
Analytical chemistry

Answers to worked examples

WE 12.1 What's in a sample for analysis?

Identify the analyte(s) and the matrix in each of the following systems:

- (a) iron in iron ore from a mine;
- (b) pesticide residues in fruit.

Strategy

Consider which of the constituents is the analyte. The remainder will be the residue.

Solution

- (a) Iron in iron ore from a mine

The analytes are the iron compounds (such as oxides and sulfides) and the matrix is all the other material that is dug out of the ground. Obtaining a representative sample will not be easy since the exact composition of the iron ore may vary widely even within a single mine. Minerals containing other metals will also occur in the ground so the analytical method must be specific for iron and not respond to the other metals.

- (b) Pesticide residues in fruit

The analyte is the pesticide while the remainder of the fruit is the matrix. Normally any pesticide is present in very concentrations. A single piece of fruit may not be representative of the whole batch. The pesticide may be present only in the skin of the fruit or it may be difficult to separate from the matrix if it interacts strongly.

WE 12.3 Spectrophotometric analysis

0.0277 g of KMnO_4 were dissolved in 250 cm^3 of water. What would be the absorbance of this solution at 520 nm?

Strategy

Calculate the amount of KMnO_4 dissolved in the water from the molar mass and hence determine the concentration of the solution.

Solution

The molar mass of KMnO_4 is

$$M = [39.10 + 54.94 + (4 \times 16.00)] = 158.04 \text{ g mol}^{-1}$$

Thus, the amount of KMnO_4 present is, from Equation 1.2

$$n = m/M = 0.0277 \text{ g} / 158.04 \text{ g mol}^{-1} = 1.75 \times 10^{-4} \text{ mol}$$

and by rearranging Equation 1.9, the concentration is

$$\begin{aligned} c &= n/V \\ &= 1.75 \times 10^{-4} \text{ mol} / 250 \text{ cm}^3 \\ &= 1.75 \times 10^{-4} \text{ mol} / 250 \times 10^{-3} \text{ dm}^3 \\ &= 7.0 \times 10^{-4} \text{ mol dm}^{-3} \end{aligned}$$

where it is important to remember to convert the volume from units of cm^3 to dm^3 in order that the final concentration is expressed in the conventional units of mol dm^{-3} . Using the Beer Lambert Law, Equation 11.8, the absorbance is thus

$$\begin{aligned} A &= \epsilon \times c \times l = 1920 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \times 7.0 \times 10^{-4} \text{ mol dm}^{-3} \times 1.0 \text{ cm} \\ &= 1.34 \end{aligned}$$

WE 12.5 Using the standard addition method to measure concentrations

What will be the absorbance of a solution of Zn^{2+} ions with a concentration of 1.0 $\mu\text{mol dm}^{-3}$ measured under the same conditions as used in the question above?

Strategy

Calculate the mass concentration of the solution from the molar concentration and the molar mass of zinc ions. Determine the absorbance as a proportion of that given in the Worked Example for a concentration of $10 \mu\text{g dm}^{-3}$.

Solution

Under these conditions, an absorbance of 0.280 corresponds to a concentration of $10.0 \mu\text{g dm}^{-3}$

The molar mass of zinc atoms is

$$M = 65.41 \text{ g mol}^{-1}$$

Thus, rearranging Equation 1.8, shows that a molar concentration of $1.0 \mu\text{mol dm}^{-3}$ is equivalent to a mass concentration of

$$c \times M = 1.0 \times 10^{-6} \text{ mol dm}^{-3} \times 65.41 \text{ g mol}^{-1} = 6.54 \mu\text{g dm}^{-3}$$

If a concentration of $10 \mu\text{g dm}^{-3}$ corresponds to an absorbance of 0.280, then a concentration of $6.54 \mu\text{g dm}^{-3}$ is equivalent to

$$A = \frac{6.54 \mu\text{g dm}^{-3}}{10 \mu\text{g dm}^{-3}} \times 0.280 = 1.83$$

Answers to boxes

Box 12.1 Analysing food contaminants

Convert the detection limit of the above analysis, 5 mg kg^{-1} to units of: (a) mg g^{-1} (b) $\mu\text{g g}^{-1}$ and (c) ppm (by mass). (Concentrations in parts per million, ppm, are defined in Box 1.5, p.37.)

Strategy

Use the SI prefixes in Table 1.3 to express the concentrations in terms of the various units.

Solution

(a)

$$\begin{aligned} 5 \text{ mg kg}^{-1} &= 5 \text{ mg} / 1 \text{ kg} \\ &= 5 \text{ mg} / 10^3 \text{ g} \\ &= 5 \times 10^{-3} \text{ mg g}^{-1} \\ &= 0.005 \text{ mg g}^{-1} \end{aligned}$$

(b)

$$\begin{aligned} 5 \text{ mg kg}^{-1} &= 5 \text{ mg} / 1 \text{ kg} \\ &= 5 \times 10^3 \mu\text{g} / 10^3 \text{ g} \\ &= 5 \mu\text{g g}^{-1} \end{aligned}$$

(c)

$$\begin{aligned} 5 \text{ mg kg}^{-1} &= 5 \text{ mg} / 1 \text{ kg} \\ &= 5 \times 10^{-3} \text{ g} / 10^3 \text{ g} \\ &= 5 \times 10^{-6} \\ &= 5 \text{ ppm} \end{aligned}$$

Box 12.3 Monitoring PCBs in the environment

Imagine that, rather than a standard sample, Figure 1 showed a chromatogram of an unknown sample. Suggest how each compound could be identified.

Strategy

Consider how each of the components with the various retention times may be identified.

Solution

The usual method for identifying compounds in gas chromatography is to compare their retention times with known samples run under identical conditions. However, a better method is to couple the gas chromatograph to a spectrometer (e.g. NMR, mass spectrometer) which can record a spectrum of the compound as it emerges from the chromatograph.

Box 12.7 A pulse oximeter

Use the absorbance spectra in Figure 1 to explain why deoxygenated blood in the veins looks bluer than arterial blood.

Strategy

Consider how the absorption spectra of oxygenated and deoxygenated haemoglobin differ at long wavelengths.

Solution

The spectra show that the absorbances of both forms of haemoglobin are similar at the short-wavelength blue end of the spectrum. However, the absorption spectra of the two do differ at the long-wavelength, red end of the spectrum. At a wavelength from 600–700 nm, in the red region, the deoxygenated form has a higher absorbance. It therefore transmits less red light and so appears bluer.

Answers to end of chapter questions

1. 0.5850 g of NaCl were dissolved in 100.0 cm³ of water. 10.0 cm³ of this solution were made up with water to 250.0 cm³. Calculate the concentration of the resulting solution in:
- (a) mol dm⁻³
 (b) mol m⁻³
 (c) mg dm⁻³
 (d) ppm (by mass).

Strategy

Determine the mass concentration of the final, diluted solution. Calculate the molar mass of NaCl and hence use Equation 1.8 to calculate the molar concentration. Use the SI prefixes in Table 1.3 to convert between units.

Solution

- (a) The mass concentration of the initial solution is

$$m/V = 0.5850 \text{ g}/100.0 \text{ cm}^3 = 5.85 \times 10^{-3} \text{ g cm}^{-3}$$

By extracting 10 cm³ of this solution and making up to 250 cm³, the mass concentration is reduced by a factor of 25 and so is

$$5.85 \times 10^{-3} \text{ g cm}^{-3}/25 = 2.34 \times 10^{-4} \text{ g cm}^{-3}$$

The molar mass of sodium chloride is

$$M = (22.99 + 35.45) \text{ g mol}^{-1} = 58.44 \text{ g mol}^{-1}$$

Thus, from Equation 1.8, the molar concentration is

$$\begin{aligned} 2.34 \times 10^{-4} \text{ g cm}^{-3}/58.44 \text{ g mol}^{-1} &= 4.00 \times 10^{-6} \text{ mol cm}^{-3} \\ &= 4.00 \times 10^{-3} \text{ mol dm}^{-3} \end{aligned}$$

- (b) Using the SI prefixes in Table 1.3 to convert between units,

$$1 \text{ dm}^3 = 1(\text{dm})^3 = 1(\times 10^{-1}\text{m})^3 = 10^{-3}\text{m}^3$$

Thus, a molar concentration of $4.00 \times 10^{-3} \text{ mol dm}^{-3}$ is equivalent to

$$4.00 \times 10^{-3} \text{ mol dm}^{-3} \times 10^3 \text{ m}^3 \text{ dm}^{-3} = 4.00 \text{ mol m}^{-3}$$

(c) From part (a), the mass concentration is $2.34 \times 10^{-4} \text{ g cm}^{-3}$, which, because $1 \text{ g} \equiv 10^3 \text{ mg}$, and $1 \text{ dm}^3 \equiv 10^3 \text{ cm}^3$ is equivalent to

$$2.34 \times 10^{-4} \text{ g cm}^{-3} \times 10^3 \text{ mg g}^{-1} \times 10^3 \text{ cm}^3 \text{ dm}^{-3} = 234 \text{ mg dm}^{-3}.$$

(d) The concentration of the solution is sufficiently low that, within the level of precision given, the mass of 1 cm^3 of solution may be considered as the same as 1 cm^3 of solution. The density of water is

$$\rho = 1.00 \text{ g cm}^{-3}$$

so that the mass of 1 cm^3 of solution is 1.00 g . From part (a), however, 1 cm^3 of solution contains a mass of NaCl of $2.34 \times 10^{-4} \text{ g}$. Thus, considering a volume of 1 cm^3 , the concentration of NaCl as a ratio by mass is

$$\begin{aligned} \frac{m_{\text{NaCl}}}{m_{\text{total}}} &\approx \frac{m_{\text{NaCl}}}{m_{\text{H}_2\text{O}}} = \frac{2.34 \times 10^{-4} \text{ g}}{1.00 \text{ g}} = 2.34 \times 10^{-4} = 2.34 \times 10^{-4} \times 10^6 \text{ ppm} \\ &= 234 \end{aligned}$$

3. In preparing a standard solution, you forget to zero the balance so that it reads 0.10 g too high. What kind of error is this? What effect would this error have on an analysis if the standard solution was used to prepare a calibration graph by dilution?

Strategy

Consider whether the error is random or systematic.

Solution

This is a systematic or determinate error. If the mass of standard was measured by difference (e.g. subtracting the mass of a container after adding to the volumetric flask from the mass before addition) then the same error will apply to both measurements and so will cancel out. If the solution is prepared using a single weighing, then the standard solution will appear to be more concentrated than expected and so the final result will be too high.

5. The fluoride ion (F^- (aq)) concentration of a solution was measured using a probe with an ion-selective electrode. When immersed in 100 cm^3 of solution, a voltage of 0.505 V was measured. When 2.0 cm^3 of 1.00 mol dm^{-3} NaF were added, the voltage changed to 0.251 V . Estimate the concentration of fluoride ions and the pF in the original solution.

Strategy

Use Equation 12.5, which expresses the relation between the measured potential difference and the concentration of fluoride ions in solution, assuming that $k = 1$. Determine the amount of NaF added and hence the change in concentration. Use Equation 12.5, with values for the potential differences and expressions for the concentrations before, and after, addition of the NaF, and solve simultaneously to find the unknown initial concentration. Use Equation 12.6 to determine the pF from the concentration.

Solution

Using Equation 12.5, the measured potential difference, measured in volts, across the electrodes is

$$V = -0.0592 \times k \times \log_{10}[F^-(aq)]_{\text{outside}} + c$$

where c is a constant. The potential difference is thus a linear function of the logarithm of the fluoride ion concentration.

A volume of $2.0 \text{ cm}^3 \equiv 2.0 \times 10^{-3} \text{ dm}^3$ of 1.00 mol dm^{-3} NaF contains an amount of fluoride ions

$$n_{F_{\text{aq}}^-} = 2.00 \times 10^{-3} \text{ dm}^3 \times 1.00 \text{ mol dm}^{-3} = 2.00 \times 10^{-3} \text{ mol}$$

which, in a solution of volume $100 \text{ cm}^3 \equiv 0.100 \text{ dm}^3$, is equivalent to a change in concentration of

$$\delta[F_{\text{aq}}^-] = n/V = 2.00 \times 10^{-3} \text{ mol}/0.100 \text{ dm}^3$$

On addition of the NaF, the volume of the solution changes from 100 cm^3 to 102 cm^3 , which represents a dilution factor of 1.02, or a change in concentration of

$$1/1.02 = 0.98$$

The concentration of fluoride ions, measured in mol dm^{-3} therefore changes from

$$[\text{F}^-(\text{aq})]_{\text{outside}} \text{ to } 0.98 \times ([\text{F}^-(\text{aq})]_{\text{outside}} + 2.00 \times 10^{-2})$$

Using Equation 12.5 to write two equations, for the potential difference before and after the addition of NaF,

$$0.505 = -0.0592 \times \log_{10}[\text{F}^-(\text{aq})]_{\text{outside}} + c$$

$$0.251 = -0.0592 \times \log_{10}\{0.98 \times ([\text{F}^-(\text{aq})]_{\text{outside}} + 2.00 \times 10^{-2})\} + c$$

Solving the equations simultaneously, by subtracting the second from the first,

$$\begin{aligned} \frac{0.505 - 0.251}{-0.0592} &= \log_{10}[\text{F}^-(\text{aq})]_{\text{outside}} \\ &\quad - \log_{10}\{0.98 \times ([\text{F}^-(\text{aq})]_{\text{outside}} + 2.00 \times 10^{-2})\} \\ -4.291 &= \log_{10} \frac{[\text{F}^-(\text{aq})]_{\text{outside}}}{0.98 \times ([\text{F}^-(\text{aq})]_{\text{outside}} + 2.00 \times 10^{-2})} \end{aligned}$$

Thus

$$10^{-4.291} = 5.117 \times 10^{-5} = \frac{[\text{F}^-(\text{aq})]_{\text{outside}}}{0.98 \times ([\text{F}^-(\text{aq})]_{\text{outside}} + 2.00 \times 10^{-2})}$$

so that

$$5.117 \times 10^{-5} \times 0.98 \times ([\text{F}^-(\text{aq})]_{\text{outside}} + 2.00 \times 10^{-2}) = [\text{F}^-(\text{aq})]_{\text{outside}}$$

and therefore

$$[\text{F}^-(\text{aq})]_{\text{outside}} = 1.00 \times 10^{-6} \text{ mol dm}^{-3}$$

Using Equation 12.6 to find the pF of the initial solution,

$$\text{pF} = -\log_{10}[\text{F}^-(\text{aq})] = -\log_{10} 1.00 \times 10^{-6} \text{ mol dm}^{-3} = 5.97$$

7. You are handed a bottle labelled 'xylene' (dimethyl benzene). A gas chromatogram gives three peaks corresponding to the 1,2-, the 1,3-, and the 1,4-isomers with peak areas in the ratio of 143.1:9.5:6.4 respectively. Assuming that the detector responds equally to each isomer, calculate the composition of the xylene.

Strategy

Find the ratio of the area under each separate peak to the total peak area.

Solution

The concentration of each component is proportional to the integrated area under each peak in the chromatogram. The total amount present (i.e. 100% of the mixture) is therefore proportional to the total area:

$$100\% = 143.1 + 9.5 + 6.4 = 159.$$

The three isomers are therefore present in the ratios:

1,2-isomer:

$$143.1/159 \times 100 = 90.0\%$$

1,3-isomer:

$$9.5/159 \times 100 = 6.0\%$$

1,4-isomer:

$$6.4/159 \times 100 = 4.0\%$$

9. The molar absorption coefficient for an aqueous solution of Fe²⁺ ions is $\epsilon = 0.3 \text{ m}^2 \text{ mol}^{-1}$ at 325 nm. When the Fe²⁺ is complexed with 1,10-phenanthroline (C₁₀H₈N₂), the [Fe(C₁₀H₈N₂)₃]²⁺ ion has a molar absorption coefficient of 1100 m² mol⁻¹ at 508 nm. If the minimum reading on a spectrophotometer is an absorbance of 0.01, what is the minimum detectable concentration of each of the ions using a 1.0 cm cell?

Strategy

Use the Beer–Lambert Law, Equation 11.8, to determine the concentration that corresponds to an absorbance of 0.01.

Solution

Rearranging the Beer–Lambert law, Equation 11.8,

$$c = A/\epsilon l$$

so, for the uncomplexed ions,

$$\begin{aligned}c &= A/\epsilon l = 0.01/(0.3 \text{ m}^2\text{mol}^{-1} \times 0.01 \text{ m}) \\ &= 3.33 \text{ mol m}^{-3} = 3.33 \text{ mol dm}^{-3}\end{aligned}$$

and for the complexed ions,

$$\begin{aligned}c &= A/\epsilon l = 0.01/(1100 \text{ m}^2\text{mol}^{-1} \times 0.01 \text{ m}) \\ &= 9.1 \times 10^{-4} \text{ mol m}^{-3} = 9.1 \times 10^{-7} \text{ mol dm}^{-3}\end{aligned}$$

- 11.** You are provided with 10 kg of soil from a site suspected of uranium contamination. Outline the steps that you would take to obtain an accurate measurement of the uranium concentration in the soil. What blank experiments would you run?

Strategy

Factors to consider will include preparation of the sample, choice of technique and tests to ensure that the measurements are not subject to systematic errors.

Solution

Firstly, ensure that the sample is well mixed and homogeneous. The soil must then be treated with a reagent to quantitatively extract all the uranium, either from the solid or by dissolving in acid and extracting the uranium by complexing with a suitable ligand and extracting into a solvent. Taking care to ensure no loss of sample, an accurately known volume of solution containing all the uranium from the soil may thus be obtained.

Choose a suitable analytical method, such as atomic absorption spectroscopy, AAS, calibrating the instrument using solutions with accurately known concentrations.

Blank experiments might include performing the same series of processes on a soil known to contain no uranium, or performing the analysis on a standard soil with an accurately known uranium concentration that has been determined using a different technique.

- 13.** Suggest, with reasons, an appropriate chromatographic technique which could be used for each of the following analyses:

- (a) the concentration of H₂S in natural gas;
- (b) trace levels of chlorinated pesticides in river water;
- (c) the concentrations of each compound in a mixture of several chiral sugars;
- (d) the concentration of cyanide ions in an aqueous industrial effluent.

Strategy

Consider the various phases and chemical nature of the individual analytes.

Solution

- (a) Since the components are gases, gas chromatography. H₂S and the components of natural gas will burn so that a flame ionisation detector will be suitable. It is sensitive, which will be needed since the concentration is (hopefully!) low.
- (b) The concentrations will be low since these compounds are not very soluble in water. A high-performance liquid chromatography, HPLC, method could be used but a sensitive detector would be needed and these compounds do not usually fluoresce. The normal method is to extract them into a suitable solvent and then to use gas chromatography employing an electron capture detector.
- (c) Sugars are not volatile and so gas chromatography is not suitable. They are soluble in water so that water would be a suitable mobile phase for high-performance liquid chromatography, HPLC. Since they are chiral, a chiral stationary phase would be used with a UV/VIS or (preferably since most sugars do not absorb strongly) a refractive index detector.
- (d) Since the cyanide ions are in solution, ion-exchange chromatography would be suitable using a conductivity detector.