes such as Ln(2-methyl lactate)$_3$ and that the different stability constants of the complexes lead to different elution characteristics.

S23-1. (a) Fraction remaining $= \dfrac{V_1}{V_1 + KV_2}$

$0.005 = \dfrac{100}{100 + (610)V_2} \;\Rightarrow\; V_2 = 32.6 \text{ mL}$

(b) $0.005 = \left(\dfrac{100}{100 + (610)V_2}\right)^4 \;\Rightarrow\; V_2 = 0.453 \text{ mL}. \quad 4 \times V_2 = 1.81 \text{ mL}$

S23-2. (a) $D + \dfrac{[HA]_{ether} + [A^-]_{ether}}{[HA]_{aq} + [A^-]_{aq}} \approx \dfrac{[HA]_{ether}}{[HA]_{aq} + [A^-]_{aq}}$

$K + \dfrac{[HA]_{ether}}{[HA]_{aq}}$

(b) $D = \dfrac{K - [H^+]}{[H^+] + K_a} = \dfrac{92 - 10^{-4.00}}{10^{-4.00} + 4.2 \times 10^{-4}} = 17.7$

(c) At pH 3.50, more of the acid will be in the form HA, which is the extractable species. Therefore the distribution coefficient will be greater than at pH 4.00.

(d) $1 = \dfrac{92 \cdot [H^+]}{[H^+] + 4.2 \times 10^{-4}} \;\Rightarrow\; [H^+] = 4.62 \times 10^{-6} \text{ M} \Rightarrow \text{pH} = 5.34$

S23-3. (a) $t'_r = 13.81 - 1.06 = 12.75 \text{ min}. \quad k' = 12.75/1.06 = 12.03$

(b) $w_{1/2} = 0.172 \text{ min} \;\Rightarrow\; N = \dfrac{5.55 \, t_r^2}{w_{1/2}^2} = \dfrac{5.55 \,(13.81)^2}{0.172^2} = 3.58 \times 10^4 \text{ plates}$

(c) $w = 0.302 \text{ min} \;\Rightarrow\; N = \dfrac{16 \, t_r^2}{w^2} = \dfrac{16 \,(13.81)^2}{0.302^2} = 3.35 \times 10^4 \text{ plates}$

(d) $H = (30.0 \times 10^3 \text{ mm})/(3.35 \times 10^4 \text{ plates}) = 0.896 \text{ mm}$

(e) Volume of 30.0 m of column $= \pi r^2 \times \text{length} = \pi (0.026\,2 \text{ cm})^2 \times 3\,000 \text{ cm}$
$= 6.47 \text{ mL}.$
Volume flow rate $= (6.47 \text{ mL}) / (1.06 \text{ min}) = 6.10 \text{ mL/min}$

S23-4. (a) $N = \dfrac{16 \, t_r^2}{w^2} = \dfrac{16 \,(12.83 \text{ min})^2}{(0.307 \text{ min})^2} = 2.80 \times 10^4 \text{ plates}$

(b) $H = (158 \text{ mm})/(2.80 \times 10^4 \text{ plates}) = 5.64 \text{ μm}$

S23-5. (a) Volume of mobile phase per cm of column $= (0.426)\pi r^2 \times (1\text{ cm}) =$
$(0.426)\pi(0.960\text{ cm})^2 \times (1\text{ cm}) = 1.23\text{ mL}$
Linear flow rate $= (2.22\text{ mL/min}) / (1.23\text{ mL/cm}) = 1.80\text{ cm/min}$

(b) $t_m = (50.6\text{ cm}) / 1.80\text{ cm/min} = 28.1_1\text{ min}$

$$k' = \frac{t_r - t_m}{t_m} \Rightarrow 8.04 = \frac{t_r - 28.11}{28.11} \Rightarrow t_r = 254\text{ min}$$

S23-6. $\alpha = (k_2') / (k_1') = 1.02; \quad k_2' = 5.10; \quad k_{av}' = 5.05$

$$\text{Resolution} = \frac{\sqrt{N}}{4}\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k_2'}{1 + k_{av}'}\right)$$

$$1.00 = \frac{\sqrt{N}}{4}\left(\frac{1.02 - 1}{1.02}\right)\left(\frac{5.10}{1 + 5.05}\right) \Rightarrow N = 5.86 \times 10^4\text{ plates}$$

$(5.86 \times 10^4\text{ plates})(155\ \mu m/\text{ plate}) = 9.08\text{ m}$

To double the resolution requires four times as many plates $= 36.3\text{ m}$.

S23-7. (a) Heptane: $t_r' = 14.56 - 1.06 = 13.50\text{ min}. \quad k' = 13.50/1.06 = 12.74$

$C_6H_4F_2$: $t_r' = 14.77 - 1.06 = 13.71\text{ min}. \quad k' = 13.71/1.06 = 12.93$

(b) $\alpha = 12.93/12.74 = 1.015$

(c) $w_{1/2}\text{ (heptane)} = 0.126\text{ min}; \quad w_{1/2}\ (C_6H_4F_2) = 0.119\text{ min}$

$$N = \frac{5.55\ t_r^2}{w_{1/2}^2} = \frac{5.55\ (14.56)^2}{0.126^2} = 7.41 \times 10^4\text{ plates for heptane}$$

$$N = \frac{5.55\ (14.77)^2}{0.119^2} = 8.55 \times 10^4\text{ plates for } C_6H_4F_2$$

(d) $w\text{ (heptane)} = 0.216\text{ min}; \quad w\ (C_6H_4F_2) = 0.196\text{ min}$

$$N = \frac{16\ t_r^2}{w^2} = \frac{16\ (14.56)^2}{0.216^2} = 7.27 \times 10^4\text{ plates for heptane}$$

$$N = \frac{16\ (14.77)^2}{0.196^2} = 9.09 \times 10^4\text{ plates for } C_6H_4F_2$$

(e) $\text{Resolution} = \dfrac{\Delta t_r}{w_{av}} = \dfrac{14.77 - 14.56}{0.206} = 1.019$

(f) $N = \sqrt{(7.27 \times 10^4)(9.09 \times 10^4)} = 8.13 \times 10^4\text{ plates}$

$$\text{Resolution} = \frac{\sqrt{N}}{4}\left(\frac{\alpha-1}{\alpha}\right)\left(\frac{k_2'}{1+k_{av}'}\right) = \frac{\sqrt{8.13\times10^4}}{4}\left(\frac{1.015-1}{1.015}\right)\left(\frac{12.93}{1+12.84}\right) = 0.984$$

(g) Fraction of time in stationary phase $= \dfrac{t_s}{t_s+t_m} = \dfrac{k't_m}{k't_m+t_m} = \dfrac{k'}{k'+1}$

$$= \frac{12.74}{12.74+1} = 0.927$$

S23-8. $\dfrac{\text{Large load}}{\text{Small load}} = \left(\dfrac{\text{large column radius}}{\text{small column radius}}\right)^2$

$$\frac{72.4\text{ mg}}{10.0\text{ mg}} = \left(\frac{3.00\text{ cm}}{\text{small column diameter}}\right)^2 \Rightarrow \text{diameter} = 1.11\text{ cm}$$

Use the same concentration $\Rightarrow$ volume $= \frac{10.0}{72.4}(0.500\text{ mL}) = 0.069\,1\text{ mL}$

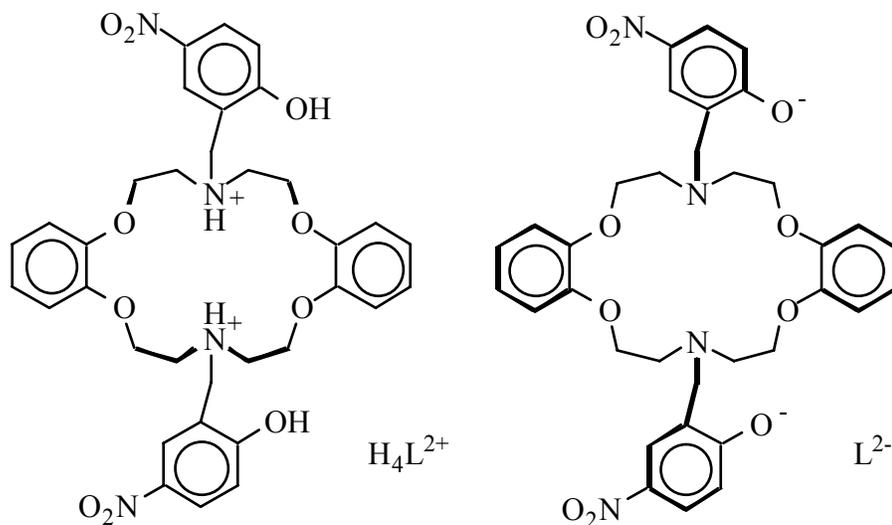**S23-9.** Flux $= -D\dfrac{dc}{dx} = -\left(2.0\times10^{-9}\dfrac{\text{m}^2}{\text{s}}\right)\left(-3.4\dfrac{\text{mol}}{\text{L·cm}}\right)$
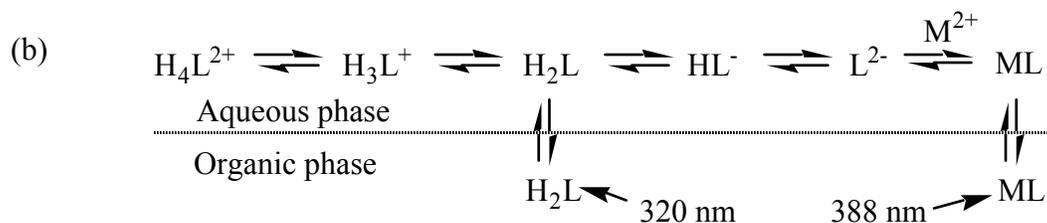
$$= \left(2.0\times10^{-9}\frac{\text{m}^2}{\text{s}}\right)\left(\frac{100\text{ cm}}{\text{m}}\right)^2\left(3.4\frac{\text{mol}}{\text{L·cm}}\right)\left(\frac{0.001\text{ L}}{\text{cm}^3}\right) = 6.80\times10^{-8}\frac{\text{mol/s}}{\text{cm}^2}$$

$$= 4.09\times10^{16}\frac{\text{ions/s}}{\text{cm}^2}$$

In 5.5 s, 2.3×10^{17} ions will cross each square centimeter.

S23-10.   (a)

(b)

$$H_4L^{2+} \rightleftharpoons H_3L^+ \rightleftharpoons H_2L \rightleftharpoons HL^- \rightleftharpoons L^{2-} \overset{M^{2+}}{\rightleftharpoons} ML$$

Aqueous phase

Organic phase

$H_2L \longleftarrow$ 320 nm   388 nm $\longrightarrow$ ML

The organic phase initially contains H_2L, which gives the peak near 320 nm. Hg(II) extracted from the aqueous phase into the organic phase gives ML, whose absorbance maximum is at 388 nm. By raising the pH of the aqueous phase, the equilibria above are driven to the right and formation of ML is favored. (At low pH, H^+ competes with Hg(II) for the ligand.) An isosbestic point is observed when there are only two predominant species and they have a constant total concentration. The isosbestic point suggests that H_2L and ML are the only significant species in the organic phase and, therefore, that very little of the crown ether goes into the aqueous phase at any pH. If the crown ether dissolved in the aqueous phase, its concentration in the organic phase would change and there would not be an isosbestic point.

S24-1. $I = 100 \left[6 + (7 - 6) \dfrac{\log(6.45) - \log(6.12)}{\log(7.20) - \log(6.12)} \right] = 632$

S24-2. (a) hexane < benzene < heptane < nitropropane < pyridine < octane < nonane

(b) hexane < heptane < benzene < octane < pyridine < nitropropane < nonane

(c) hexane < heptane < octane < nonane < benzene < pyridine < nitropropane

S24-3. $TZ = \dfrac{18.5 - 14.3}{0.5 + 0.5} - 1 = 3.2$