

ATOMIC SPECTROSCOPY

S21-1. Calculate the Doppler linewidths for the 248-nm line of Fe and for the 254-nm line of Hg, each at 3 000 K and 6 000 K.

S21-2. The first excited state of Cu is reached by absorption of 327 nm light.

(a) What is the energy difference (kJ/mol) between the ground and excited states?

(b) The relative degeneracies are $g^*/g_0 = 3$ for Cu. What is the ratio N^*/N_0 at 2 400 K?

(c) By what percentage will the fraction in part b be changed by a 15 K rise in temperature?

(d) What will be the ratio N^*/N_0 at 6 000 K?


S21-3. A sample containing 23.6 $\mu\text{g Mo/mL}$ gave an absorbance of 0.025. If "sensitivity" is defined as the concentration of Mo giving 99% transmittance, estimate the sensitivity for Mo.

S21-4. A series of Ca and Cu samples was run to determine the atomic absorbance of each element.

Ca($\mu\text{g/mL}$)	$A_{422.7}$	Cu ($\mu\text{g/mL}$)	$A_{324.7}$
1.00	0.086	1.00	0.142
2.00	0.177	2.00	0.292
3.00	0.259	3.00	0.438
4.00	0.350	4.00	0.579

(a) Find the average relative absorbance ($A_{422.7}/A_{324.7}$) produced by equal concentrations ($\mu\text{g/mL}$) of Ca and Cu.

(b) Copper was used as an internal standard in a Ca determination. A sample known to contain 2.47 $\mu\text{g Cu/mL}$ gave $A_{422.7} = 0.218$ and $A_{324.7} = 0.269$. Calculate the concentration of Ca in micrograms per milliliter.

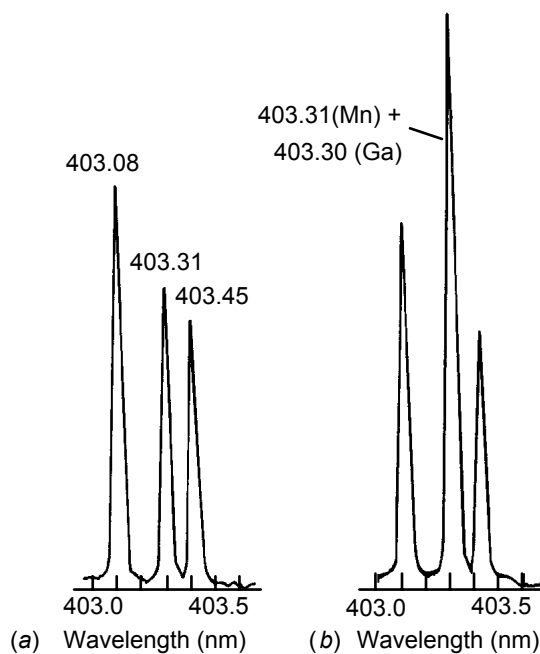
S21-5.  The following nonlinear calibration data were obtained in an atomic absorption experiment.

(a) Use the quadratic equation spreadsheet in Supplementary Problem S17-33 to find the best fit to the data in the form $y = A + Bx + Cx^2$.

- (b) Use the method of Box 5-1 to estimate the concentration (and its uncertainty) of an unknown with a signal intensity of 344.0 ± 2.2 .

Concentration of standard ($\mu\text{g/mL}$)	Signal intensity (arbitrary meter units)
0	0.1
1.00	49.0
2.00	96.5
3.00	142.4
4.00	183.3
5.00	222.1
6.00	258.9
7.00	293.0
8.00	321.2
9.00	350.8
10.0	377.8

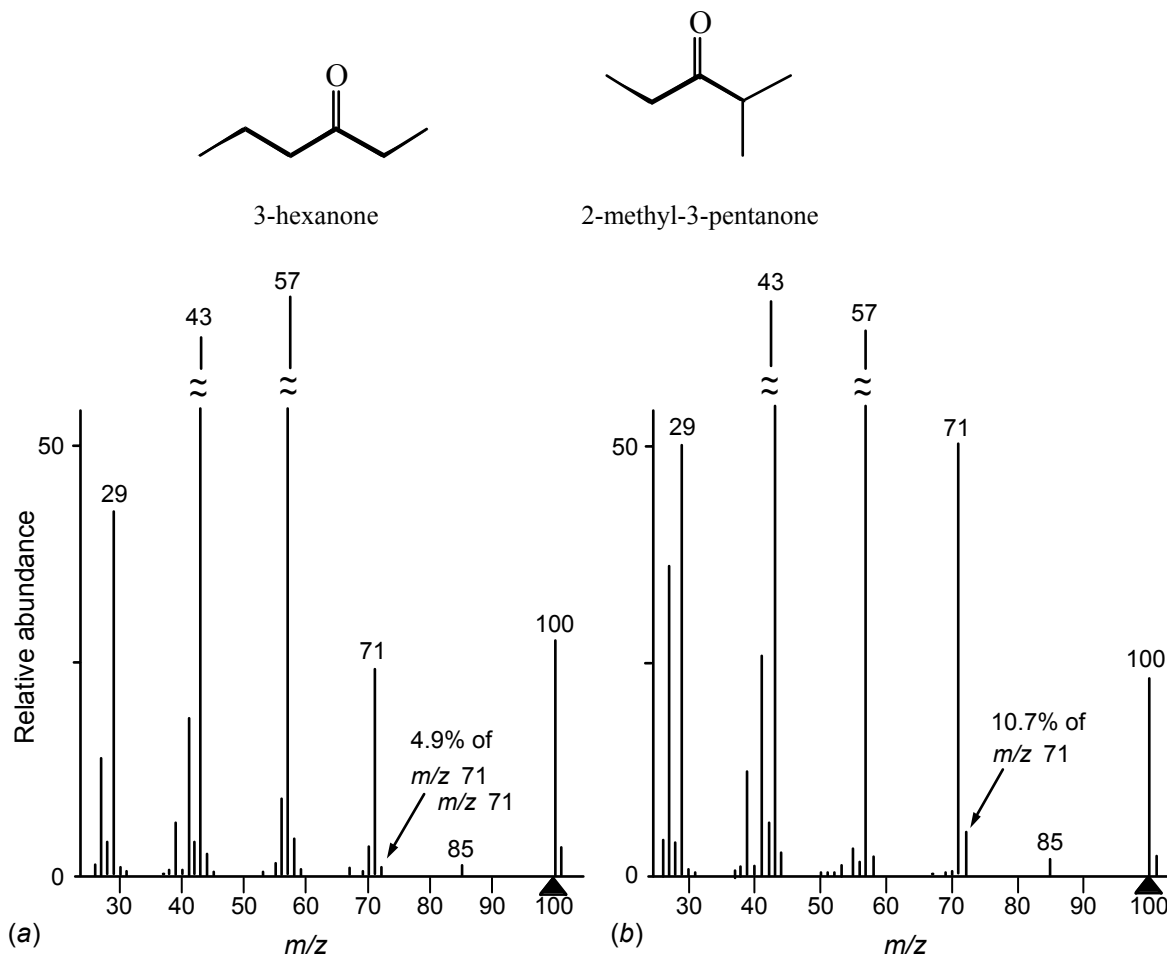
- S21-6.** In the excitation spectra below, the Ga line is within 0.2 nm of all three Mn lines. Explain why there is no spectral interference by Ga in the laser atomic fluorescence excitation analysis of Mn, even though the detector monochromator bandwidth is 1.0 nm.



Fluorescence excitation of solution containing (a) $1 \mu\text{g Mn/mL}$ and (b) $1 \mu\text{g Mn/mL}$ plus $5 \mu\text{g Ga/mL}$. [S. J. Weeks, H. Haraguchi, and J. D. Winefordner, *Anal. Chem.* **1978**, *50*, 360.]

MASS SPECTROSCOPY

- S22-1.** (a) The two mass spectra belong to the isomers of $C_6H_{12}O$ below. The peak at m/z 71 is $C_4H_7O^+$, which comes from loss of an ethyl group (CH_3CH_2 , 29 Da). What is the expected intensity of m/z 72 relative to that of m/z 71?



Mass spectra of isomeric ketones with the composition $C_6H_{12}O$ from NIST/EPA/NIH Mass Spectral Database.

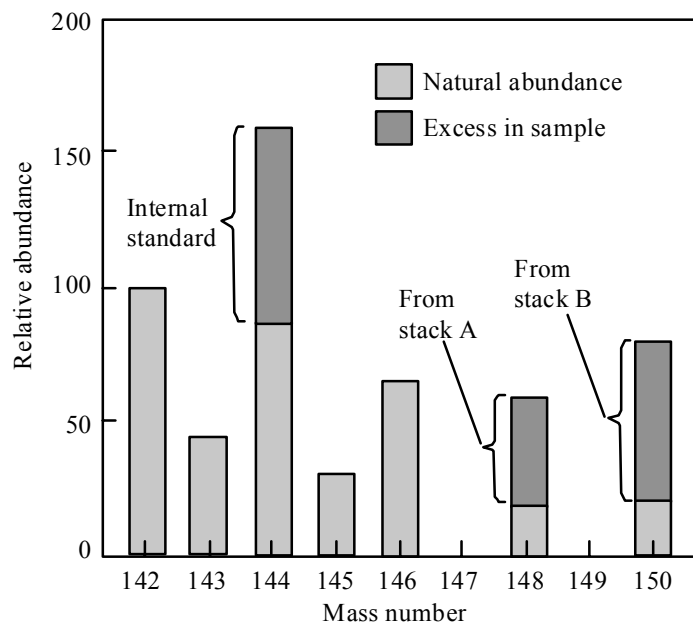
- (b) There is extra intensity at m/z 72 in spectrum (b) beyond what is expected for the isotopic partner of m/z 72. Assuming that the extra intensity is real, explain how to tell which compound corresponds to spectrum

- S22-2.** *Isotope patterns.* Predict the ratio $^{12}C_3H_6 : ^{12}C_2^{13}CH_6 : ^{12}C^{13}C_2H_6 : ^{13}C_3H_6$ for cyclopropane from the expansion of $(a + b)^3$.

Note that $(a + b)^n = a^n + na^{n-1}b + \frac{n(n-1)}{2!} a^{n-2}b^2 + \frac{n(n-1)(n-2)}{3!} a^{n-3}b^3 + \dots$

S22-3. *Isotopic tracers in environmental analysis.* Stable isotopes of lanthanide elements can be used as *tracers* to tag and study the spread of microscopic particles (called fly ash) from smokestacks. [J. M. Ondov and W. R. Kelly, "Tracing Aerosol Pollutants With Rare Earth Isotopes," *Anal. Chem.* **1991**, *63*, 691A.] The goal in this problem is to determine what fractions of fly ash collected at a university campus came from smokestack A (15 km to the south) and from smokestack B (30 km to the west). The figure and table show the natural abundance of neodymium isotopes and the abundance in the experimental sample. Here is how the experiment was done:

1. Neodymium was introduced into each smokestack by thermal decomposition of volatile Nd compounds. Ash emerging from smokestack A contained 10.2 ppm (10.2 $\mu\text{g/g}$) of added ^{148}Nd and ash from smokestack B had 11.4 ppm of added ^{150}Nd .
2. Airborne dust was collected at the university campus by sucking a large volume of air through a filter that trapped particles larger than 0.3 μm . The dust (1.00 g) was dissolved (digested) in HF/HNO_3 with microwave heating. A solution containing 0.100 μg of *internal standard*, ^{144}Nd , was then added to the dissolved dust.
3. For mass spectrometric analysis, it is necessary to isolate the Nd and to remove 99.995% of any samarium from the Nd, because Sm has some isotopes with the same masses as Nd isotopes. Rare earth ions were separated from other components of the dust by chromatography on AG50-X8 cation-exchange resin (H^+ form) eluted with 6 M HCl. The rare earth fraction of eluate was then chromatographed on AG50-X8 resin (NH_4^+ form) eluted with 0.225 M 2-methyl lactic acid to separate Nd(III) from Sm(III).
4. A mass spectrum of the purified Nd was obtained by aspirating eluate into an inductively coupled plasma interfaced to a mass spectrometer.



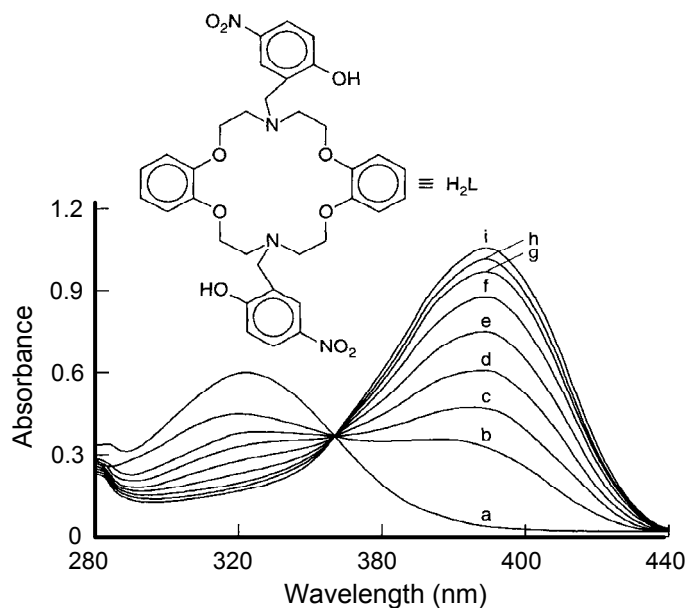
Isotope	Atomic mass	Natural abundance	Abundance in sample
^{142}Nd	141.907 5	100.00	100.00
^{143}Nd	142.909 6	44.89	44.89
^{144}Nd	143.909 9	87.97	160.53
^{145}Nd	144.912 2	30.62	30.62
^{146}Nd	145.912 7	64.99	64.99
^{148}Nd	147.916 5	21.14	59.87
^{150}Nd	149.920 7	20.73	80.10

- (a) The experimental sample contains some amount of Nd found in dust in the air and is enriched in ^{144}Nd (the internal standard), ^{148}Nd (from smokestack A), and ^{150}Nd (from smokestack B). Subtract the natural abundance of each isotope from the experimental abundance to find the excess ^{144}Nd , ^{148}Nd , and ^{150}Nd . The mass spectral signal is proportional to the number of ions of each isotope reaching the detector. Based on the known quantity of ^{144}Nd added to the dust sample, how many micrograms of ^{148}Nd and ^{150}Nd were in 1.00 g of dust?
- (b) How many milligrams of ash from smokestack A and how many milligrams from smokestack B were in the 1.00-g dust sample?
- (c) Explain the purpose of the two ion-exchange separation steps and rationalize (make up a plausible reason) the two choices of ion-exchange conditions.

- S23-1.** (a) What volume of chloroform is needed to extract 99.5% of a solute from 100 mL of water, if the partition coefficient is $C_{\text{CHCl}_3}/C_{\text{H}_2\text{O}} = 610$?
- (b) What will be the total volume of chloroform needed to remove 99.5% of the solute in four equal extractions instead?
- S23-2.** The acid HA ($K_a = 4.2 \times 10^{-4}$) equilibrates between water and ether.
- (a) Define the distribution coefficient (D) and the partition coefficient (K) for this system.
- (b) Calculate D at pH 4.00 if $K = 92$.
- (c) Will D be greater or less at pH 3.50 than at pH 4.00? Explain why.
- (d) At what pH will D be unity?
- S23-3.** The chromatogram in Problem 23-44 has a peak for isooctane at 13.81 min. The elution time for unretained solute is 1.06 min and the column is 30.0 m long.
- (a) Find the adjusted retention time and capacity factor for isooctane.
- (b) Measuring $w_{1/2}$, find the number of theoretical plates for this peak.
- (c) Measure the width (w) at the base of the peak to find the number of plates.
- (d) Using the answer from part (c), find the plate height.
- (e) The open tubular column has an inner diameter of 524 μm . Given that the linear flow rate is 30.0 m/1.06 min, find the volume flow rate.
- S23-4.** (a) How many theoretical plates produce a chromatography peak eluting at 12.83 min with a width at the base of 18.4 s?
- (b) If the length of the column is 15.8 cm, find the plate height.
- S23-5.** (a) A chromatography column with a length of 50.6 cm and inner diameter of 19.2 mm is packed with a stationary phase that occupies 57.4% of the volume. Find the linear flow rate (cm/min) if the volume flow rate is 2.22 mL/min.
- (b) Find the retention time for a solute with a capacity factor of 8.04.
- S23-6.** Two compounds with capacity factors of 5.00 and 5.10 are separated on a column with a plate height of 155 μm . What length of column is required to give a resolution of 1.00? Of 2.00?

- S23-7.** Consider the peaks for *n*-heptane and *p*-difluorobenzene in the chromatogram in Problem 23-44. The elution time for unretained solute 1.06 min. The open tubular column is 30.0 m in length and 0.530 mm in diameter, with a 3.0 μm thick layer of stationary phase on the inner wall.
- Find the adjusted retention times and capacity factors for both compounds.
 - Find the relative retention.
 - Measuring $w_{1/2}$ on the chromatogram, find the number of plates (N_1 and N_2) and the plate height for these two compounds.
 - Measuring the width (w) at the baseline on the chromatogram, find the number of plates for these two compounds.
 - Use your answer to part d to find the resolution between the two peaks.
 - Using the number of plates ($N = \sqrt{N_1 N_2}$), with values from part (d), the relative retention, and the capacity factors, calculate what the resolution should be and compare your answer to the measured resolution in part e.
 - What fraction of the time does heptane spend in the stationary phase?
- S23-8.** A 3.00-cm-diameter column with a length of 32.6 cm gives adequate resolution of a 72.4 mg mixture of unknowns, initially dissolved in 0.500 mL. If you wish to scale down to 10.0 mg of the same mixture with minimum use of chromatographic stationary phase and solvent, what length and diameter column would you use? In what volume would you dissolve the sample?
- S23-9.** Potassium ion diffuses down a steady concentration gradient of $dc/dx = 3.4 \text{ M/cm}$. If the diffusion coefficient is $2.0 \times 10^{-9} \text{ m}^2/\text{s}$, find the number of ions crossing a 1 cm^2 area in 5.5 s.

S23-10. The figure shows spectral changes in a 25- μM solution of a crown ether (designated H_2L) in 1,2-dichloroethane solvent before (a) and after (b-i) extracting $\text{Hg}(\text{II})$ from aqueous 1.0 mM $\text{Hg}(\text{II})$ solutions adjusted to pH 2.0 (b), 2.2 (c), 2.5 (d), 2.7 (e), 3.0 (f), 3.2 (g), 3.4 (h), and 3.9 (i). H_2L is soluble in 1,2-dichloroethane but has negligible solubility in water. The metal complex HgL has no net charge.



- (a) Draw the structures of H_4L^{2+} and L^{2-} .
- (b) Explain the spectral changes in the organic phase. Which species is responsible for the absorbance maximum near 320 nm? Which is responsible for the maximum near 388 nm? Why does the 388-nm peak grow as the pH of the extracted aqueous solution is raised? What does the isosbestic point at 348 nm tell you? Make a diagram showing the species and acid/base and complex formation equilibria in each phase. Use the abbreviations H_4L^{2+} , H_3L^{2+} , etc.

S24-1. Retention times in a gas chromatogram are 1.21 min for CH₄, 7.33 min for hexane, 7.66 min for unknown, and 8.41 min for heptane. Find the Kovats retention index for the unknown.

S24-2. Referring to Table 24-3, what is the order of elution of the hexane, heptane, octane, nonane, benzene, nitropropane and pyridine from

(a) (diphenyl)_{0.05}(dimethyl)_{0.95}polysiloxane

(b) (cyanopropylphenyl)_{0.14}(dimethyl)_{0.86}polysiloxane

(c) (biscyanopropyl)_{0.9}(cyanopropylphenyl)_{0.1} polysiloxane

S24-3. *Separation number.* In chromatography, the separation number for peaks 1 and 2 is defined as

$$\text{separation number} = TZ = \frac{t_{r2} - t_{r1}}{w_2 + w_1} - 1$$

where t_{ri} is the retention time of peak i and w_i is the width of peak i at half-height. (The symbol TZ comes from the German word *trennzahl*, meaning "separation number.") If all peak widths are equal, TZ tells us how many peaks can be placed between peaks 1 and 2, with a resolution (Figure 23-10) of 1.17 between all peaks. In Figure 23-7, suppose that $t_r(\text{octane}) = 14.3$ min, $t_r(\text{nonane}) = 18.5$ min, and $w = 0.5$ min for both peaks. Calculate the separation number. Does it look as though this many peaks can be placed between octane and nonane in Figure 23-7?