
Analytical chemistry

Answers to worked examples

WE 11.1 What's in a sample for analysis? (on p. 517 in *Chemistry*³)

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 11.2 Mean and standard deviation (on p. 520 in *Chemistry*³)

If another 20 titrations were performed under the same conditions, how many results would you expect to lie between 12.14 cm³ and 12.26 cm³?

Strategy

Express the range of values in terms of the mean and standard deviation of the distribution. Use Figure 11.3 to find the proportion of values that will fall within this range.

Solution

The mean of the readings was

$$\bar{x} = 12.20 \text{ cm}^3$$

and standard deviation was

$$\sigma = 0.06 \text{ cm}^3$$

Therefore, the range 12.14 cm³ and 12.26 cm³ corresponds to $\bar{x} - \sigma$ to $\bar{x} + \sigma$ so for a normal distribution such as this, Figure 11.3 shows that 68% of readings would be expected to lie within these limits and 32% of readings outside. Hence, 68% of the 20 readings, which is equivalent to

$$\frac{68}{100} \times 20 = 14$$

readings would lie between these values.

WE 11.3 Spectrophotometric analysis (on p. 544 in *Chemistry*³)

0.0277 g of KMnO₄ were dissolved in 250 cm³ of water. What would be the absorbance of this solution at 520 nm in the same cell?

Strategy

Calculate the amount of KMnO₄ dissolved in the water from the molar mass and hence determine the concentration of the solution.

Solution

The molar mass of KMnO₄ 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 10.8, 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 11.4 Measuring concentrations using atomic emission spectrometry (on p. 549 in *Chemistry*³)

A mineral water has a concentration of Li^+ ions of 0.25 mg dm^{-3} . What would be the emission intensity from the spectrometer used under the conditions above?

Strategy

Use the calibration graph to determine the emission expected from a sample of this concentration.

Solution

The emission of a 0.25 mg dm^{-3} solution can be read from the calibration graph as 365.

WE 11.5 Using the standard addition method to measure concentrations (on p. 552 in *Chemistry*³)

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 1.2, 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 11.1 Analysing food contaminants (on p. 522 in *Chemistry*³)

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.34.)

Strategy

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

Solution

(a)

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

(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 11.2 Rapid blood analysis using electrochemical methods (on p. 526 in *Chemistry*³)

Explain how the principle of the techniques for measuring concentrations of H^+ , Na^+ , K^+ and Ca^{2+} ions differs from those for measuring O_2 and CO_2 concentrations in blood.

Strategy

Consider the different methods outlined in Section 11.2.

Solution

The techniques for measuring concentrations of H⁺, Na⁺, K⁺ and Ca²⁺ ions rely on potentiometric methods in which the voltage generated by an ion selective electrochemical cell is measured. The techniques for measuring O₂ and CO₂ concentrations are, however, different and rely upon a galvanic method involving measuring the current generated in an electrolytic cell.

Box 11.3 Monitoring PCBs in the environment **(on p. 537 in *Chemistry*³)**

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 11.6 Alcohol analysis and drink driving **(on p. 542 in *Chemistry*³)**

Suggest why the O–H bond stretching vibration at 3650 cm^{-1} is not used for the analysis of ethanol in breath.

Strategy

Consider how the absorption arising from the O–H stretching vibration differs from that for the C–H vibration.

Solution

The absorption arising from the O–H stretching vibration is weaker than that for

the C–H stretch. Use of the more intense C–H peak therefore provides greater relative sensitivity than the O–H band.

Box 11.7 A pulse oximeter (on p. 546 in *Chemistry*³)

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.

Box 11.8 Why is the temperature so important in atomic emission spectrometry? (on p. 547 in *Chemistry*³)

- Calculate the ratio of the numbers of excited state to ground state sodium atoms 5000 K.
- Calculate the temperature needed for this ratio to be 0.1.
- Calculate the ratio at 2510 K. Compare your answer with the value given above for 2500 K and comment on the result in terms of the experimental requirements atomic emission spectrometry.

Strategy

Calculate the relative populations using the Boltzmann distribution, Equation 10.9.

Solution

- Using the Boltzmann distribution, with the energy separation and degeneracies given

$$\frac{n_{3p}}{n_{3s}} = \frac{3}{1} e^{-\left\{ \frac{3.37 \times 10^{-19} \text{ J}}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (5000 \text{ K})} \right\}} = 0.023$$

(b) If

$$\frac{n_{3p}}{n_{3s}} = 0.1 = \frac{3}{1} e^{-\left\{ \frac{3.37 \times 10^{-19} \text{ J}}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times T} \right\}}$$

then, rearranging

$$-\frac{3.37 \times 10^{-19} \text{ J}}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times T} = \ln \left(0.1 \times \frac{1}{3} \right)$$

so that

$$T = -\frac{3.37 \times 10^{-19} \text{ J}}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (\ln 0.033)} = 7170 \text{ K}$$

(c) Using the same method as (a),

$$\frac{n_{3p}}{n_{3s}} = \frac{3}{1} e^{-\left\{ \frac{3.37 \times 10^{-19} \text{ J}}{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (2510 \text{ K})} \right\}} = 1.80 \times 10^{-4}$$

As stated in Box 11.8, at 2500 K, the fraction is 1.71×10^{-4} . So, a change of only 10 K increases the ratio by about 5%. This limits the accuracy and precision of the method and explains the requirement to keep the temperature of the flame (governed by the fuel to air ratio) very constant.

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 1.2 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 1.6, 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

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

2. A gravimetric determination (see Section 1.5, p.39) of the chloride ion, Cl^- , content of a mineral water was carried out by precipitating as silver chloride. If the balance available can weigh to $\pm 0.1 \text{ mg}$, what is the detection limit for Cl^- (aq)? ($M_r(\text{AgCl}) = 143.4$)

Strategy

Use the molar mass to determine the amount of silver chloride that is equivalent to the uncertainty in the balance of $\pm 0.1 \text{ mg}$.

Solution

$$M_r(\text{AgCl}) = 143.4. \quad 1 \text{ mol} = 143.4 \text{ g}$$

If the molar mass is 143.4 g mol^{-1} , then, from Equation 1.2, an uncertainty of $\pm 0.1 \text{ mg}$ is equivalent to

$$n = m/M = (0.1 \text{ mg}) / \overbrace{(143.4 \text{ g mol}^{-1})}^{\text{molar mass, } M} = \pm 6.97 \times 10^{-7} \text{ mol}$$

The detection limit is thus $6.97 \times 10^{-7} \text{ mol dm}^{-3}$.

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.

4. Ten determinations of the sulphate ion content in ppm (by mass) of a water sample were made using two different methods. For each method, calculate:
- the mean value;
 - the standard deviation;
 - the range;
 - the coefficient of variation.

Comment on the values you obtain.

Strategy

- Substitute the results into Equation 11.1 to find the mean, \bar{x} . Many scientific calculators will perform this function automatically.
- Find the difference between each result, find the mean and sum the square of the values and substitute into Equation 11.2 to find the standard deviation. Once again, many scientific calculators will calculate the standard deviation of a distribution without needing to calculate the individual differences.
- Subtract the lowest reading from the highest to find the range.
- Use Equation 11.3 to find the coefficient of variation.

Solution

	Method 1	Method 2
(a) Mean / ppm	10.09	10.09
(b) Standard deviation / ppm	0.324	0.037
(c) Range / ppm	0.98	0.12
(d) Coefficient of variation / %	3.21	0.365

Both methods give the same mean from the 10 readings. However, Method 2 gives less scattered results and so is more precise.

5. A laboratory operates two methods for determining the concentration of lead in water. To check the method, a Certified Reference Material containing a known Pb concentration of $20.00 \mu\text{g dm}^{-3}$ is analysed ten times using each of the two methods. The first method gives a mean concentration of $21.9 \mu\text{g dm}^{-3}$ with a standard deviation of $0.5 \mu\text{g dm}^{-3}$. The second method gives a mean and standard deviation of $19.4 \mu\text{g dm}^{-3}$ and $2.1 \mu\text{g dm}^{-3}$, respectively.

Comment on these results in terms of the accuracy and precision of the two analytical methods. (Section 11.1)

Strategy

Assume that the measurements for both methods are randomly distributed. Use the mean of the measurements, \bar{x} , as an indication of the centre of the distribution and the standard deviation, σ , as an indication of the width of the distribution.

Solution

The first method appears to be precise, because the standard deviation, and thus the width of the distribution of measurements is relatively small. The method yields reproducible values. The coefficient of variation for this method is, from Equation 11.3,

$$CV = \frac{\sigma}{\bar{x}} \times 100 = \frac{0.5 \mu\text{g dm}^{-3}}{21.9 \mu\text{g dm}^{-3}} \times 100 = 2.3 \text{ per cent}$$

For a random distribution, 99% of measurements lie within two standard deviations from the mean and we typically quote results as

$$\bar{x} \pm 2\sigma$$

Thus, for the first method, we might quote the Pb concentration as $21.9 \pm 1.0 \mu\text{g dm}^{-3}$. This implies that the method is not accurate. The range of possible values, which included 99% of all measurements, does not include the known Pb concentration of the Certified Reference Material.

The second method is not as precise as the first. From Equation 11.3, the coefficient of variation is

$$CV = \frac{\sigma}{\bar{x}} \times 100 = \frac{2.1 \mu\text{g dm}^{-3}}{19.4 \mu\text{g dm}^{-3}} \times 100 = 11 \text{ per cent}$$

We would quote the results as $19.4 \pm 2.1 \mu\text{g dm}^{-3}$. This implies that the second method is more accurate than the first. Not only is the mean Pb concentration closer to that of the Certified Reference Material, but the range is also sufficiently wide to incorporate the known value.

The second method is thus less precise than the first, but more accurate.

6. The electric potential of a glass pH electrode was measured as a function of pH with the following results.

pH	2.0	4.0	5.0	6.0	8.0	9.0	10.0
Potential / V	+0.300	+0.168	+0.081	+0.035	-0.092	-0.168	-0.235

Under the same conditions, analysis of a carbonated drink gave a potential of +0.240 V while a sample of water gave a potential of -0.005 V. Find the pH of the drink and of the water. (Section 11.2)

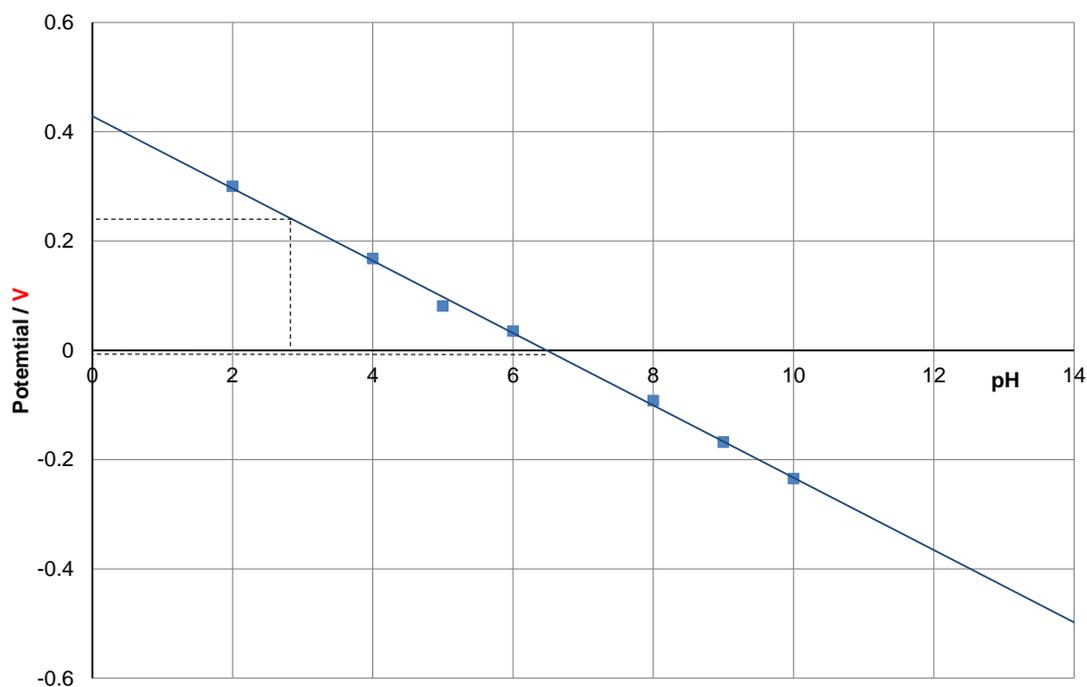
Strategy

Use the data to construct a calibration graph. The pH of the drink and the water

sample may then be read off the graph by finding the points that correspond to the measured potentials.

Solution

A calibration graph of measured potential against pH is shown in the accompanying figure. We may see that a potential of +0.240 V corresponds to pH = +2.8 for the sample of drink and -0.005 V to pH = 6.4 for the sample of water.



7. An ion-selective electrode was used for the analysis of benzoate ion in aqueous solution. The electric potential of the electrode varied with benzoate concentration as shown.

[Benzoate] / mol dm ⁻³	1.0×10^{-3}	2.0×10^{-4}	1.0×10^{-4}	1.0×10^{-5}	1.0×10^{-6}
Potential / mV	190	152	136	95	40

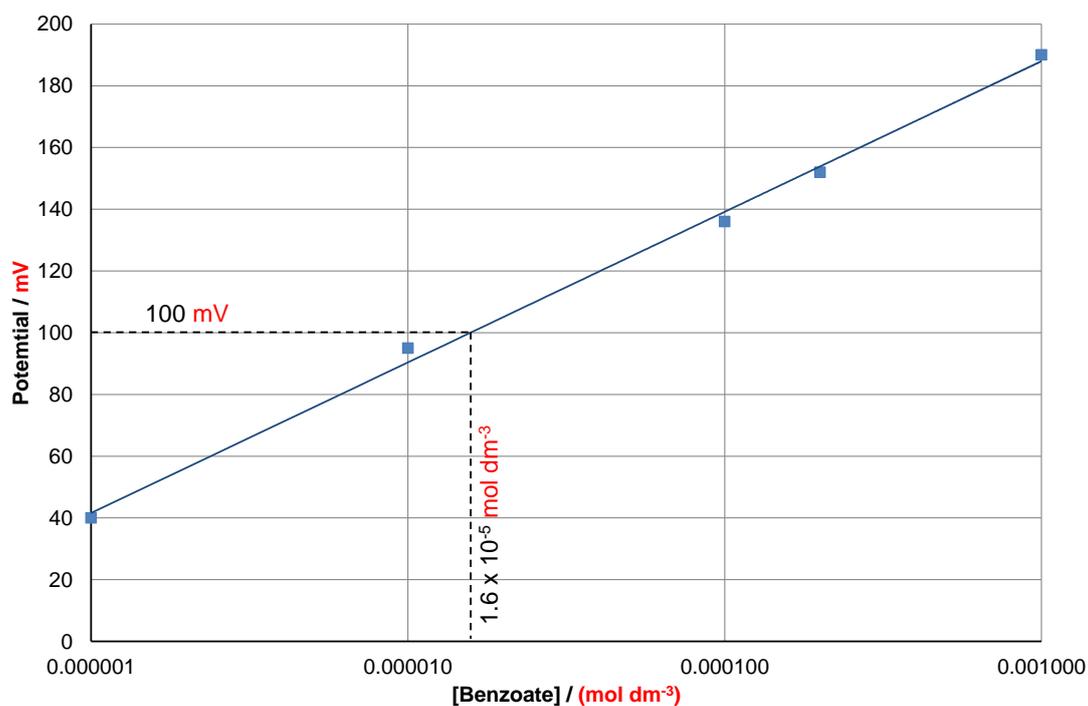
Analysis of a solution of benzoate ions gave a potential of 100 mV under these conditions. Using a calibration curve, determine the concentration of benzoate ions in solution. (Section 11.2)

Strategy

Draw a calibration curve and use it to determine the concentration of benzoate ions for a measured potential of 100 mV.

Solution

The accompanying calibration curve shows how the measured potential varies with the concentration of benzoate ions. The data have been plotted on a logarithmic scale, which results in a near linear calibration line with evenly spaced points that is easier to interpret. We may see that a potential of 100 mV corresponds to a concentration of benzoate ions of $1.6 \times 10^{-5} \text{ mol dm}^{-3}$.



8. 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 11.5, 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. By substituting the values for the potential differences into the expressions for the concentrations before, and after, addition of the NaF, to solve simultaneously to find the unknown initial concentration. Use Equation 11.6 to determine the pF from the concentration.

Solution

Using Equation 11.5, the measured potential difference, measured in volts, across the electrodes is

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

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

$$n_{\text{F}_{\text{aq}}^-} = (1.00 \text{ mol dm}^{-3}) \times (2.00 \times 10^{-3} \text{ dm}^3) = 2.00 \times 10^{-3} \text{ mol}$$

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

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

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 11.5 to write two equations, for the potential difference before and after the addition of NaF,

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

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

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

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

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

Thus

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

so that

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

and therefore

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

Using Equation 11.6 to find the pF of the initial solution,

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

9. An ion selective electrode is designed to measure the concentration of perchlorate ions (ClO_4^-). The electrode was immersed in 50.0 cm^3 of a perchlorate solution and registered a potential of 358.7 mV against a standard electrode. 0.50 cm^3 of a solution with concentration 0.10 mol dm^{-3} NaClO_4 was then added and the potential changed to 346.1 mV. What was the concentration of ClO_4^- ions in the original solution?

Strategy

From the relation between the potential of an ISE and concentration, you can use the change in voltage which must be due to the added perchlorate ions, to find the concentration in the original solution.

Solution

The relation between the measured voltage and the ion concentration in solution (assuming $k = 1$) is

$$\text{Measured voltage, } V = \text{constant} + 0.0592 k \log_{10} [\text{ClO}_4^- (\text{aq})]$$

so V is therefore a linear function of $\log_{10} [\text{ClO}_4^- (\text{aq})]$.

The amount of ClO_4^- added is

$$0.50 \text{ cm}^3 \text{ of } 0.10 \text{ mol dm}^{-3} \text{ NaClO}_4^- \text{ i.e. } 0.50 \text{ cm}^3 \times \frac{0.10 \text{ mol dm}^{-3}}{1000 \text{ cm}^3 \text{ dm}^{-3}} = 5 \times 10^{-5} \text{ mol}$$

This was added to 50 cm^3 so change of concentration is $1 \times 10^{-3} \text{ mol dm}^{-3}$
 $= 0.001 \text{ mol dm}^{-3}$

You now have two voltages at two different concentrations so:

$$\text{Before addition: } 0.3587 \text{ V} = \text{constant} - 0.0592 \text{ V} \log_{10} [\text{ClO}_4^- (\text{aq})] \quad (1)$$

$$\text{After addition: } 0.3461 \text{ V} = \text{constant} - 0.0592 \text{ V} \log_{10} [\text{ClO}_4^- (\text{aq}) + 0.001] \quad (2)$$

Subtracting (1) from (2) gives

$$\begin{aligned} 0.3587 \text{ V} - 0.3461 \text{ V} \\ = \{ \text{constant} + 0.0592 \log_{10} [\text{ClO}_4^- (\text{aq}) + 0.001] \} - \{ \text{constant} + 0.0592 \log_{10} [\text{ClO}_4^- (\text{aq})] \} \end{aligned}$$

$$0.0126 \text{ V} = 0.0592 \text{ V} \log_{10} [\text{ClO}_4^- (\text{aq}) + 0.001] - 0.0592 \text{ V} \log_{10} [\text{ClO}_4^- (\text{aq})]$$

$$0.213 = (\log_{10} [\text{ClO}_4^- (\text{aq}) + 0.001] - \log_{10} [\text{ClO}_4^- (\text{aq})])$$

$$0.213 = \log_{10} \left(\frac{[\text{ClO}_4^- (\text{aq}) + 0.001]}{[\text{ClO}_4^- (\text{aq})]} \right)$$

$$\left(\frac{[\text{ClO}_4^- (\text{aq}) + 0.001]}{[\text{ClO}_4^- (\text{aq})]} \right) = 10^{0.213} = 1.63$$

$$[\text{ClO}_4^- (\text{aq}) + 0.001] = 1.63 [\text{ClO}_4^- (\text{aq})]$$

$$[0.001] = 0.63 [\text{ClO}_4^- (\text{aq})]$$

$$[\text{ClO}_4^- (\text{aq})] = [0.001] / 0.63 = 1.6 \times 10^{-3} \text{ mol dm}^{-3}$$

10. A solute has a partition coefficient of 28.7 between trichloromethane (CHCl₃) and water. 20 cm³ of CHCl₃ were added to 100 cm³ of an aqueous solution of the solute. At equilibrium, the aqueous layer contained a concentration of 0.005 mol dm⁻³. What was the concentration of the organic layer?

Strategy

Use Equation 11.8, which expresses how the concentration of the two layers is related to the partition function.

Solution

Using Equation 11.8, the value of the partition coefficient K is given by the ratio of the concentrations in the organic and aqueous phases,

$$K = \frac{c_{\text{CH}_3\text{Cl}}}{c_{\text{H}_2\text{O}}}$$

Thus,

$$c_{\text{CH}_3\text{Cl}} = K \times c_{\text{H}_2\text{O}} = 28.7 \times (0.005 \text{ mol dm}^{-3}) = 0.144 \text{ mol dm}^{-3}$$

11. 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:

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

- 12.** Suggest, with reasons, an appropriate chromatographic technique that could be used for each of the following analyses. (Section 11.3)
- (a) the concentration of H₂S in natural gas;
 - (b) trace concentrations of chlorinated pesticides in river water;
 - (c) the concentration of each compound in a mixture of several chiral sugars.

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.

13. Suggest suitable forms of chromatography to investigate the following situations.
(Section 11.3)

(a) You are an analyst in a dairy. It is claimed that a consignment of milk has been contaminated with a toxic organochlorine pesticide at ppb levels. How would you identify and measure the concentration of the pesticide?

(b) Your colleagues in a pharmaceutical company have developed a new high-yield route to a single enantiomer of a chiral target compound. You are asked to check the purity of the product and to identify any by-product impurities in it and measure their concentrations. How might you do this?

Strategy

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

Solution

(a) The initial isolation of the pesticide contaminant could be performed by extraction using an appropriate solvent. The resulting extract could then be analysed using gas–liquid chromatography, GLC, in which the volatile pesticide, and other impurities evaporate and pass through a liquid-phase column. Detection could be performed using a mass spectrometer, which would allow the identity of the pesticide to be confirmed. Such GC–MS techniques are sufficiently sensitive to allow detection at the ppb levels required.

(b) In general, we would not expect either the target compound or any impurities to be volatile and you must therefore use liquid rather than gas-phase chromatography. The choice of a suitable mobile phase for high-performance liquid chromatography, HPLC, will depend upon whether the components are soluble in water. The target compound is chiral, and a chiral stationary phase must be used to separate out the different enantiomers. Detection could be performed using either UV/VIS a detector, or if the compounds do not absorb strongly in this region of the spectrum, a refractive index detector.

14. Four solutions of a dye were prepared in water. In a 1.00 cm cell, the percentage of light at a particular wavelength transmitted through each solution is given in the following table:

Concentration / mol dm ⁻³	0.004	0.010	0.020	0.040
Percentage light transmitted	79	56	32	10

Confirm that these data obey the Beer–Lambert Law and calculate the molar absorption coefficient, ϵ , at this wavelength.

Strategy

Calculate the absorbance from the percentage of light transmitted using Equation 10.7. Plot a graph of absorbance against concentration and determine the value of the molar absorption coefficient from the gradient of the graph using Equation 10.8.

Solution

According to Equation 10.7, the absorbance is related to the logarithm of the percentage of light transmitted, T

$$A = \log_{10}(I_0/I_t) = -\log_{10}(I_t/I_0) = -\log_{10} T$$

If the data obey the Beer–Lambert Law, Equation 10.8,

$$A = -\log_{10} T = \epsilon \times c \times l$$

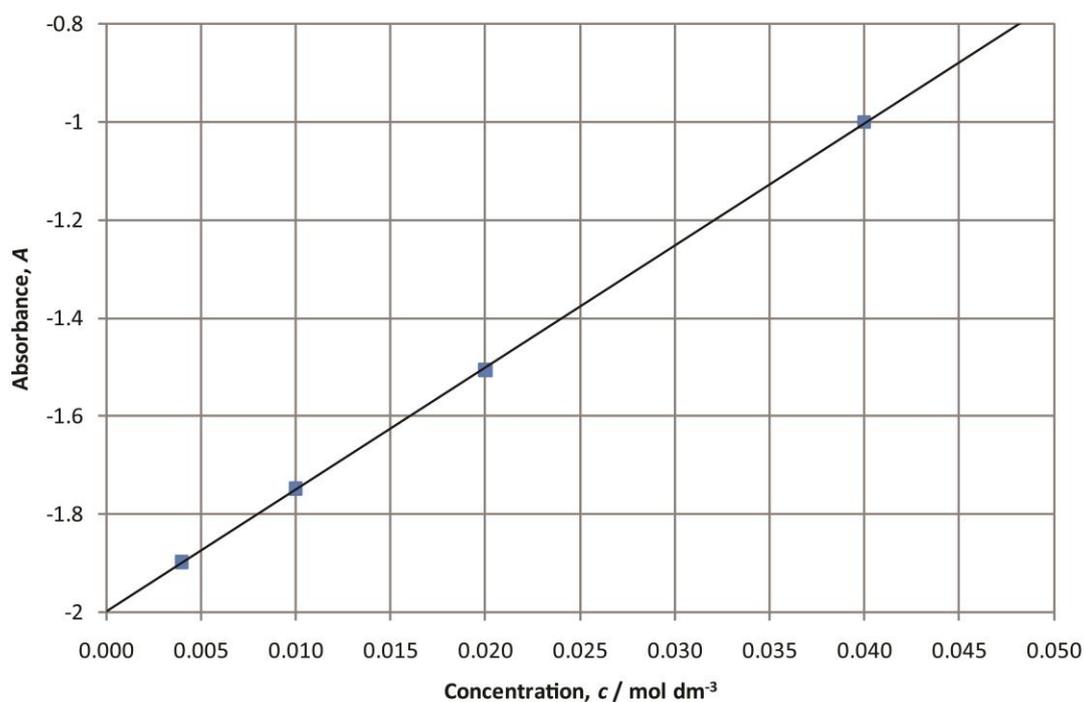
and so a plot of the negative logarithm of the light transmitted versus concentration should be linear, with a gradient of

$$m = \epsilon \times l$$

Taking logarithms to calculate the absorbance allows a graph to be plotted.

Concentration / mol dm ⁻³	0.004	0.010	0.020	0.040
Percentage light transmitted	79	56	32	10

Absorbance	0.102	0.251	0.490	1.00
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The gradient of the graph is

$$m = \epsilon \times l = 24.92 \text{ (mol dm}^{-3}\text{)}^{-1}$$

Thus, because the path length of the sample is 1.00 cm \equiv 0.100 dm, then

$$\epsilon = m/l = (24.92 \text{ mol}^{-1}\text{dm}^3)/(0.100 \text{ dm}) = 249.2 \text{ mol}^{-1}\text{dm}^2$$

This is equivalent to

$$\epsilon = 249.2 \text{ mol}^{-1}(10^{-1}\text{m})^2 = 2.492 \text{ mol}^{-1}\text{m}^2$$

- 15.** The molar absorption coefficient for an aqueous solution of Fe^{2+} ions is $\epsilon = 0.3 \text{ m}^2 \text{ mol}^{-1}$ at 325 nm. When the Fe^{2+} is complexed with 1,10-phenanthroline ($\text{C}_{10}\text{H}_8\text{N}_2$), the $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]^{2+}$ ion has a molar absorption coefficient of $1100 \text{ m}^2 \text{ mol}^{-1}$ 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 10.8, to determine the concentration that corresponds to an absorbance of 0.01.

Solution

Rearranging the Beer–Lambert law, Equation 10.8,

$$c = A/\epsilon l$$

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,

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

- 16.** As part of an investigation into the harmful effects of petrol engine emissions, a 10 g sample of grass from a roadside verge was analyzed for its lead content. The grass was burned to ash in oxygen to remove organic material and the inorganic residue was dissolved in 20 cm³ of dilute acid. Under certain conditions, this gave an absorbance of 0.72 on an atomic absorption spectrophotometer. A standard solution containing 1.0 μg cm⁻³ of lead was available. Aliquots of this were made up to 50 cm³ with dilute acid and the absorbances measured as shown.

Volume of standard solution in 50 cm ³ / cm ³	5	10	15	20	25
Absorbance	0.26	0.52	0.81	1.04	1.30

Calculate the concentration of lead in the grass in parts per million (by mass).

Strategy

Calculate the mass concentrations of each of the standard solutions and so prepare a calibration graph of absorbance versus mass concentration. Use the

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graph to determine the mass concentration of the unknown solution. Hence determine the mass, and thus the proportion, of lead in the grass.

Solution

The standard solution contains $1.0 \mu\text{g cm}^{-3}$ so that each cm^3 added adds $1.0 \mu\text{g}$.

So, the solution which contained 5 cm^3 of standard, contains

$$5 \times 1.0 \mu\text{g} = 5.0 \mu\text{g}$$

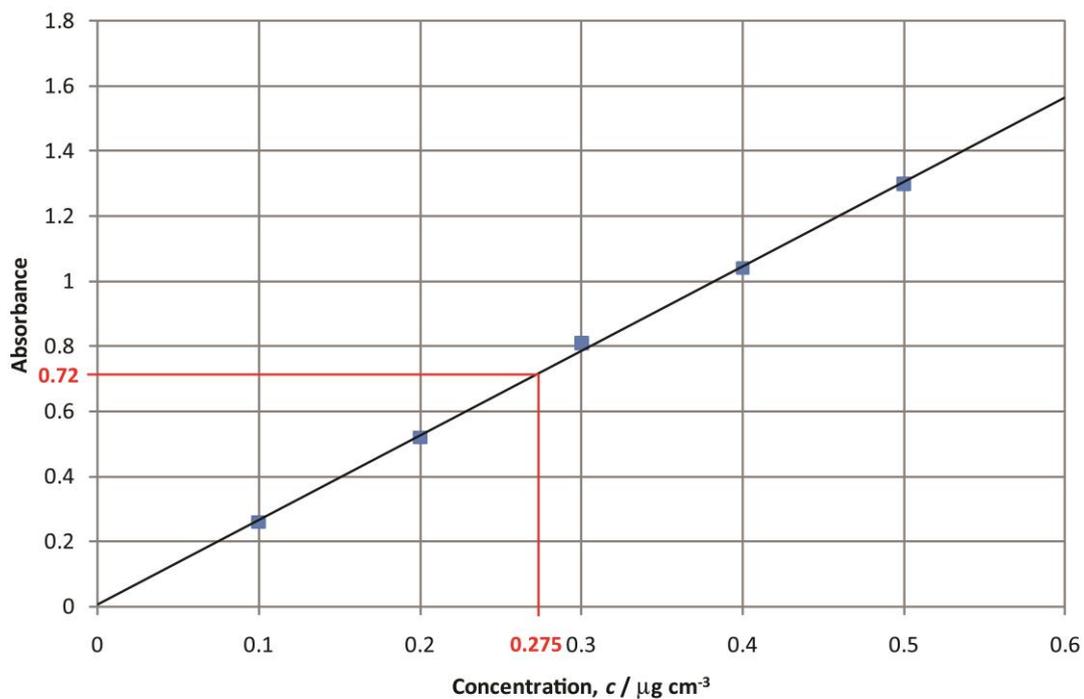
in 50 cm^3 , giving a mass concentration of

$$(5.0 \mu\text{g}) / (50 \text{ cm}^3) = 0.10 \mu\text{g cm}^{-3}$$

Similar calculations may be performed for the other solutions, so that

Volume of standard solution in $50 \text{ cm}^3 / \text{cm}^3$	5	10	15	20	25
Concentration / $\mu\text{g cm}^{-3}$	0.10	0.20	0.30	0.40	0.50
Absorbance	0.26	0.52	0.81	1.04	1.30

yielding a calibration graph



The solution being analysed gave an absorbance of 0.72. From the graph (either reading directly or using the equation of the line), this corresponds to a mass concentration of $0.275 \mu\text{g cm}^{-3}$, which is equivalent to $275 \mu\text{g dm}^{-3}$.

The volume of solution was 20 cm^3 , which was derived from 10 g of grass, thus contained a mass of lead of

$$m = c \times V = 20 \text{ cm}^3 \times 0.275 \mu\text{g cm}^{-3} = 5.50 \mu\text{g}$$

which is equivalent to a proportion of

$$\{(5.50 \times 10^{-6} \text{ g}) / (10 \text{ g})\} \times 10^6 = 0.55 \text{ ppm}$$

17. A drug with a molar mass of 190 g mol^{-1} is formed into a tablet with a matrix that does not absorb visible light. The drug strongly absorbs at 450 nm with a molar absorption coefficient of $1650 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. A tablet weighing 0.438 g is dissolved in 500 cm^3 water and gives an absorbance in a 1.0 cm cell of 0.475 at 450 nm . Find the percentage by mass of the drug in the tablet. (Section 11.4)

Strategy

Use the Beer–Lambert law, Equation 10.8, to calculate the molar concentration of the drug in solution. Then use the molar mass of the drug to find the mass of the drug dissolved in the solution. Hence find the percentage by mass of drug by calculating the ratio of the mass of the drug to the total mass of the tablet.

Solution

Rearranging the Beer–Lambert law, Equation 10.8, the concentration of the drug in the sample is

$$c = \frac{A}{\epsilon L} = \frac{0.475}{(1650 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \times (1.0 \text{ cm})} = 2.9 \times 10^{-4} \text{ mol dm}^{-3}$$

The amount of drug dissolved in the 500 cm^3 sample is therefore

$$n = cV = \overbrace{(2.9 \times 10^{-4} \text{ mol dm}^{-3})}^{\text{concentration, } c} \times \overbrace{(0.500 \text{ dm}^3)}^{\text{volume, } V} = 1.4 \times 10^{-4} \text{ mol}$$

which corresponds to a mass

$$m = nM = \overbrace{(1.4 \times 10^{-4} \text{ mol})}^{\text{amount, } n} \times \overbrace{(190 \text{ g mol}^{-1})}^{\text{molar mass, } M} = 0.027 \text{ g}$$

The percentage by mass of drug in the tablet is thus

$$\{(0.027 \text{ g}) / (0.438 \text{ g})\} \times 100 = 6.2 \text{ per cent}$$

- 18.** A sample of sodium sulfate is known to be contaminated with copper ions. Analysis of reference solutions containing copper ions at known concentration gave the absorbances shown in the table. Under the same conditions, a solution made by dissolving 1.00 g of the sodium sulphate sample in 1.00 dm³ distilled water gave an absorbance of 0.20. What was the purity of the sodium sulphate, assuming that the copper ions are the only impurity. (Section 11.4)

Concentration of Cu ²⁺ / ppm	2.0	4.0	6.0	8.0	10.0
Absorbance	0.06	0.12	0.18	0.24	0.30

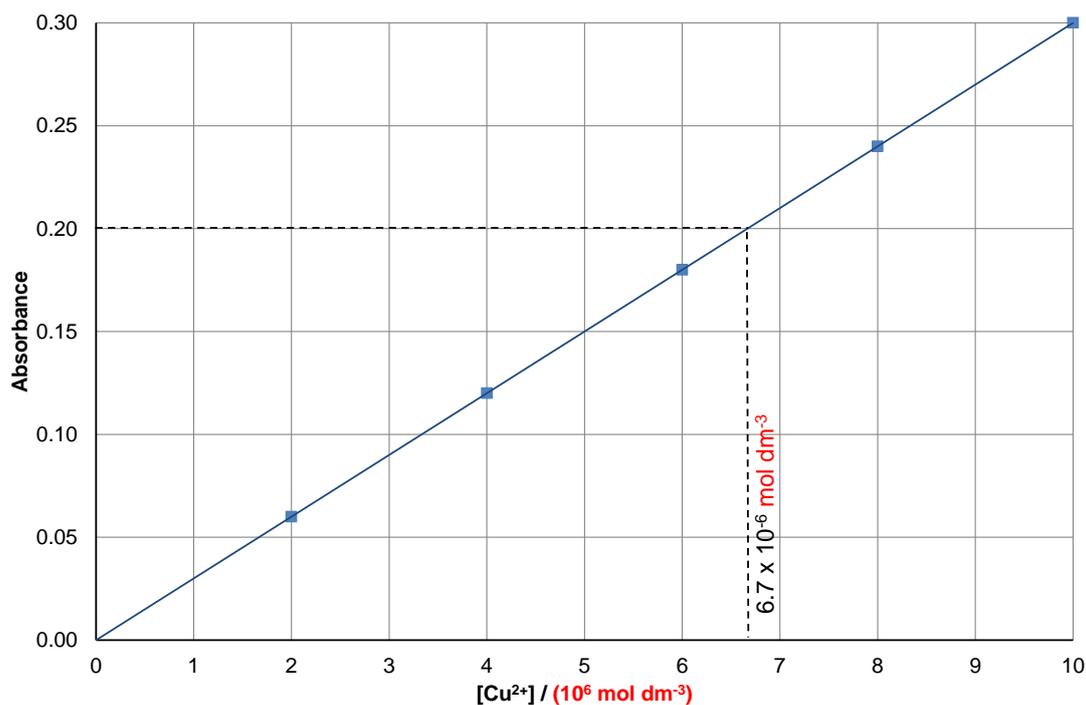
Strategy

Use the data to construct a calibration graph and so determine the concentration of copper ions in the sample, expressed as a fraction of the mass of the solution. Assume that the solution is sufficiently dilute that the density is the same as pure water, so that a volume of 1.00 dm³ of solution has a mass of 1.00 kg. Hence calculate the mass of copper ions present. Finally, express the purity of the sample as a percentage by mass of sodium sulphate.

Solution

The following calibration chart shows how absorbance varies with the concentration of copper ions. The graph is a straight line because the absorption follows the Beer–Lambert law, Equation 10.8

$$A = \epsilon cl$$



Reading from the calibration graph, an absorbance of 0.20 corresponds to a concentration of copper ions in solution of 6.7 ppm, or 6.7×10^{-6} g per 1 g of solution. We may assume that the solution is sufficiently dilute that the density is the same as pure water, so that a volume of 1.00 dm³ of solution has a mass of 1.00 kg = 1.00×10^3 g. Thus, 1.00 dm³ of solution, made up using 1.00 g of tablet, therefore contains a mass of impurities

$$(6.7 \times 10^{-6}) \times (1.00 \times 10^3 \text{ g}) = 6.7 \times 10^{-3} \text{ g}$$

This is equivalent to a percentage impurity by mass of

$$\frac{(6.7 \times 10^{-3} \text{ g})}{(1 \text{ g})} \times 100 = 0.0067 \text{ per cent}$$

or a percentage purity of

$$\left\{ 1 - \frac{(6.7 \times 10^{-3} \text{ g})}{(1 \text{ g})} \right\} \times 100 = 99.33 \text{ per cent}$$

- 19.** A sample of soil is to be analysed for the presence of trace amounts of an organic contaminant. 5.00 g of soil were extracted with 20.0 cm³ of dichloromethane, a good solvent for the contaminant. An injection of 1.0 microlitre (1 μL) of the

extract onto a HPLC instrument with a UV/Visible detector gave rise to a peak signal with an area of 250 arbitrary units. A separate injection of 1.0 μL of a 0.001 ppm reference solution of the contaminant under the same conditions gave a signal of 310 units. Find the concentration (in ppm) of contaminant in the soil. (Section 11.4)

Strategy

Calculate the concentration of contaminant in the extract by reference to the signal obtained for the standard solution. Use the density of dichloromethane to express the concentration as a mass of contaminant per unit volume of solution and hence as a fraction of the mass of the original sample of soil.

Solution

Assuming that signal from the UV/Visible detector depends linearly upon the concentration of the solution, the concentration of the unknown sample must be

$$\frac{250}{310} \times 0.001 \text{ ppm} = 8.06 \times 10^{-4} \text{ ppm} = 8.06 \times 10^{-10}$$

Thus, 1 g of extracted solution contains 8.06×10^{-10} g of contaminant. The density of dichloromethane is 1.33 g cm^{-3} . We may therefore express the concentration per unit volume of solution as

$$(8.06 \times 10^{-10} \text{ g}) / (1.33 \text{ g cm}^{-3}) = 6.06 \times 10^{-10} \text{ g cm}^{-3}$$

But, the solution contains $(5.00 \text{ g}) / (20.0 \text{ cm}^3) = 0.250 \text{ g cm}^{-3}$ of soil, so that this is equivalent to a concentration of contaminant per unit mass of soil of

$$\frac{(6.06 \times 10^{-10} \text{ g cm}^{-3})}{(0.25 \text{ g cm}^{-3})} = 2.43 \times 10^{-9}$$

or 0.00243 ppm.

- 20.** 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.

21. 100 g of a soil sample was treated chemically to extract all the uranium into 1.00 dm³ of solution. In an atomic absorption spectrophotometer, this solution gave an absorbance of 0.427. The spectrophotometer was calibrated using a standard solution with a uranium concentration of 1.00×10^{-6} mol dm⁻³. Various volumes of the standard solution were diluted with water to prepare 1.00 dm³ of solution.

Volume of standard in 1.00 dm ³ / cm ⁻³	5.0	10.0	15.0	20.0	25.0
Absorbance	0.130	0.275	0.412	0.550	0.687

Calculate the concentration of uranium (in ppm by mass) in the soil.

Strategy

Calculate the molar concentrations of each of the standard solutions and so prepare a calibration graph of absorbance versus molar concentration. Use the graph to determine the mass concentration of the unknown solution. Hence determine the mass, and thus the proportion, of uranium in the soil.

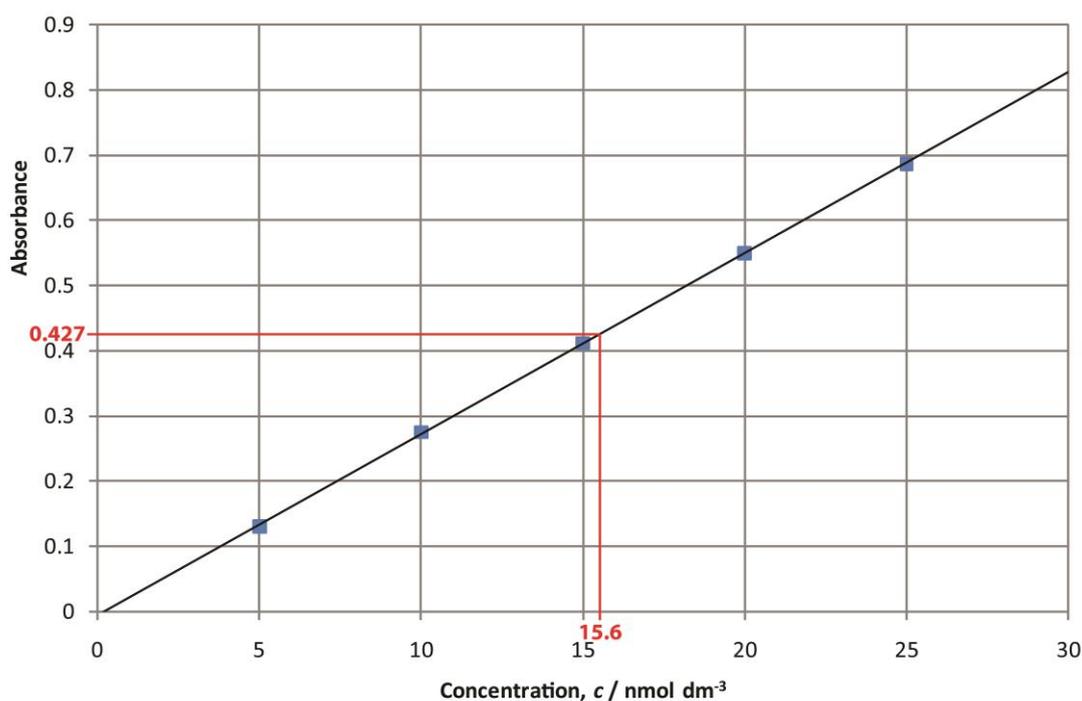
Solution

The standard solution has a uranium concentration of $1.00 \times 10^{-6} \text{ mol dm}^{-3}$, and so if 5.0 cm^3 of the solution are taken and diluted to a total volume of $1.00 \text{ dm}^3 \equiv 1000 \text{ cm}^3$, then the concentration of the resulting solution is

$$\begin{aligned} \{(5.0 \text{ cm}^3)/(1000 \text{ cm}^3)\} \times (1.00 \times 10^{-6} \text{ mol dm}^{-3}) &= 5.0 \times 10^{-9} \text{ mol dm}^{-3} \\ &= 5.0 \text{ nmol dm}^{-3} \end{aligned}$$

Preparing a calibration graph of absorbance against concentration,

Volume of standard in $1.00 \text{ dm}^3 / \text{cm}^3$	5.0	10.0	15.0	20.0	25.0
Concentration / nmol dm^{-3}	5.0	10.0	15.0	20.0	25.0
Absorbance	0.130	0.275	0.412	0.550	0.687



The solution being analysed gave an absorbance of 0.427. From the graph (either reading directly or using the equation of the line), this corresponds to a concentration of $15.6 \text{ nmol dm}^{-3}$. This came from 1.0 dm^3 of solution so that the amount of uranium was 15.6 nmol . This is equivalent to a mass

$$m = n \times M = \overbrace{(15.6 \times 10^{-9} \text{ mol})}^{\text{amount, } n} \times \overbrace{(238.0 \text{ g mol}^{-1})}^{\text{molar mass, } M} = 3.78 \times 10^{-6} \text{ g}$$

This was the mass contained in 100 g of sample, so that the proportion of uranium by mass must be

$$\{(3.78 \times 10^{-6} \text{ g}) / (100 \text{ g})\} \times 10^6 = 0.037 \text{ ppm}$$

22. A water company needed to measure the concentration of iron in a contaminated supply. A determination of Fe by atomic absorption spectrophotometry gave an absorbance of the water of 0.323 after diluting it ten times with pure water.

A standard Fe solution was prepared by dissolving 0.1200 g of iron wire in 1.00 dm^3 of acid. After a further $\times 100$ dilution the solution had an absorbance of 0.813. Find the concentration in **ppm** of iron in the water supply. How could this estimate be improved?

Strategy

You can use the standard addition method. Since you can calculate how much iron was contained in the standard solution which was added. The change in absorbance must be due to this concentration so that, knowing the absorbance of the original water, its iron concentration can be found by proportion.

Solution

For the standard solution, the concentration is

$$0.12 \text{ g dm}^{-3} = (0.12 \text{ g} / 55.845 \text{ g mol}^{-1}) = 2.15 \times 10^{-3} \text{ mol dm}^3.$$

This was diluted 100 fold so the aspirated standard had a concentration of $2.15 \times 10^{-5} \text{ mol dm}^3$

Hence, absorbance of 0.813 corresponds to a concentration of $2.15 \times 10^{-5} \text{ mol dm}^3$

The original water supply gives an absorbance of 0.323, corresponding to a concentration of

$$(0.323 / 0.813) \times 2.15 \times 10^{-5} \text{ mol dm}^3 = 8.54 \times 10^{-6} \text{ mol dm}^{-3}.$$

However, this has been diluted by 10 so the concentration is $8.54 \times 10^{-5} \text{ mol dm}^{-3}$

$$8.54 \times 10^{-5} \text{ mol dm}^{-3} = (8.54 \times 10^{-5} \text{ mol dm}^{-3} \times 55.845 \text{ g mol}^{-1}) = 0.0048 \text{ g dm}^{-3} = 4.80 \text{ ppm}$$

The analysis could be improved since only one standard sample was used. It would be better to use several independently prepared standards and/or use the standard addition method.

- 23.** Tributyl tin chloride, TBT, was commonly added to marine paints used to prevent the growth of barnacles on the hulls of ships although it is now banned due to its toxicity. A common method for analysing TBT in marine sediments is graphite furnace atomic absorption spectrophotometry (AAS). In a particular analysis, 0.500 g of a sediment was dissolved in 10.0 cm³ of acid. Aspiration into a graphite furnace AAS gave an absorbance of 0.44.

A standard solution of tin with an accurately known concentration of 1.0 µg dm⁻³ (1.0 ppb) was available. Known volumes of this were added to 1.00 dm³ volumetric flasks and made up to the mark with pure water. Aspiration under identical conditions gave the following results.

Volume standard added / cm ³	Absorbance
5	0.13
10	0.26
15	0.39

20	0.52
25	0.65

Find the concentration of TBT in the sediment.

Strategy

You know that the absorbance should be a linear function of concentration and so can plot a calibration graph. From the graph, you can read off the concentration corresponding to the absorbance of the sediment solution.

Solution

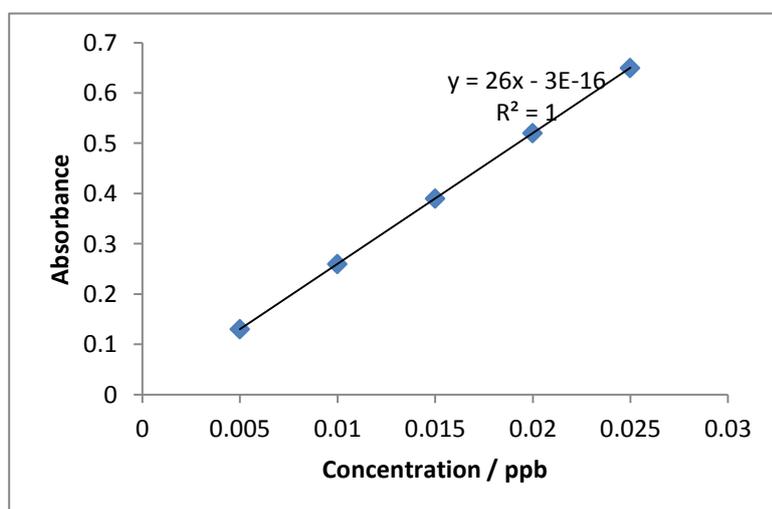
For the first standard solution, the concentration is given by:

$$5 \text{ cm}^3 \times 1.0 \text{ } \mu\text{g dm}^{-3} \times 0.001 \text{ dm}^3 \text{ cm}^{-3} = 0.005 \text{ } \mu\text{g} \text{ made up to } 1.0 \text{ dm}^{-3}$$

The concentrations of each solution can be calculated and a calibration graph plotted.

From the calibration data,

$$A = 26 \times (\text{concentration in ppb}).$$



The sediment sample had $A = 0.44$ corresponding to 0.017 ppb .

$0.017 \text{ ppb} = 0.017 \text{ ng cm}^{-3}$ so 10 cm^{-3} contained 0.17 ng . This came from 0.5 g sediment so 1 g contained 0.34 ng

Hence, sediment is 0.34 ng g^{-1}

- 24.** Suggest suitable analytical procedures to investigate the following situations. More than one technique may be appropriate depending on the circumstances. What are the factors that need to be considered in each case?
- (a) A mixture of tablets of analgesic drugs, including aspirin, paracetamol and morphine.
 - (b) A mixture of organic dyes in aqueous solution.
 - (c) A white powder found near the scene of a crime.
 - (d) The residue from a can of petrol suspected of being used in arson.
 - (e) The concentration of mercury in a freshwater lake.

Strategy

Consider whether and how the various components may be separated. Decide on a method that will allow the separate components to be distinguished.

Solution

- (a) There is more than one species to analyse so some separation is needed. The tablets are not volatile (so gas chromatography is not suitable) but do dissolve in water. Thus, high-performance liquid chromatography, HPLC, is suitable.
- (b) Since the dyes absorb strongly in the visible, UV/visible spectrophotometry would be suitable provided that the dyes absorb at different wavelengths.
- (c) As a preliminary method, the powder could be dissolved in a suitable solvent and the components separated and identified by thin-layer chromatography, TLC, through comparison with known compounds.
- (d) Petrol is volatile and so its components can be analysed by gas chromatography with FID detection. The proportions of each component can be compared with known samples to identify the petrol used.
- (e) The water can be analysed using atomic absorption spectrophotometry. Choosing the appropriate hollow cathode lamp means that only mercury will be measured and the concentration can be determined by calibrating the spectrophotometer with standard solutions.