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CHAPTER 1

1. *The chemical characterization of matter.*
2. *Qualitative analysis deals with the identification of the presence of a particular substance or substances in a sample. Quantitative analysis deals with determining how much is present.*
3. *Define the problem, obtain a representative sample, dry the sample if required, measure its weight or volume, dissolve the sample and prepare the solution for the measurement step, measure the analyte, calculate the amount or concentration of analyte in the sample, and compute the precision of the analysis.*
4. *A sample represents the material to be analyzed. The analyte is the substance to be measured or determined. Hence, we determine the analyte by analyzing the sample.*
5. *A blank consists of all chemicals used in an analysis, run through the analytical procedure, to determine impurities that might be added to the analytical result, and which must be subtracted.*
6. *Gravimetry, volumetric analysis, instrumental analysis, kinetic methods of analysis, and combinations of these*
7. *Precipitation (gravimetry), chromatography, solvent extraction, volatilization (distillation)*
8. *The measurement of a physical property of the sample*
9. *A calibration curve represents an instrument (detector) response as a function of concentration. It may be a linear or a nonlinear response. An unknown analyte concentration in a sample solution is determined by comparison of the response with the calibration curve.*

CHAPTER 3

From Equation 3.25,

$$s_m = \sqrt{(0.01_0)/(30.00 - 100.00/4)} = \pm 0.004_5 \text{ absorbance/ppm}$$

$$m = 0.205 \pm 0.004$$

From Equation 3.26,

$$s_b = 0.01_0 \sqrt{30.00/[4(30.00) - 100.00]} = \pm 0.01_2 \text{ absorbance}$$

$$b = 0.00_0 \pm 0.01_2$$

The phosphorus concentration in the urine sample is given by

$$x = [(0.62_5 \pm 0.01_0) - (0.00_0 \pm 0.00_1)] / (0.205 \pm 0.004) = 3.05 \pm ?$$

$$s_{num} = \sqrt{(\pm 0.01_0)^2 + (\pm 0.00_1)^2} = \pm 0.01_0$$

$$(s_{div})_{rel} = \sqrt{(\pm 0.01_0/0.62_5)^2 + (\pm 0.004/0.205)^2} = \pm 0.02_5$$

$$s_{div} = 3.05 (\pm 0.02_5) = \pm 0.07_6$$

$$x = 3.05 \pm 0.08 \text{ ppm P in urine}$$

40. % yeast extract (x_i)

Toxin, mg (y_i)

1.000
0.200
0.100
0.010
0.001

0.487
0.260
0.195
0.007
0.002

$\Sigma 1.311$

$\Sigma 0.951$

$$\bar{x}_i = 1.311/5 = 0.262$$

$$\bar{y}_i = 0.951/5 = 0.190$$

$$\Sigma x_i^2 = 1.050$$

$$\Sigma y_i^2 = 0.343$$

$$n = 5$$

$$\Sigma x_i y_i = 0.559$$

CHAPTER 3

$$r = (n \Sigma x_i y_i - \Sigma x_i \Sigma y_i) / \{ [n \Sigma x_i^2 - (\Sigma x_i)^2] [n \Sigma y_i^2 - (\Sigma y_i)^2] \}^{1/2}$$

$$= (2.795 - 1.247) / \{ [(5.250 - 1.719)(1.715 - 0.904)] \}^{1/2} = 0.915 \text{ (See CD)}$$

$$r^2 = 0.84$$

∴ There is a good correlation between yeast extract concentration and the amount of toxin produced.

Toxin, mg (x_i)	Dry weight (y_i)
0.487	116
0.260	53
0.195	37
0.007	8
0.002	1
0.951 = Σx_i	215 = Σy_i

$$\bar{x}_i = 0.951 / 5 = 0.190$$

$$\bar{y}_i = 215 / 5 = 43$$

$$\Sigma x_i^2 = 0.343$$

$$\Sigma y_i^2 = 17699$$

$$\Sigma x_i y_i = 77.5$$

$$r = (387.5 - 204.5) / \sqrt{(1.715 - 0.904)(88495 - 46225)} =$$

$$(183.0) / \sqrt{(0.811)(42270)} = (183.0) / (185) = 0.989; r^2 = 0.978 \text{ (See CD)}$$

∴ There is a strong correlation between fungal dry weight and amount of toxin produced.

42. Enzyme method (See CD for spreadsheet calculations)

Enzyme method (x_i)	Colorimetric method (y_i)	D_i	$D_i - D$	$(D_i - D)^2$	$x_i y_i$	x_i^2	y_i^2
305	300	5	1	1	91,500	93,025	90,000
385	392	-7	-11	121	150,920	148,225	153,664
193	185	8	4	16	35,705	37,249	34,225
162	152	10	6	36	24,624	26,244	23,104
478	480	-2	-6	36	229,440	228,484	230,400
455	461	-6	-10	100	209,755	207,025	212,521
238	232	6	2	4	55,216	56,644	53,824
298	290	8	4	16	86,420	88,804	84,100
408	401	7	3	9	163,608	166,464	160,801
323	315	8	4	16	101,745	104,329	99,225
$\Sigma 3,245$	$\Sigma 3,208$	$\Sigma 37$		$\Sigma 355$	$\Sigma 1,148,933$	$\Sigma 1,156,493$	$\Sigma 1,141,864$

CHAPTER 11

3. From the appendix, K_{sp} of $AgIO_3 = 3.1 \times 10^{-8}$ and K_a of $HIO_3 = 2 \times 10^{-1}$. The equilibria are



$$K_{sp} = [Ag^+][IO_3^-] = [Ag^+]C_{HIO_3}\alpha_1 \quad (3)$$

where α_1 is the fraction of the total iodate (C_{HIO_3}) that exists as IO_3^- .

Then,

$$K_{sp}/\alpha_1 = K_{sp}' = [Ag^+]C_{HIO_3} = s^2 \quad (4)$$

where s is the water solubility. First calculate α_1 .

$$C_{HIO_3} = [HIO_3] + [IO_3^-] \quad (5)$$

But, $[HIO_3] = [H^+][IO_3^-]/K_a$. So,

$$C_{HIO_3} = [H^+][IO_3^-]/K_a + [IO_3^-] \quad (6)$$

from which

$$1/\alpha_1 = C_{HIO_3}/[IO_3^-] = [H^+]/K_a + 1 = 1.5 \text{ (at } 0.100 \text{ M acid)}$$

$$K_{sp}' = (3.1 \times 10^{-8})(1.5) = s^2$$

$$s = 2.1 \times 10^{-4} \text{ M} = [Ag^+] = C_{HIO_3}$$

(This is only increased from $1.8 \times 10^{-4} \text{ M}$ in the absence of acid, since HIO_3 is a fairly strong acid.)

$$\alpha_1 = 0.67; \alpha_0 = 1 - 0.67 = 0.33$$

$$\therefore [IO_3^-] = (2.1 \times 10^{-4})(0.67) = 1.5 \times 10^{-4} \text{ M}$$

CHAPTER 11

4. From the appendix, K_{sp} of $CaF_2 = 4.0 \times 10^{-11}$ and K_a of $HF = 6.7 \times 10^{-4}$. The equilibria are



$$K_{sp} = [Ca^{2+}][F^-]^2 = [Ca^{2+}]C_{HF}^2\alpha_1^2 \quad (3)$$

(since $[F^-] = C_{HF}\alpha_1$.)

$$K_{sp}/\alpha_1^2 = K_{sp}' = [Ca^{2+}]C_{HF}^2 = (s)(2s)^2$$

As in the preceding problem,

$$1/\alpha_1 = [H^+]/K_a + 1 = 1.51 \times 10^2 \text{ (At } 0.100 \text{ M acid)}$$

$$K_{sp}' = (4.0 \times 10^{-11})(1.51 \times 10^2)^2 = (s)(2s)^2$$

$$s = 6.1 \times 10^{-3} \text{ M} = [Ca^{2+}] = 1/2 C_{HF}$$

$$\alpha_1 = 6.62 \times 10^{-3}; \alpha_0 = 1 - 6.62 \times 10^{-3} = 0.993$$

$$\text{Since } C_{HF} = 2 \times 6.1 \times 10^{-3} = 1.21 \times 10^{-2} \text{ M,}$$

$$[HF] = (1.21 \times 10^{-2})(0.993) = 1.20 \times 10^{-2} \text{ M}$$

$$[F^-] = (1.21 \times 10^{-2})(6.62 \times 10^{-3}) = 8.01 \times 10^{-5} \text{ M}$$

Essentially all of the fluoride exists as HF and its concentration is twice that of the calcium. About 12% of the HCl was consumed in forming HF. Recalculation (reiteration) using 0.088 M HCl would result in a minor correction in the calculation ($s = 5.6 \times 10^{-3} \text{ M}$).

5. From the appendix, K_{sp} of $PbS = 8 \times 10^{-28}$ and $K_{a1} = 9.1 \times 10^{-8}$,

$K_{a2} = 1.2 \times 10^{-15}$ for H_2S . The equilibria are:



Handwritten notes on the right side of the page:

$$\alpha_1 = \frac{[F^-]}{C_{HF}}$$

$$K_a = \frac{[H^+][F^-]}{[HF]} = K_a$$

$$\alpha_1 = \frac{K_a}{K_a + [H^+]}$$

Handwritten notes on the left side of the page:

$$K_a = \frac{[H^+][IO_3^-]}{[HIO_3]}$$

$$1/\alpha_1 = \frac{[HIO_3]}{[IO_3^-]} = \frac{[H^+]}{K_a} + 1$$

CHAPTER 16

1. In the far infrared region, quantized rotational energy transitions occur in absorption. In the mid-infrared region, these are superimposed on quantized vibrational transitions. In the visible and ultraviolet regions, quantized electronic transitions occur in addition to the rotational and vibrational transitions.

2. Paired nonbonding outershell electrons (n electrons) and pi (π) electrons in double or triple bonds

3. Transitions to a π^* antibonding orbital ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions). At wavelengths less than 200 nm, $n \rightarrow \sigma^*$ transitions may also occur. $\pi \rightarrow \pi^*$ transitions are the most intense ($\epsilon = 1000 - 100,000$ vs. 1000 for $n \rightarrow \pi^*$).

Examples are: $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ - ketones

$n \rightarrow \pi^*$ - ethers, disulfides, alkyl halides, etc. at < 200 nm.

4. There must be a change in the dipole moment of the molecule.

5. Stretching and bending.

6. Absorption in the near-IR region (0.75 - 2.5 μm) is the result of vibrational overtones which are weak and featureless. They are due mainly to C-H, O-H and N-H band stretching and bending motions. NIR is useful for analyzing "neat", i.e., undiluted, samples, and as such, is useful for non-destructive analysis.

7. chromophore - an absorbing group

auxochrome - enhances absorption by a chromophore or shifts its wavelength of absorption

bathochromic shift - λ_{max} shifted to longer wavelength

hypsochromic shift - λ_{max} shifted to shorter wavelength

hyperchromism - absorption intensity increased

hypochromism - absorption intensity decreased

8. (a) $\text{CH}_2=\text{CHCO}_2\text{H}$ (c)

(b) $\text{CH}_3\text{C}=\text{C}=\text{CCH}_3$



9. (a) Bathochromic shift, increased absorption

(b) bathochromic shift, increased absorption

(c) no shift, but increased absorption

CHAPTER 16

10. They are highly conjugated and in alkaline solution loss of a proton affects the electron distribution and hence the wavelength of absorption.

11. Excitation of the metal ion or of the ligand, or via a charge transfer transition (movement of electrons between the metal ion and ligand).

12. absorption = fraction of light absorbed = $1 - (P/P_0)$

absorbance = $-\log (P/P_0)$ and is proportional to the concentration.

percent transmittance = percent of light transmitted = $(P/P_0) \times 100$

transmittance = fraction of light transmitted = (P/P_0)

13. Absorptivity is the proportionality constant, a , in Beer's law, when the concentration units are expressed in g/L. Molar absorptivity, ϵ , is the proportionality constant when the concentration is expressed in mol/L and is equal to $a \times \text{f.w.}$

14. At an absorption maximum, the average absorptivity of the band of wavelengths passed remains more nearly constant as the concentration is changed. The steepness of an absorption shoulder increases as the concentration increases, with the result that the average absorptivity of the wavelengths passed may change.

15. Ultraviolet region: the solvents listed in Table 16.3.

Visible region: any colorless solvent, including those listed in Table 14.3.

Infrared region: carbon tetrachloride or carbon disulfide to cover the region of 2.5-15 μm .

16. An isobestic point is the wavelength at which the absorptivities of two species in equilibrium with each other are equal, i.e., where their absorption spectra overlap. The absorbance at this wavelength remains constant as the equilibrium is shifted, e.g., by varying pH.

17. Deviations from Beer's law can be caused by chemical equilibria in which the equilibria are concentration-dependent. These can usually be minimized by suitable buffering. Other deviations can be caused by instrumental limitations, particularly by the fact that a band of wavelengths is passed by the instrument, rather than monochromatic light. These are apparent deviations, which can be minimized or corrected for. Real deviations from Beer's law occur when the concentration is so high that the index of refraction of the solution is changed, or when the index of refraction of the sample solvent is different from that of the reference solvent.

13. 2-D PAGE is 2-dimensional polyacrylamide gel electrophoresis. It separates proteins, first by isoelectric focusing based on charge, and then by gel electrophoresis based on molecular size.

14. MALDI-TOF is matrix assisted laser desorption ionization – time-of-flight mass spectrometry. It is a soft ionization technique for large molecules that produces single peaks from singly charged molecules. It is used to identify the masses of peptides in protein digestions mixtures.

15. Theoretical protein amino acid fingerprints are constructed from a combination of a knowledge of the gene codons and a large protein database. The experimental fingerprint is compared with the theoretical ones to identify the protein from fingerprints of as few as 5 or 6 peptides.

16. The first sequence is:

GATCCAATTGCAT

The second is:

GATCCACATTCCGTA

They overlap as follows:

GATCCAATTGCAT
GATCCACATTCCGTA

The sequence is:

ATTGATTCCGTA

1. Vacuum source, meter, collector
2. Impingers are used to sample aerosols in air.
3. Acidity, alkalinity, BOD, DO, conductivity, CO_2 , Cl_2 , F^- , NH_3 , PO_4^{3-} , NO_3^- , SO_3^{2-} , metal ions, etc.
4. Protect from heat and light.
5. pH, dissolved gases, temperature
6. For 1 mole, $V = (1 \text{ mol})(0.082 \text{ L atm/K mol})(293 \text{ K})/(1 \text{ atm}) = 24.0 \text{ L}$
 $(2.8 \times 10^{-6} \text{ L/L}_{\text{air}})/(24.0 \text{ L/mol}) = 1.17 \times 10^{-7} \text{ mol/L}_{\text{air}}$
 $(1.17 \times 10^{-7} \text{ mol/L}_{\text{air}})(28.0 \text{ g/mol}) = 3.3 \times 10^{-6} \text{ g/L}_{\text{air}}$
7. $0.50 \text{ } \mu\text{g/L} = 0.50 \text{ ppb} = 500 \text{ ppt}$
 $(97/128) \times 500 \text{ ppt} = 380 \text{ ppt toluene.}$