

# CHAPTER 1

## FUNDAMENTAL CALCULATIONS IN ANALYTICAL CHEMISTRY

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### OBJECTIVES AND SCOPE

This chapter summarizes the units and the expressions of concentrations employed more often in the calculations associated to the analytical techniques presented in this book. How to (inter) convert them is also discussed, with special emphasis on conversion factors and mathematical relations between expressions/definitions. In our experience, this is a point where students present difficulties frequently throughout their B.S. degree. Another main objective here is to present a systematic approach for the student to deliver a final result taking into account every working step of the operational treatment of the samples or standards (drying, dissolution, dilution, concentration, digestion, etc.). This is an issue that will be reinforced in many examples throughout the other chapters contained in this book.

### 1. INTRODUCTION

It is critical for students to be aware of the importance of using the measurement units properly, to express the concentrations correctly and to consider the adequate number of significant figures. Throughout their professional careers, they will unavoidably have

to master every operation related to scientific notation, conversions among units and relationships between concentration forms. The adequate development of any analytical procedure depends on that, from its inception and planning to the preparation of the reagents, the choice of suitable laboratory material and the final result and its interpretation.

The calculations reflect the different stages of the analytical process and, so, the more complex the analytical procedures become, the more intertwined the required calculations will be. In general, calculations are not too complex although it is essential to understand what is going on chemically in each step of the analysis. This would allow students to establish the appropriate mathematical relationships between the various stages of the analytical process.

To achieve satisfactory learning outcomes, you should be able to understand and justify every operation or calculation rather than only performing them mechanically, so that you yourself should be able to detect any gross error in the final solution. There is no single ‘magic’ formula to solve all exercises. Students have to learn problem-solving strategies and start developing some chemical intuition (‘the chemical criterion’). This means that they must develop critical thinking skills to succeed in their professional lives.

A fundamental starting point that falls outside the scope of this book is that the students should know how to formulate (and name) all the compounds involved in the exercises to correctly write and balance the chemical reactions. (S)He has to know how to perform the necessary basic stoichiometric calculations. Without this essential background, (s)he will not achieve satisfactory results in their degrees or, worse, they will fail as chemists. When the compounds mentioned into the numerical exercises are not of common use, their chemical structure will be shown. This will be particularly so in Chapter 6.

### 1.1. Relevant units and expressions of concentration

Initially, it is worth starting this chapter by presenting some basic recommendations. As a general rule, scientific notation must be used

in order to avoid working with very large or very small numbers, being advisable to obtain a number between 1 and 10, and to express its magnitude through an exponent. Thus, large numbers have positive exponents and small numbers have negative exponents.

Another way for chemists to avoid using very large or very small numbers is by selecting the most suitable measuring unit or concentration expression for each number. Furthermore, the units of measurement have a major role in making the numbers meaningful. In effect, a number itself makes little sense. If you read in a laboratory manual: mix 1 of sodium carbonate and 2 of sodium hydrogen carbonate, what would you do? You should ask for the lost units!

### 1.1.1. Units

From the previous discussions, it turns out that the value of a quantity should be reported as the product of a number and a unit. The number multiplying the unit is the numerical value of the quantity expressed in that unit.

For scientific measurements, the most convenient metric system is the *International System of Units* (*Système International d'Unités*) with the international abbreviation **SI**, which is used worldwide, although in the United States of America and most countries associated in the Commonwealth, the so-called *English system* is applied frequently. This uses traditional units such as inches, yards and pounds instead of the metric system such as centimeters, meters and kilograms (see Table 1 for some examples).

The SI defines a set of basic units, prefixes and derived units. All related information is exhaustively compiled and updated at the official website of the responsible organization, the *Bureau International des Poids et Mesures*, BIPM [1].

Following International Union for Pure and Applied Chemistry (IUPAC) recommendations [2], the symbol of the unit is placed after the numerical value, separated by a space (i.e.,  $t = 25$  mL instead of 25mL); it is written in roman (upright) type (km instead *km*); it should remain unaltered in the plural (i.e., 10 cm, not 10 cms) and

Table 1. Some common units and equivalences between the SI and the English system.

	International system (SI)	English system
Mass	1 kilogram (kg)	2.205 pounds (lb)
	453.59 grams (g)	1 pounds (lb)
	28.35 grams (g)	1 ounce (oz)
Volume	1 liter (L)	1.057 quarts (qt)
	3.785 liters (L)	1 U.S. gallon (gal)
	100 milliliters (mL)	6.10 cubic inch (in <sup>3</sup> )

should not be followed by a full stop (but at the end of a sentence). The symbols should be printed in lowercase letters, except for those derived from a personal name. An exception is the symbol for the liter, which can be uppercase (L, more advisable) and lowercase (l), to avoid its confusion with a one.

It is also advisable not to mix information with unit symbols. For example, the form ‘the copper content is 5 mg/kg’ should be used instead of ‘5 mg Cu/kg’ or ‘5 mg of copper/kg’. When mathematical operations are performed, it should be made clear to which unit symbol a numerical value belongs to. Thus, 12 cm × 3 cm is used and not 12 × 3 cm; 54 mg ± 1 mg or (54 ± 1) mg, but not 54 ± 1 mg [3].

Commas are not used to separate digits into groups of three but a plain space, counting from both the left and the right of the decimal symbol. For example, 5 425.123 12 instead of 5,425.12312 is preferred.

When scientific measurements or results are reported, the number should be written according to some additional criteria as, for instance, the number of significant figures. The result should only contain digits which are considered ‘correct’ except for the last digit, which indicates that such digit is not ‘certain’, but estimated. Students should be familiar with the basic rules for setting significant figures for the results, as well as their rounding. These issues are not considered here due to space restrictions but the student can find them in almost all classical textbooks on analytical chemistry.

### 1.1.2. Some important terminologies

In this section, we will try to summarize different terminologies intended to indicate the concentration of a mixture, solution, sample, etc. Please bear in mind that not always the recommendations from competent organizations, as NIST or IUPAC, are applied in every academic and scientific text. Nevertheless, we will resume here, as practically as possible, the most widely used terms, as well as some indications on their limitations.

The term *concentration* is related to the composition of a mixture in which we need to describe the amount of one or more substances ('constituents' or 'components' are preferred terms) that are present. According to IUPAC, the term concentration includes four quantities characterizing the composition of a mixture with respect to the volume of the mixture [4]: mass, amount, volume and number concentration. Also, the term concentration is a shortcut for *amount-of-substance concentration* or *amount concentration*.

The SI unit for the amount of substance is the mole ( $n$ ): defined as the *amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12* [2]. IUPAC recommends that this physical quantity ('amount of substance') is no longer called 'number of moles', just as the physical quantity 'mass' should not be called 'number of kilograms'. This unit is selected so that the *atomic mass* (expressed in the unified atomic mass unit, u) and the *molar mass* (in grams/mol) have the same numerical value (*Note*: the abbreviation amu is not an acceptable unit symbol nowadays for the unified atomic mass unit).

In general, the calculations that involve moles of a substance require the use of the molar mass of that substance. The terms *atomic weight* and *molecular weight* are obsolete and, thus, should be avoided. They have been replaced by the equivalent but preferred terms *relative atomic mass* and *relative molecular mass*, respectively, which are simple dimensionless numbers. When they are expressed as g/mol, they are designated as *molar mass*, represented by  $M$ , for both atoms and molecules.

The concentration or *amount-of-substance concentration* ( $c_A$ ) is the amount of a substance,  $A$ , divided by the volume of the mixture in which it is present:  $c_A = n_A/V$ . The common unit is  $\text{mol/dm}^3$  or  $\text{mol/L}$ . Molarity ( $M$ ) is commonly used instead of these terms. Thus, the molarity for a  $0.5 \text{ mol/dm}^3$  solution is said to be  $0.5 M$  ( $0.5$  molar solution). However, NIST's Guide [3] prefers the original term because it is unambiguous; they recommend that the term molarity and the  $M$  symbol should no longer be used because they are obsolete. However, its use is so rooted and broadly extended in chemistry that this change will, likely, be difficult.

Related terms are: (i) *substance content*, defined as the amount-of-substance of a component ( $n$ ) divided by the mass of the system ( $m$ ); (ii) *number concentration* ( $C$ ), the number of entities of a constituent in a mixture divided by the volume of the mixture; (iii) *mass concentration*, mass of a constituent divided by the volume of the mixture; (iv) *volume fraction*, volume of a constituent of a mixture divided by the sum of volumes of all constituents before mixing them.

The relationship between all these terms is summarized in Figure 1. In general, the term level as a synonym for content is obsolete.

### 1.1.3. Specifying the concentrations of solutions

A *solution* is a liquid or a solid phase containing more than one substance. One of them is called the solvent, whereas the other(s) is(are) called solute(s). When the sum of the mole fractions of solutes is small compared with unity, as it is frequently (but not necessarily) the case, the solution is called a *diluted solution*. That is, the solutes are the minor constituents and the solvent is the major constituent. A *concentrated solution* contains large amounts of solute relative to the solvent.

A *standard solution* is a solution of accurately known concentration, prepared using standard substances in one of several ways.

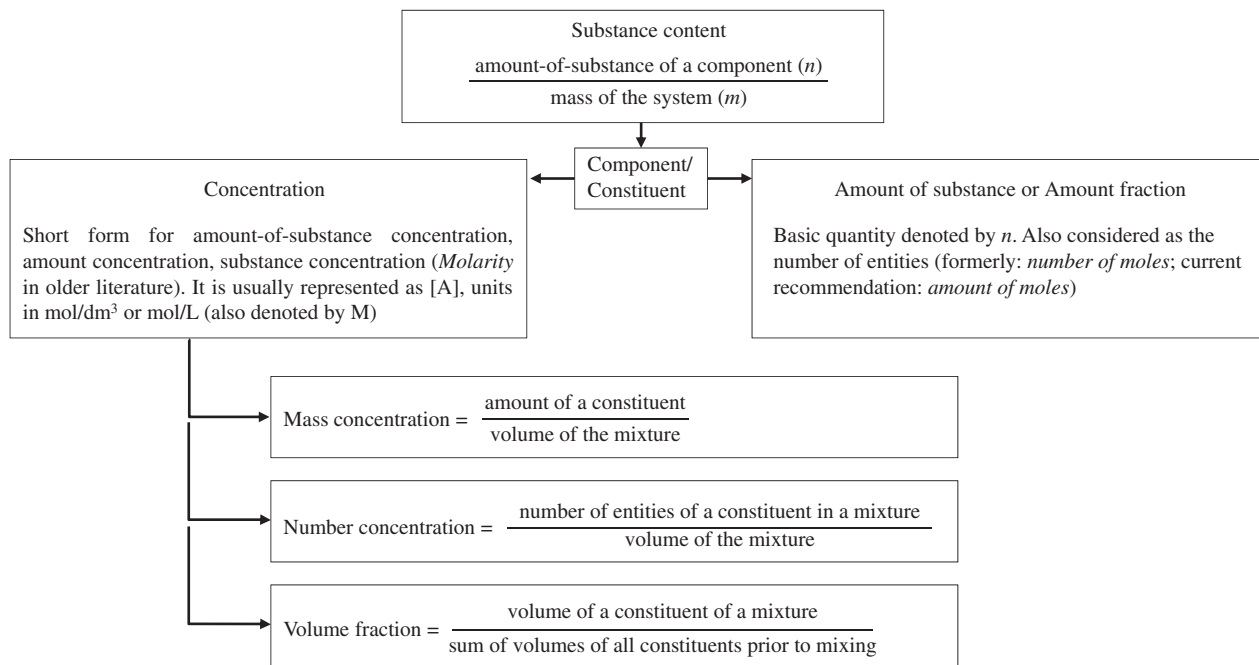


Figure 1. Definitions of the main terms related to the composition of a mixture (adapted from Ref. [4]).

A primary standard is a substance of known high purity which may be dissolved in a known volume of solvent to give a primary standard solution. A secondary standard is a substance whose active agent has been found by comparison against a primary standard. Their concentrations may be expressed in  $\text{mol/dm}^3$ , although due to traditional customs, they are frequently reported as M (molarity) or N (normality).

In general, the concentration of a solution is defined as the amount-of-substance (in plain language, amount) of solute per given amount of solution. It is expressed in a variety of ways although only a handful of them are frequent. Students often have difficulties in correctly interconverting them, even in highest courses of the Degree, which should not occur at all. Table 2 shows the most common expressions used by chemists to indicate a solution concentration.

The most important notion required for a concentration conversion step is to define and (re)write the concentration units in their simplest forms. Of course, you must know the definitions of the individual concentration units and how to rewrite the units.

The combinations of letters like ‘ppm’, ‘ppb’ and ‘ppt’ (and, so, the terms part per million, part per billion, part per trillion and the like) should not be employed to indicate the values of quantities or concentration. The following forms are recommended instead: for example,  $2.0 \mu\text{L/L}$  or  $2.0 \times 10^{-6} \text{ V}$ ,  $4.3 \text{ nm/m}$  or  $4.3 \times 10^{-9} \text{ l}$ ,  $7 \text{ ps/s}$

Table 2. Common expressions for solution concentration.

Expression	Symbol	Definition
Molarity	M	Moles of solute dissolved per 1 L of solution
Mass percent	% (m/m)	Grams of solute dissolved per 100 g of solution
Volume percent	% (v/v)	Milliliters of solute per 100 mL of solution
Mass per volume	mg/L	Mass in grams of solute per 1 L of solution
Mole fraction	$\chi$	Moles of solute per total amount of moles
Molality	m	Moles of solute per 1 kg of solvent
Normality	N	Equivalents of solute per 1 L of solution.



or  $7 \times 10^{-12} t$ , where  $V$ ,  $l$  and  $t$  are the adequate quantity symbols for volume, length, and time respectively [4].

Some old expressions for the concentration are ubiquitous since they are still present in many fields such as regulations, textbooks and scientific reports, to cite but a few. Thus, as it was commented already for the molarity, the term *normality* and its symbol,  $N$ , should no longer be used because they are obsolete. The main limitation of this term is that there is no unique expression for its calculation because it is a function of the reaction that takes place, which usually represents a big difficulty for students. However, it is very useful and convenient to carry out many calculations. Two typical examples are the Faraday's statements on electrical deposition and the calculations associated to many electroanalytical measurements.

Normality is an old term in chemistry based on the concept of equivalence between the amounts of reacting substances. It has played a fundamental role in the history of quantitative analysis (all reactions take place on an equivalent-to-equivalent basis). Today, its role in titrimetric analysis and electrochemistry studies is still very important. The equivalent of a species must be specified with respect to a definite reaction. For instance:

- (i) For acid–base reactions, 1 equivalent equals 1 mole of hydrogen ions donated or accepted.
- (ii) For oxidation–reduction reactions, 1 equivalent equals 1 mole of electrons.
- (iii) For determining electrolyte concentration, 1 equivalent equals 1 mole of electrical charge.

A direct relation between molarity and normality is derived easily considering their definitions:  $N = M \cdot K$ , where  $K$  denotes the amount of equivalents (corresponding to moles of hydrogen ions, electrons or charge, depending on the type of reaction). To reach this formula, the term equivalent weight (EW) must be considered as the mass of a compound that contains an equivalent (e.g., the equivalent weight of an acid is the mass of acid required to generate one mole of hydrogen ion — hydronium — in aqueous solution). It is calculated as:  $EW = M/\text{amount of equivalents}$ .

The use of percentages also leads to confusing situations for students, mainly due to the diversity of terms related to this expression: percentage by weight, percentage by mass, percentage by volume, percentage by amount of substance, percentage solution, etc.; as well as the symbology to denote them: % (by weight), % (by volume), % (mol/mol), etc. Thus, somehow contrary to common practices in laboratories, NIST [3] discourages the use of phrases like ‘percentage by weight’, ‘percentage by mass’, and the like. Similarly, one should avoid writing, for instance, ‘% (m/m)’, ‘% (by weight)’, ‘% (v/v)’, ‘% (by volume)’, or ‘% (mol/mol)’. The preferred forms are ‘the mass fraction is 0.10’ or ‘the mass fraction is 10 %’, or ‘the amount-of-substance fraction is 0.10’, or ‘the amount-of-substance fraction is 10 %’.

In the next sections, the term ‘percent solution’ will be always related to either ‘mass percent’ (often designed by m/m) or ‘volume percent’ (v/v), avoiding other ambiguous terms. The resulting number is dimensionless. The term mass/volume percent (m/v) is discouraged because numerator and denominator have different units and, therefore, this concentration unit is not a true relative unit. However, it is often employed as a simple-to-use concentration unit since volumes of solvent and solutions are easier to measure than weights. Moreover, since the density of dilute aqueous solutions is close to  $1 \text{ g/cm}^3$ , if the volume of a solution is measured in mL (as per definition), then this well approximates the mass of the solution in grams (making a true relative unit) [5].

## 1.2. Preparing solutions from solids or liquids

Solutions are commonly made in the laboratory from solid materials, from liquids or from other solutions. It is very advisable to use the correct terminology in each instance. Thus, the process of dissolving a solute in a solvent is called *dissolution* (dissolving) and when the solution is prepared from a liquid, the process is called *dilution* (diluting).

Note that when solid materials or reagents are considered, a solvent will only dissolve a limited quantity of solute, at a given

temperature, according to the salt solubility (a physical property of the salt). However, the rate at which the solute dissolves can be accelerated by triturating the solid, heating the solvent and/or agitating the mixture.

To calculate the mass of a reagent required to prepare a solution, it is very important to consider whether that reagent has water molecules of hydration. If it does, they must be included in the molar mass because, otherwise, a serious error (by default) is committed.

In many cases, solutions are prepared from a liquid reagent or stock solution by addition of a known amount of solvent, usually deionized water. Thus, a volume of a stock solution is combined with the appropriate volume of solvent to achieve the desired concentration in the diluted solution.

Usually, a very simple, common equation is applied to perform the calculations related to dilution. It combines the concentrations and volumes of both the concentrated and the diluted dissolutions, and considers that the amount of solute that is finally present in the diluted solution proceeds uniquely from the volume of the concentrated stock solution. Figure 2 shows the basic operations implied in this typical procedure.

$$C_{\text{concentrated}} \cdot V_{\text{concentrated}} = C_{\text{diluted}} \cdot V_{\text{diluted}}$$

$$C_1 \cdot V_1 = C_2 \cdot V_2$$

Although it might be ambiguous and confusing for students, the notation ‘:’ is still used to designate dilutions (this option is not recommended by NIST). For example, a 1:10 dilution (verbalize as ‘1 to 10’ dilution) entails combining one unit volume of the solution to be diluted plus nine unit volumes of the solvent.

An important caveat is not to confound the act of preparing a solution by mixing parts or volumes of different solutions (even deionized water) with a simple dilution step. In doubt, ask always to

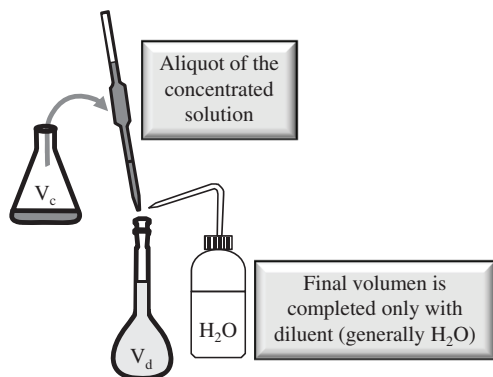


Figure 2. Basic operations for dilution.

avoid misunderstanding. Thus, to prepare a 1:4 acetic acid–ethanol solution, you should mix one unit volume of acetic acid and four unit volumes of ethanol. However, to make a 1:4 dilution of acetic acid in ethanol, you should mix one unit volume of acetic acid with three unit volumes of ethanol (to make four unit volumes of solution).

Another aspect that may mislead students is that many times, the volume to prepare the final solution is not indicated explicitly. They must decide it in accordance to the needs of the assay.

### 1.3. General operational treatments before the analysis

Another embarrassing question for students is usually associated to the calculations involved in multistage sample (standard) treatment to bring it to a state suitable to perform an experimental measurement. For example, the sample is solid and we have to analyze a solution which is obtained after applying a series of treatments. This will be discussed in this section and many examples will be proposed throughout Chapters 5 and 6, mainly.

When we consider the analysis of a *sample* (consider this term in a chemical sense, not in a statistical one as in Chapter 2), we are thinking on withdrawing a portion of material from a larger quantity of that material and, then, analyzing only that portion. But that

term can be ambiguous if we do not specify what type of sample we are considering; namely, bulk sample, representative sample, primary sample, test sample, etc. The existence of a sampling error when obtaining such portion has to be assumed, which means that the results gathered from different portions extracted from the bulk (or lot) are only estimates of the true concentration of the constituent of interest in it. The portion removed from the bulk is called a *test portion* or *aliquot* (or specimen, in some cases).

The term *aliquot*, a known amount of a homogeneous material, is usually applied properly to fluids, although there are some difficulties when solids are considered. Sometimes, it matches with *test portion*, which is the amount or volume of the test sample taken for the analysis, usually of known weight or volume.

The solution prepared from the test portion to perform the analytical measurement is called *test solution* (proportions of the test portion and solvent are normally known). If the test solution has been subjected to reaction or separation procedures prior to measurement, the resulting solution is called *treated solution* [4].

In general, the objective of an analysis is to determine/quantitate an *analyte*. Thus, the analyte is the component of a system we are interested in, and which has to be measured [4]. It is differentiated from the other components of the sample which, in conjunction, is called *matrix*. *Qualitative analysis* involves identifying the analyte: atoms, molecules or functional groups. It indicates the *presence* of the analyte in the matrix. *Quantitative analysis* involves measuring the amount or concentration of the analyte in the sample. It indicates the magnitude of the property being measured and it commonly (but not necessarily) relates to the *concentration* of analyte in the matrix, it could be any other physical, chemical or biological property.

### 1.3.1. Drying

Many samples are wet originally and they must be dried before they can be analyzed. Sometimes, this step is mandatory because of the

nature of the next step of the analytical procedure (grinding, sieving, digestion, etc.) and in other cases, it is made to get a dried sample with a constant mass to which the content of the analyte investigated in the analysis can be easily referred to.

Drying can also be required for chemical reagents prior their use. This is usually the case for hygroscopic salts which should be dried first in order to weight them accurately. Drying is very important whenever standard solutions are prepared from solid primary standards and its correct performance is crucial to achieve reliable results, because drying a substance under improper conditions can result in the loss of target elements (or even in the transformation to a different compound).

Constant weight is obtained by removing the water from the sample, that is, by drying it. Mathematically, the water content (moisture) of the sample can be calculated usually in the form of a mass percent (%). Experimentally, moisture is determined by measuring the mass of a sample before and after water is removed by drying. Then, we apply the mass percent expression, as follows:

$$\text{Moisture (\%)} = \frac{M_{\text{initial}} - M_{\text{dried}}}{M_{\text{initial}}} \cdot 100$$

Here,  $M_{\text{initial}}$  and  $M_{\text{dried}}$  are the mass of sample before and after drying, respectively. Their difference represents the water content of the sample.

### 1.3.2. Dissolution, digestion and extraction

Most methods of analysis necessitate a more or less simple (more often than not, complex) preparation of the sample. Only few direct methods allow the introduction of the sample without any preparation.

When solid samples are analyzed, and even some complex liquid matrices, a partial or total dissolution is needed prior to their instrumental analysis. A variety of ‘sample treatment’ methods have been developed and reported in literature, depending on the type of matrix, analyte, methodology, instrumentation used, etc. They

can involve dissolution, digestion, extraction of the sample, and any combination among them.

In quantitative analysis, it is essential to consider mathematically all treatments of the sample to reach the objective, which is to determine the amount or concentration of analyte in the sample. The process can be schematized briefly as: a given mass of sample is submitted to a series of treatments to finally obtain a solution. This is the test portion which, when analyzed yields a result that must be converted through adequate calculations to the concentration of the constituent we are interested in.

The biggest difficulties that many students face consist often of relating each intermediate dissolution with the corresponding changes in analyte concentration, deciding if a particular treatment modifies the analyte concentration, i.e., whether it increases (decreases) the concentration.

In almost all circumstances, the solution to these problems is very simple: depict graphically the process you are studying, set each step and the numerical information you have, write each number with its correct units and identify somehow (by a letter, a number, etc.) each solution obtained during the analytical procedure and, finally, evaluate whether it is a dilution or a concentration. In this way, you will assure that each unit will be canceled out correctly, and check easily whether the correct units for your numerical result were obtained.

The steps of a basic analytical procedure to analyze a solid sample or complex liquid sample are presented in Figure 3a. Despite how complex it may appear, it can be simplified largely to perform the necessary calculations (Figure 3b).

Finally, remember that the enunciates of the numerical exercises will contain (almost all) data you will need to solve them (tables are contained in the introductory sections and students have to realize when they need them). Therefore, read them carefully and discriminate between queries and supplied information, otherwise mistakes occur frequently. For instance, in some exercises, the questions may be formulated in one direction or in another, that is, you may be asked to calculate the concentration in the sample

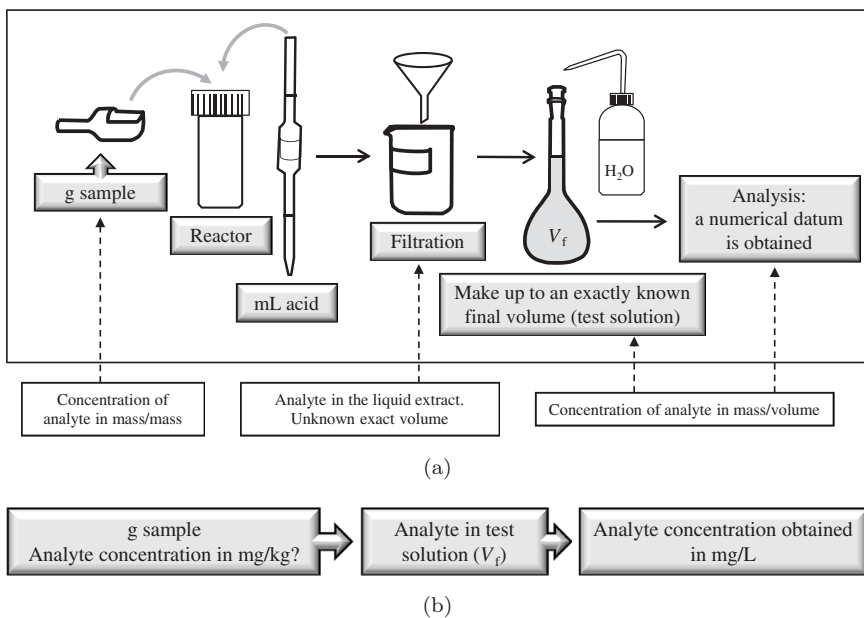


Figure 3. (a) Graphical representation of a typical sample treatment procedure and (b) its conceptual simplification to perform the final calculations.

or in the test portion. For both situations, the multistep conversion procedure seen above will be valid.

Units are critical in calculations. You should always include units in your calculations, they will help you determine the correct solving approach. Converting from one unit to another is simply made by multiplying, dividing and canceling units like any other algebraic quantity.

### 1.3.3. Dilution and concentration of test solutions

Sometimes, when analyzing a test portion, the result gathered from the instrumental system is out of the calibration range where accuracy was validated (this is explained in more detail in Chapter 2). When this occurs, the test portion of the sample must be diluted, if it is above the limits; or concentrated, if it is below them. Next,



they have to be measured again and the new result used to calculate the concentration of analyte in the original sample. Dilution and concentration factors, respectively, are considered usually in such situations, although IUPAC discourages their use.

The dilution factor (DF) is equal to the final volume of the solution to be measured (volume of the test portion plus volume of the diluent) divided by the volume of the original test portion.

Dilution factor (DF)

$$= \frac{\text{Final volume of the solution to be measured } (V_f)}{\text{Original test portion } (V_o)} = \frac{V_f}{V_o}$$

The concentration factor (CF) is calculated analogously as the final volume of the solution to be measured divided by the original volume of the test portion.

A simplified way to solve this type of calculation consists of using the same approach as for preparing solutions by diluting a concentrated stock solution:

$$C_1 \cdot V_1 = C_2 \cdot V_2$$

$$C_{\text{initial}} \cdot V_{\text{initial}} = C_{\text{final}} \cdot V_{\text{final}}$$

Here,  $C_{\text{initial}}$  and  $V_{\text{initial}}$  refer to the concentration and volume of the concentrated solution, respectively. When a known and exact amount of solvent is added to this solution, a diluted solution is obtained, being  $C_{\text{final}}$  its concentration and  $V_{\text{final}}$  its volume.

Note that it does not matter what the units of  $C$  and  $V$  are; but of course, they have to be the same on each side of the equation. Keep your units coherent!

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## WORKED EXERCISES

### Some preliminary notes:

- (1) Every number (result) you write down in science should have some units accompanying it. Quite often, undergraduates perform calculations and they report only numbers in their notebooks, without units. This is a serious mistake that may cause them many problems in their professional life.
- (2) Identify the solute, solvent and solution (solution = solute + solvent).
- (3) Identify each quantity symbol with their corresponding substance. For this, it is generally preferable to place symbols for substances in parentheses immediately after the quantity symbol, for example  $n(\text{NaOH})$ ,  $M(\text{H}_2\text{SO}_4)$ ; or as a subscript,  $C_{\text{Hg}}$ .
- (4) Whenever you solve any kind of quantitative exercise/calculation, you must check whether it makes sense.
- (5) Usually, there are many ways to solve a problem. If the one you apply has no conceptual drawbacks (too frequent in

students!), makes you feel comfortable, you really understand it, you can justify it, and it delivers correct results always, go ahead and follow it!

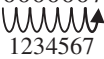
- (6) When the sample to be analyzed has to be submitted to several sample treatment steps, we strongly recommend to depict the analytical process in order to avoid typical missing calculations associated with sample treatment.
- (7) In this chapter, the numerical exercises will discriminate with detail the data which are given in the enunciate and those which are requested for you to calculate. In the other chapters, this task is let to the student. Remember that it is always advisable to write down this scheme before starting the exercise.

1. The visible region of the electromagnetic spectrum corresponds to wavelengths from about  $0.00000078 \text{ m}$  to  $0.00000038 \text{ m}$ . Express this range in (a) scientific notation, (b) adequate units.

SOLUTION:

**Question a:**

To convert these numbers to scientific notation, move the decimal point to the right 7 decimal places. For this reason, the exponent will be 7. The sign of the exponent is negative as the decimal point moves to the right.

Strategy:  $0.00000078$   
  
 1234567

Solution:  $7.8 \times 10^{-7} \text{ m}$  and  $3.8 \times 10^{-7} \text{ m}$ .

**Question b:**

To select the most adequate units (SI) for a value, it is advisable to obtain a number higher than 1 and lower than 1000. Moreover, scientific criteria should be applied, according to our previous knowledge of the particular subject, to assess its significance.

Taking into account that the exponent that converts these numbers into an integer is  $-7$ , the unit that has a similar relation with the meter is nanometer ( $10^{-9}$  m).

$$7.8 \cdot 10^{-7} \text{ m} \cdot \frac{10^9 \text{ nm}}{1 \text{ m}} = 7.8 \cdot 10^2 \text{ nm} = 780 \text{ nm}$$

The results you were asked for are 780 nm and 380 nm.

2. Calculate the concentration of a solution prepared by mixing 24.0 g of potassium chloride with 126.0 g of water. Express it as (a) mass percent and (b) molality.

**SOLUTION:**

You can follow the next steps: (1) Define clearly the quantities you get in the enunciate and the quantities you are requested to calculate, (2) write down the concentration expression you need, (3) substitute solute and solvent (solution) quantities into the equation and perform the calculations.

<i>Data</i>	<i>Given by enunciate:</i>	<i>Have to find out:</i>
	24.0 g solute	% KCl
	126.0 g H <sub>2</sub> O	m

**Question a:**

$$\begin{aligned} \%(m/m) &= \frac{\text{mass of solute}}{\text{mass of solution}} \cdot 100 \\ \%(m/m) &= \frac{24.0}{24.0 + 126.0} \cdot 100 = 16 \% \end{aligned}$$

**Question b:**

$$m = \frac{n \text{ solute}}{\text{mass (kg) solvent}} = \frac{\text{mass (g) solute/molar mass solute}}{\text{mass (kg) solvent}}$$

$$M(\text{KCl}): 39.1 + 35.5 = 74.6 \text{ g/mol}$$

$$m = \frac{24.0 \text{ g solute}}{126.0 \text{ kg solvent}} \cdot \frac{1 \text{ mole solute}}{74.6 \text{ g solute}} = 0.0025 \text{ m}$$

The final solution has 16 % of potassium chloride and a molality of  $2.5 \times 10^{-3}$ .

3. The European guideline value for total inorganic mercury in drinking water is  $6 \mu\text{g/L}$ . Two laboratories reported average results for the analysis of two spring water samples, which were 1 mM (sample A) and  $2 \cdot 10^{-5} \%$  (in w/v, sample B), can you drink them safely?

### SOLUTION:

To compare these concentrations is mandatory to express them in the same units. Thus, taking into account that the guideline value is given in  $\mu\text{g/L}$ , we will consider this unit as the reference one ( $C_{\text{Hg}}$ ).

<i>Data</i>	<i>Given by enunciate:</i>	<i>Have to find out:</i>
	Guideline value: $6 \mu\text{g/L Hg}$	$C_{\text{Hg}}$ in $\mu\text{g/L}$
	Sample A: 1 mM Hg	
	Sample B: $2 \cdot 10^{-5} \%$ (m/v) Hg	

Now, the next steps for sample A should be done:

- Rewrite 1 mM (millimolar) as a function of M:  $1 \text{ mM} = 10^{-3} \text{ M}$
- Express M in its simplest possible units:  $10^{-3} \text{ mol/L}$
- Convert molarity to g/L multiplying by the molar mass of the analyte ( $M(\text{Hg}) = 206.6 \text{ g/mol}$ ), and finally convert g to  $\mu\text{g}$ :

$$C_{\text{Hg}} = 10^{-3} \frac{\text{mol}}{\text{L}} \cdot \frac{206.6 \text{ g}}{1 \text{ mol}} \cdot \frac{10^3 \mu\text{g}}{1 \text{ g}} = 206.6 \mu\text{g/L}$$

For sample B:

- Rewrite % (w/v) in its simplest possible units:  $2 \cdot 10^{-5} \text{ g/100 mL}$
- Divide to obtain:  $2 \cdot 10^{-7} \text{ g/mL}$

- Convert g in  $\mu\text{g}$  and mL in L with the appropriate conversion factor:

$$C_{\text{Hg}} = 2 \cdot 10^{-7} \frac{\text{g}}{\text{mL}} \cdot \frac{10^6 \mu\text{g}}{1 \text{ g}} \cdot \frac{10^3 \text{ mL}}{1 \text{ L}} = 2 \cdot 10^2 \mu\text{g/L}$$

Accordingly, the solution to this exercise is: Both samples, A and B, exceeded the guideline value for total inorganic mercury as  $206.6 \mu\text{g/L}$  and  $200 \mu\text{g/L}$  and are higher than  $6 \mu\text{g/L}$  and, so, they should not be drunk.

Observe that, as it will occur many times in Chapter 2, the solution to the exercise is not a value, but a statement or conclusion. When solving out the exercises, do not forget to keep your units!

4. What is the concentration of the  $\text{Cu}^{2+}$  ion, expressed as molarity, in a solution prepared by dissolving 1.25 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in enough water to give 50.0 mL of solution?

SOLUTION:

The highlight of this problem is that the salt used to prepare the solution is hydrated. Thus, we have to consider those molecules of hydration water in the calculation of its molar mass:  $M(\text{CuSO}_4 \cdot 5\text{H}_2\text{O})$ :  $159.5 + 5 \cdot 18 = 249.5 \text{ g/mol}$ .

<i>Data</i>	<i>Given by enunciate:</i>	<i>Have to find out:</i>
	1.25 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	$M(\text{Cu}^{2+})$
	50 mL solution	

$$\begin{aligned}
 & \frac{1.25 \text{ g } \text{CuSO}_4 \cdot 5\text{H}_2\text{O}}{50 \text{ mL solution}} \cdot \frac{1 \text{ mol } \text{CuSO}_4 \cdot 5\text{H}_2\text{O}}{249.5 \text{ g } \text{CuSO}_4 \cdot 5\text{H}_2\text{O}} \\
 & \cdot \frac{1 \text{ mol } \text{Cu}^{2+}}{1 \text{ mol } \text{CuSO}_4 \cdot 5\text{H}_2\text{O}} \cdot \frac{10^3 \text{ mL}}{1 \text{ L}} \\
 & = 0.10 \text{ mol/L}
 \end{aligned}$$

Molarity concentration of  $\text{Cu}^{2+} = 0.10 \text{ M}$

5. Prepare 150 mL of 4%  $\text{Na}_2\text{CO}_3$  from a 6.00 M stock solution of this salt.

### SOLUTION:

This problem calls for the use of the  $V_1 \cdot C_1 = V_2 \cdot C_2$  formula, since a stock concentrated solution is used to prepare a diluted solution of the same solute. But the concentrations given in the enunciate are in different units; therefore, one of them must be converted to match the other. It does not matter which unit of concentration is chosen. Let us convert them to molarity.

Firstly, we must know the type of percent solution. When no description accompanies the unit, a mass percent solution is assumed (m/m).

A practical way to convert % to M, as well as to other expressions, is to use concentrations as *conversion factor*:

Mass percent	Meaning	Conversion factors	
4 %	4 g of $\text{Na}_2\text{CO}_3$ in 100 g of solution	$\frac{4 \text{ g of Na}_2\text{CO}_3}{100 \text{ g of solution}}$	$\frac{100 \text{ g of solution}}{4 \text{ g of Na}_2\text{CO}_3}$

Now, the adequate conversion factor is employed to transform the 4 % value, as well as additional conversion factors to pass g of salt to mole (using molar mass) and to convert g of solution to L of solution. This requires a value for the density of the solution but that was not given, so we considered it equal to the water density ( $1 \text{ g/cm}^3$ , at  $25^\circ\text{C}$ ). This is true in dilute aqueous solutions.

$$\begin{aligned}
 & \frac{4 \text{ g Na}_2\text{CO}_3}{100 \text{ g solution}} \cdot \frac{1 \text{ mol Na}_2\text{CO}_3}{106 \text{ g Na}_2\text{CO}_3} \cdot \frac{1 \text{ g solution}}{1 \text{ cm}^3 \text{ solution}} \\
 & \cdot \frac{10^3 \text{ cm}^3 \text{ solution}}{1 \text{ L solution}} = 0.38 \text{ mol/L}
 \end{aligned}$$

So, the 4%  $\text{Na}_2\text{CO}_3$  stock solution has a molarity of 0.38 M.

Now using the dilution formula, we can calculate the volume of 6.00 M  $\text{Na}_2\text{CO}_3$  stock that is needed to prepare 150 mL of 0.38 M solution.

$$C_1 \cdot V_1 = C_2 \cdot V_2$$

Data are replaced:  $6.00 \text{ M} \cdot V_1 = 0.38 \text{ M} \cdot 150 \text{ mL}$

$$V_1 = \frac{0.38 \text{ M} \cdot 150 \text{ mL}}{6.00 \text{ M}}$$

After canceling the units,  $V_1 = 9.5 \text{ mL}$ .

Finally, to prepare a 4%  $\text{Na}_2\text{CO}_3$  solution, 9.5 mL of a 6 M solution will be measured and the volume completed with distilled water to 150 mL.

The use of concentrations as *conversion factor* simplified the calculations, but it is impossible to correctly apply them if the corresponding units are omitted!

When a percent concentration is given without specifying the type of percent concentration (not a desirable situation, although frequent), you have to assume that it is mass percent (m/m).

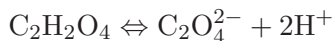
6. A 0.10 M solution of oxalic acid will be used as titrant in an acid–base titration. To facilitate further volumetric calculations, express its concentration as normality.

**SOLUTION:**

The relation between both units is:  $N = M \cdot K$ , where  $K$  is an integer constant  $\geq 1$  and for a particular species is defined by the reaction type and the balanced chemical reaction. In this case, the enunciate indicates that the type of reaction is acid–base. Hence,  $K$  is the number of moles of  $\text{H}^+$  produced or neutralized per mole of acid or base supplied. In this case, we consider the



ionization equilibrium of the oxalic acid:



- This acid produces 2 moles of  $\text{H}^+$
- Calculate:  $N = 0.10 \cdot 2 = 0.20 \text{ N}$ .

The normality of the oxalic acid is twice its molarity, as it can offer two protons per mole of compound.

The solution we are looking for is: 0.20 N.

It is common (mainly in exams and laboratories) that students get doubts on whether the correct equation is  $N = M \cdot K$  or  $M = N \cdot K$ . In doubt, first write their definitions and see where  $K$  is needed to make them equal.

7. Although HCl is not a primary standard, their solutions are widely used as titrants. How would you prepare 100 mL of a 0.10 M HCl solution knowing that the density and richness of a commercial acid are 1.37 g/mL and 37 %, respectively?

SOLUTION:

We start the calculations by considering the volume and concentration of the solution that we must prepare. Then, using the density and richness of the commercial solution (commercial solution is denoted as c.s. in the calculations), it is possible to convert the moles of solute required to prepare the solution into the volume of commercial solution.

<i>Data</i>	<i>Given by enunciate:</i>	<i>Have to find out:</i>
	100 mL solution	$V(\text{HCl c.s.})$
	0.10 M HCl	
	$d = 1.37 \text{ g/mL}$	
	37 %	

Taking into account that the units of the density refer always to the solution and not to the solute/solution ratio, the exercise can be solved.

For instance, 1.37 g/mL verbalizes 1.37 g of solution per mL of solution, instead of 1.37 g of solute per mL of solution. Be careful, this is a common confusion!

Write the necessary conversion factors, operate and check that the units cancel out properly.

$$100 \text{ mL} \cdot \frac{1 \cancel{\text{L}}}{10^3 \cancel{\text{mL}}} \cdot \frac{0.1 \cancel{\text{mol HCl}}}{1 \cancel{\text{L}}} \cdot \frac{36.45 \cancel{\text{g HCl}}}{1 \cancel{\text{mol HCl}}} \cdot \frac{100 \cancel{\text{g c.s.}}}{37 \cancel{\text{g HCl}}} \cdot \frac{1 \text{ mL c.s.}}{1.37 \cancel{\text{g c.s.}}} = 0.719 \text{ mL}$$

Therefore, 0.72 mL of the commercial acid must be pipetted, introduced into a volumetric flask (which already has some pure water) and finally, the volume made up to 100 mL.

8. From a 100 mg/L sodium stock standard solution, five calibration solutions (2–10 mg/L) have to be prepared by dilution. Present the adequate calculations to get: (a) 500 mL of the stock standard solution from commercial solid sodium chloride, and (b) 50 mL of each calibration solution.

SOLUTION:

<i>Data</i>	<i>Given by enunciate:</i>	<i>Have to find out:</i>
	500 mL of 100 mg/L	Mass NaCl (g)
	Na <sup>+</sup> , stock solution from NaCl	stock solution volumes

### Question a:

Many solutions used in the laboratory are prepared from solid chemical reagents, according to the general steps depicted in Figure 4.

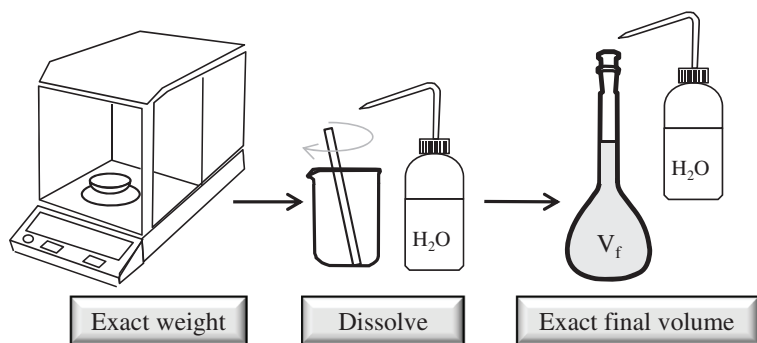


Figure 4.

We have to calculate the mass of salt to be weighed to obtain the 100 mg/L Na<sup>+</sup> solution. For this, we should consider the stoichiometric ratio:  $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$ . Thus, 1 mole of sodium ion is obtained per mole of salt. The richness of the salt is not specified, so we consider it pure (100 %).

$$\begin{aligned}
 & 500 \text{ mL} \cdot \frac{1 \text{ L}}{10^3 \text{ mL}} \cdot \frac{100 \text{ mg Na}^+}{1 \text{ L}} \cdot \frac{1 \text{ g}}{10^3 \text{ mg}} \cdot \frac{1 \text{ mol Na}^+}{23 \text{ g Na}^+} \\
 & \cdot \frac{1 \text{ mol NaCl}}{1 \text{ mol Na}^+} \cdot \frac{58.5 \text{ g NaCl}}{1 \text{ mol NaCl}} \\
 & = 0.127 \text{ g}
 \end{aligned}$$

Accordingly, 0.127 g of NaCl should be weighed, dissolved in deionized water and then made up to 100 mL in a volumetric flask with water.

### Question b:

The calibration solutions are prepared by dilution of the sodium stock standard solution. Hence, we must calculate the required volume of the concentrated solution ( $V_1$ ) for each one. This volume will be brought to final volume of 50 mL ( $V_2$ ) with distilled water.

$$100 \text{ mg/L} \cdot V_1 = 2 \text{ mg/L} \cdot 50 \text{ mL}$$

$$V_1 = \frac{2 \text{ mg/L} \cdot 50 \text{ mL}}{100 \text{ mg/L}}$$

After canceling the units,  $V_1 = 1 \text{ mL}$ .

The same calculations should be made for the remaining calibration solutions, but as their concentrations were not specified (only their range, from 2 mg/L to 10 mg/L), we decided to prepare the solutions as follows: 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L and 10 mg/L.

The following table shows the volumes required to prepare them.

Concentration (mg/L)	2	4	6	8	10
Stock solution volume (mL)	1	2	3	4	5

9. According to the World Health Organization (WHO), household bleach is one of the recommended standard disinfectants to use against the Ebola virus. Household bleach is a solution of sodium hypochlorite which generally contains 5% available chlorine. Diluted solutions 1:10 are used as strong disinfectants for bodies, spills of blood/body fluids; whereas 1:100 bleach solutions are recommended to disinfect surfaces, medical equipment, etc. How would you prepare 2 L of each solution? Express the concentration of both solutions in percent and in g/L.

**SOLUTION:**

These solutions are prepared directly by dilution of the concentrated solution, 5%.

<i>Data</i>	<u><i>Given by enunciate:</i></u>	<u><i>Have to find out:</i></u>
	5% available $\text{Cl}_2$	Final concentration in
	2 L solutions	% and g/L
	1:10	
	1:100	

Before applying the formula that relates the concentrated and diluted solutions, it is necessary to convert the 1:10 and 1:100

ratios to percentages. They are verbalized as a part of solute (in this case, the 5 % available  $\text{Cl}_2$ ) per 10 parts of solution, and a part of solute per 100 parts of solution, respectively.

$$(5\%) \frac{1}{10} = 0.5\%$$

$$(5\%) \frac{1}{100} = 0.05\%$$

Consequently, the final solutions will exhibit a 10-fold lower concentration and a 100-fold lower concentration than the original, respectively.

Now, the dilution formula can be applied.

$$C_1 \cdot V_1 = C_2 \cdot V_2$$

Data are replaced to get the first solution:  $5\% \cdot V_1 = 0.5\% \cdot 2\text{ L}$

$$V_1 = \frac{0.5\% \cdot 2\text{ L}}{5\%} = 0.2\text{ L}$$

$$V_1 = 0.20\text{ L} \cdot \frac{10^3\text{ mL}}{1\text{ L}} = 200\text{ mL}$$

In the same way, the second solution is obtained:

$$V_1 = 0.02\text{ L} \cdot \frac{10^3\text{ mL}}{1\text{ L}} = 20\text{ mL}$$

In both cases, the volumes obtained for household bleach (200 mL and 20 mL) are diluted to a 2 L final volume with water.

Finally, the concentrations must also be reported in g/L. By definition, a 0.5 % solution contains 0.5 g of solute per 100 g of solution. Considering a diluted aqueous solution, its density is taken as that for pure water (1 g/mL, 25 °C).

$$C = \frac{0.5\text{ g solute}}{100\text{ g solution}} \cdot \frac{1\text{ g solution}}{1\text{ mL solution}} \cdot \frac{10^3\text{ mL}}{1\text{ L}} = 5\text{ g/L}$$

For the 1:100 solution, calculations are performed in the same manner, obtaining 0.5 g/L.

The following table summarizes the results obtained.

<i>Data</i>	<u><i>Given by enunciate:</i></u>	<u><i>Calculated:</i></u>
	1:10	5 g/L, 0.5 %
	1:100	0.5 g/L, 0.05 %

10. A method based on the complexation of metals with ammonium pyrrolidine dithiocarbamate (APDC) and extraction into methyl isobutyl ketone (MIBK) is employed to determine Cd, Co, Cu and Pb in a seawater sample [1]. Thus, 100 mL of seawater were placed in a separating funnel and pH was adjusted to 4.1 with an acetic buffer. Around 1 mL of 1 % APDC and 5 mL of MIBK were added. The funnel was shaken for 5 min and allowed to stand for 20–30 min for phase separation. The lower seawater phase was drained and the organic phase was transferred to a separating funnel for back-extraction with 5 mL of 4 M HNO<sub>3</sub>, shaking for 10 min. After phase separation was obtained, the lower aqueous phase was transferred to a test tube for its final analysis by inductively coupled plasma mass spectrometry (ICP-MS) (this technique will be studied in Chapter 5). The extract showed the following metal concentrations (value  $\pm$  confidence interval, in  $\mu\text{g/L}$ ):  $13.62 \pm 0.07$ ,  $52.80 \pm 0.18$ ,  $83.25 \pm 0.32$  and  $61.11 \pm 0.58$  for Cd, Pb, Cu and Cr, respectively. Determine the metal concentrations in the seawater sample, expressed as  $\mu\text{g/L}$ .

#### SOLUTION:

The contents of heavy metals in seawater are usually very low, their analyses requiring currently some preconcentration steps. In addition, the analyte should be separated from the aqueous matrix due to the high complexity of the latter (large quantities of salts, biological products, etc.). For aqueous samples, liquid–liquid extraction is a widespread, suitable option. The experimental procedure described in this exercise involves many typical steps (Figure 5a).

While all these steps must be taken into account in the laboratory, for the calculations, they are reduced to a very simple scheme (Figure 5b).

The initial ( $V_i$ ) and final ( $V_f$ ) volumes of the sample aliquot can be considered in the same way as in a typical dilution/concentration calculation. Therefore, we can apply the well-known expression:

$$C_i \cdot V_i = C_f \cdot V_f$$

To start with (for instance) Cd, the experimental values yield:

$$C_i \cdot 100 \text{ mL} = 13.62 \mu\text{g/L} \cdot 5 \text{ mL}$$

By algebraic arrangement:

$$C_i = \frac{13.62 \mu\text{g/L} \cdot 5 \text{ mL}}{100 \text{ mL}}$$

After canceling the units,  $C_i = 0.681 = 0.68 \mu\text{g/L}$ .

Before proceeding, you should verify that this result is logical. Comparing both concentration values,  $C_i$ , and  $C_f$ , it is seen that:  $C_i = 0.68 \mu\text{g/L} < C_f = 13.62 \mu\text{g/L}$ , which agrees with the preconcentration treatment performed (when concentrating, the final concentration of the analyte should be greater than in the original solution).

Now, the same calculations can be performed for the other metals, as well as for their confidence intervals. The following table shows the results:

Metal	Cd	Pb	Cu	Cr
Concentration ( $\mu\text{g/L}$ )	$0.68 \pm 0.004$	$2.64 \pm 0.01$	$4.16 \pm 0.02$	$3.06 \pm 0.03$

11. A soil sample is submitted to a microwave-assisted acid digestion based on the 3051EPA Method (Environmental Protection

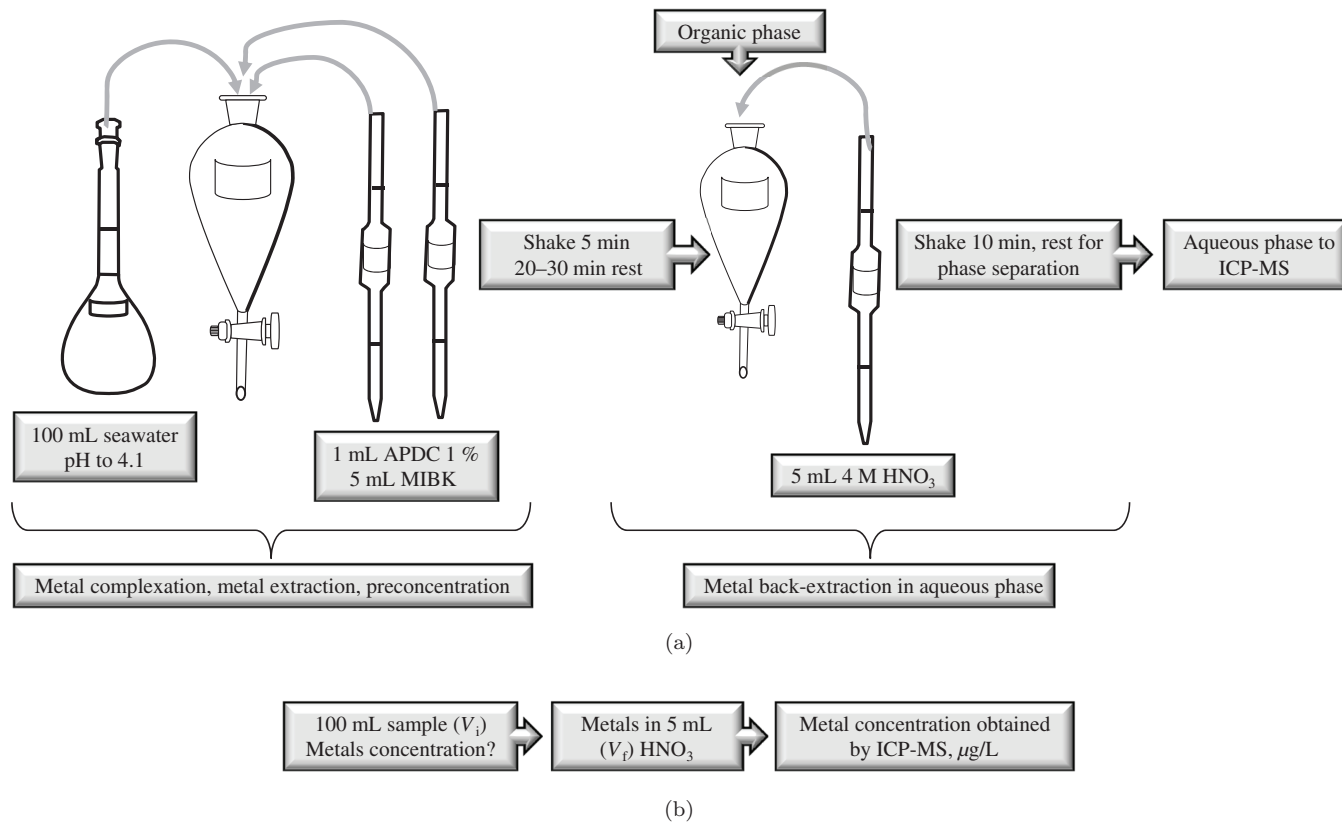


Figure 5.



Agency) for metal analysis. An aliquot of 0.5000 g of wet sample was digested with 10 mL of nitric acid in a closed reactor, microwave-heated until 170 °C during 10 min. The extract was filtered and made up to 20.00 mL with deionized water in a volumetric flask. This test solution was analyzed directly to determine Cd as a trace element; whereas iron was determined in a 20-fold diluted portion. The concentrations obtained were 8.24  $\mu\text{g/L}$  and 2.55 mg/L for Cd and Fe, respectively. If a separate portion of soil was used to determine its moisture, which resulted to be 36 %, calculate the concentrations of Cd and Fe in the original sample, on both a wet and a dry basis.

### SOLUTION:

The analytical procedure can be depicted (Figure 6a) and simplified to make calculations (Figure 6b).

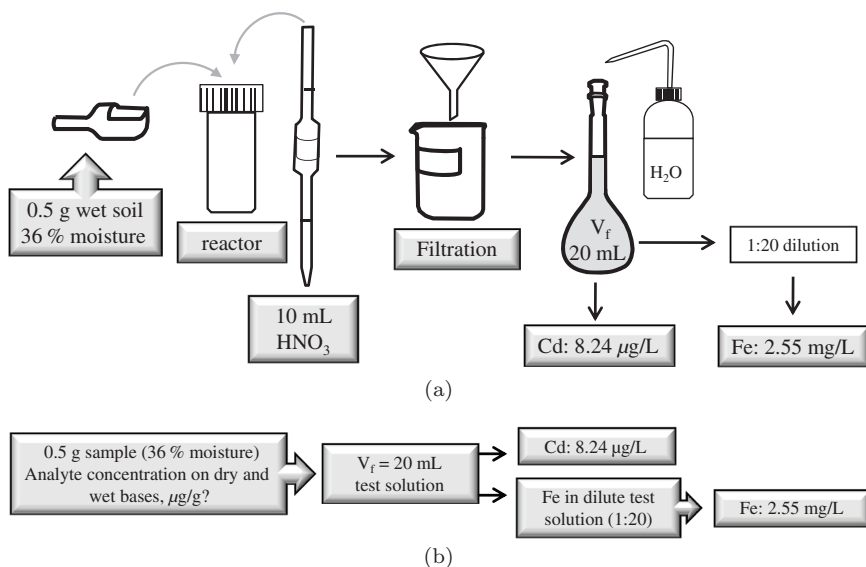


Figure 6.

<i>Data</i>	<i>Given by enunciate:</i>	<i>Have to find out:</i>
	0.5000 g wet soil	Cd, Fe concentration
	36 % moisture	on wet and dry
	$V_f$ test solution 20 mL	bases.
	8.24 $\mu\text{g/L}$ Cd	
	2.55 mg/L Fe in 1:20 solution	

To solve this problem, calculations should be carried out from the last working step to the starting point of the analytical procedure. For cadmium, calculations are presented first on a wet basis:

$$C_{\text{Cd}}(\text{wet soil}) = 8.24 \frac{\mu\text{g}}{\text{L}} \cdot \frac{1 \text{ L}}{10^3 \text{ mL}} \cdot \frac{20 \text{ mL}}{0.5 \text{ g wet soil}} = 0.33 \mu\text{g/g}$$

To convert to the dry basis, we need to take into account the percentage of moisture, which means that there are 36 g of water per each 100 g of wet soil, therefore, there will be  $100 - 36 = 64$  g of dry soil.

$$C_{\text{Cd}}(\text{dry soil}) = 0.33 \frac{\mu\text{g Cd}}{\text{g wet soil}} \cdot \frac{100 \text{ g wet soil}}{64 \text{ g dry soil}} = 0.52 \mu\text{g/g}$$

For iron, an additional dilution of the test solution was necessary since this element is a major component in soils.

$$2.55 \frac{\text{mg}}{\text{L}_{\text{diluted}}} \cdot \frac{1 \text{ L}_{\text{diluted}}}{10^3 \text{ mL}_{\text{diluted}}} \cdot \frac{20 \text{ mL}_{\text{diluted}}}{1 \text{ mL}_{\text{test solut}}} \cdot 20 \text{ mL}_{\text{test solution}} = 1.02 \text{ mg}$$

$$C_{\text{Fe}}(\text{wet soil}) = \frac{1.02 \text{ mg}}{0.5 \text{ g wet soil}} = 2.04 \text{ mg/g}$$

$$C_{\text{Fe}}(\text{dry soil}) = 2.04 \frac{\text{mg Cd}}{\text{g wet soil}} \cdot \frac{100 \text{ g wet soil}}{64 \text{ g dry soil}} = 3.19 \text{ mg/g}$$

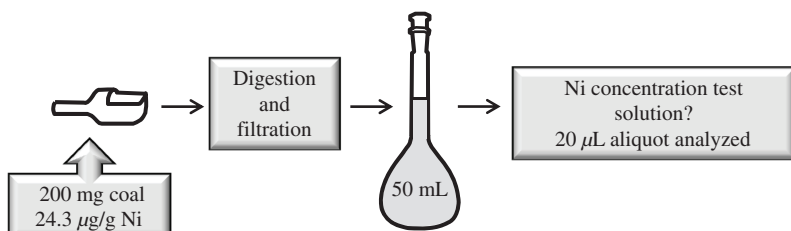
As expected, the metal concentration in a dry basis is higher than on a wet basis.

12. A coal sample has a concentration of  $24.3 \mu\text{g/g}$  of nickel. A 200 mg aliquot of this coal is digested in an acid medium, filtered and brought to a final volume of 50.00 mL (in a volumetric flask) with deionized water. Determine the concentration of Ni in the test solution if a  $20 \mu\text{L}$  aliquot was analyzed.

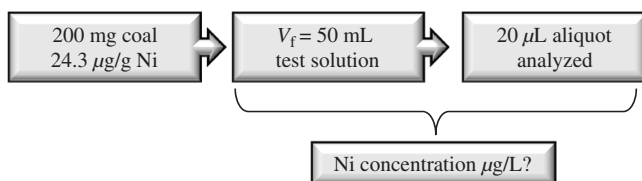
**SOLUTION:**

This situation is somehow different from what we usually need in the laboratory, but sometimes it is indeed necessary to check what concentration would you obtain with a certain procedure for a given sample; for instance, when a certificated reference material with a known analyte concentration is studied (Figure 7a).

<i>Data</i>	<i>Given by enunciate:</i>	<i>Have to find out:</i>
	200 mg coal	Ni concentration in test solution
	$24.3 \mu\text{g/g}$ Ni	
	$V_f$ test solution 50 mL	
	$20 \mu\text{L}$ aliquot analyzed	



(a)



(b)

Figure 7.

It is worth noting that all nickel in coal has been dissolved and is in the 50 mL solution (test solution). The 20  $\mu\text{L}$  aliquot analyzed of this solution, obviously, will exhibit the same Ni concentration (Figure 7b).

$$C_{\text{Ni}} = 24.3 \frac{\mu\text{g}}{\text{g}_{\text{coal}}} \cdot \frac{1 \text{ g}}{10^3 \text{ mg}} \cdot \frac{200 \text{ mg}_{\text{coal}}}{50 \text{ mL}_{\text{test solution}}} = 0.0972 \mu\text{g/mL}$$

Now, the result can be expressed in more appropriated units.

$$C_{\text{Ni}} = 0.0972 \frac{\mu\text{g}}{\text{mL}} \cdot \frac{10^3 \text{ mL}}{1 \text{ L}} = 97.2 \mu\text{g/L}$$

13. Polycyclic aromatic hydrocarbons (PAHs) are genotoxic carcinogens being their contents in foodstuffs legislated strictly. A method reported for their analysis in apples employs solid–liquid extraction using 20 g of homogenized sample mixed with 80 g of anhydrous sodium sulfate, and extracted in a Soxhlet extractor with 170 mL of a hexane–acetone mixture (1:1) for 6 h [2]. The extraction solvent was evaporated to dryness in vacuum at 40 °C. The residue after evaporation was quantitatively transferred into a 10.00 mL volumetric flask with chloroform. A cleanup procedure was carried out and the purified extracts were evaporated to dryness, and the residue was dissolved in 0.5 mL of acetonitrile before its high performance liquid chromatography with fluorescence detection (HPLC-FLD) determination. An injection volume of 20  $\mu\text{L}$  was used. The mean value ( $n = 3$ ) for the content of total PAHs was 9.30  $\mu\text{g/kg}$ , and 0.03 ng/g for benzo(*a*)pyrene, B[*a*]P, which is employed frequently as a marker compound representing carcinogenic PAHs. If the concentrations refer to ‘fresh weight’ calculate: (a) the percentage of B[*a*]P among the total PAHs, (b) the concentrations on a dry basis considering a dry matter content of 14.7 %.

SOLUTION:

<i>Data</i>	<i>Given by enunciate:</i>	<i>Have to find out:</i>
	20 g apple	B[a]P percent
	PAHs 9.30 $\mu\text{g}/\text{kg}$	Concentrations on a dry basis
	B[a]P 0.03 $\text{ng}/\text{g}$	
	14.7 % dry matter	

**Question a:**

First, it is necessary to express both concentrations in the same units. In some cases, like this, they seem different but they represent the same analyte/sample ratio.

$$9.30 \frac{\mu\text{g}}{\text{kg}} \cdot \frac{1 \text{ kg}}{10^3 \text{ g}} \cdot \frac{10^3 \text{ ng}}{1 \mu\text{g}} = 9.30 \text{ ng/g}$$

Note that many units used frequently are interchangeable:

$$\frac{\text{mg}}{\text{kg}} = \frac{\mu\text{g}}{\text{g}}$$

$$\frac{\mu\text{g}}{\text{L}} = \frac{\text{ng}}{\text{mL}}$$

To calculate the percentage of B[a]P:

$$(\%) \text{B[a]P} = \frac{0.03 \text{ ng B[a]P}}{\text{g}_{\text{apple}}} \cdot \frac{\text{g}_{\text{apple}}}{9.30 \text{ ng PAHs}} \cdot 100 = 0.32 \%$$

**Question b:**

$$C_{\text{B[a]P}} (\text{dry matter}) = 0.03 \frac{\text{ng B[a]P}}{\text{g}_{\text{fresh apple}}} \cdot \frac{100 \text{ g}_{\text{fresh apple}}}{14.7 \text{ g dry matter}}$$

$$= 0.20 \text{ ng/g}$$

$$C_{\text{PAHs}} (\text{dry matter}) = 9.30 \frac{\text{ng PAHs}}{\text{g}_{\text{fresh apple}}} \cdot \frac{100 \text{ g}_{\text{fresh apple}}}{14.7 \text{ g dry matter}}$$

$$= 63.26 \text{ ng/g}$$

**EXERCISES PROPOSED TO THE STUDENT**

14. Select the most appropriate units to express the concentration of a solution prepared by dissolving 125 mg of copper (II) sulfate in 500 mL of water.

Solution: 0.25 g/L.

15. How would you prepare 50.00 mL of a 3 % (m/v) solution from 100 % pure sodium chloride?

Solution: weigh 1.5 g of solute, dissolve it in water and make up to 50.00 mL.

16. 8.00 g of calcium chloride is dissolved in 25.00 mL of distilled water. (A) Set the concentration of this solution in mol/L. (B) What are the molar concentrations of both the chloride and calcium ions?

Solution: (a) 2.12 M, (b) 4.24 M and 2.12 M for  $\text{Cl}^-$  and  $\text{Ca}^{2+}$ , respectively.

17. How many milliliters of an ammonia stock solution are needed to prepare 200 mL with a 5 % volume?

Solution: 10 mL.

18. Determine the volume of each of the following solutions that contains 0.05 mol of potassium ion: (a) 0.200 M  $\text{KNO}_3$ , (b) 0.350 M  $\text{K}_2\text{Cr}_2\text{O}_7$ , (c) 1.5 M  $\text{KHC}_8\text{H}_4\text{O}_4$

Solution: (a) 0.25 L, (b) 71.4 mL, (c) 33.3 mL.

19. You have a 0.65 g/mL  $\text{HNO}_3$  solution. Express its concentration in terms of both molarity and normality.

Solution: 10.32 M, 10.32 N (*Hint*: this acid gives 1 mol of  $\text{H}^+$ ).

20. How much sodium hydroxide is required to prepare 1.5 L of a 2.5 % solution, whose density is 1.126 g/cm<sup>3</sup>? What is its normality?

Solution: 42.2 g, 0.7 N.

21. Calculate the molarity and normality of a 1 %  $\text{KMnO}_4$  solution used as titrant (assume that its density is that of water at 25 °C).

Solution: 0.063 M, 0.316 N (*Hint*: 5 moles of electrons per mole of  $\text{MnO}_4^-$  ion).

22. How would you prepare 50.0 mL of a 1 : 3 ethanol–water mixture  
Solution: 12.5 mL ethanol plus 37.5 mL H<sub>2</sub>O.

23. How many milliliters of a commercial solution of nitric acid (69 % purity; 1.41 g/cm<sup>3</sup> density) are needed to prepare 100 mL of a 10 % solution?

Solution: 10.28 mL (the density of the diluted solution is estimated as that for water at 25 °C).

24. How many mL of an HCl stock solution (35 % purity, specific gravity of 1.19) would be needed to prepare 1 L of a 0.2 N solution?

Solution: 17.50 mL.

25. A maximum 1000 mg/L level of phosphate in milk (expressed as P<sub>2</sub>O<sub>5</sub>) has been regulated. What volume of milk (in milliliters) contains 50 mg of P?

Solution: 114.5 mL.

26. Some countries had adopted salt fluorination schemes instead of water fluorination to prevent dental caries, mainly in young population [3]. A fixed amount of a fluoride compound (mostly NaF) is added to a fixed amount of refined common salt to achieve a maximum concentration of 250 mg/kg of fluoride. WHO recommends a maximum intake of 5 mg of common salt per day. If a maximum of 250 mg of fluoride per kg of salt is the established value, you are asked to calculate: (a) the mass percent of fluoride in salt, (b) what mass of fluoride should be ingested daily (at maximum)? (c) how much sodium fluoride should be added per each kilogram of salt?

Solution: (a) 0.025 %, (b) 1.25 μg, (c) 553 mg NaF.

27. Phenolphthalein is widely employed as an acid–base indicator. For this, a 0.1 % (m/m) solution is used. Taking into account that this solute is insoluble in water, an alcoholic solvent must be used, e.g., ethanol (density 0.789 g/cm<sup>3</sup>). You are asked to report the calculations to prepare 50.00 mL of the 0.1 % required solution. Also calculate the concentration of this solution in g/L.

Solution: 39.45 mg, 0.79 g/L (the density of the solution is considered as that for pure ethanol, at 25 °C).

28. To prepare a pH = 4 buffer solution, 5.10 g of potassium hydrogen phthalate ( $\text{KHC}_8\text{H}_4\text{O}_4$ ) were dissolved in 250 mL of deionized water, 0.50 mL of 0.10 M hydrochloric acid added, and then the mixture was diluted to 500.00 mL. Calculate the molarity of both the salt and the acid in the buffer solution.

Solution: 0.05 M  $\text{KHC}_8\text{H}_4\text{O}_4$ , 0.1 mM HCl.

29. To prepare a pH = 9.2 buffer solution, a solution containing 0.1 mol/L of ammonium chloride and 0.1 mol/L of ammonia is needed. How would you prepare 50 mL of such a solution? (for ammonia, consider 25 % purity and 0.91 g/cm<sup>3</sup>).

Solution: 0.37 mL  $\text{NH}_3$ , 0.27 g  $\text{NH}_4\text{Cl}$ .

30. A fuel oil sample is analyzed to determine its concentration of Ni. A 0.5000 g aliquot was weighed accurately and dissolved in 2.00 mL of toluene. A test portion of 200  $\mu\text{L}$  was used to prepare 1.00 mL emulsion with ethanol, nitric acid and xylene. After the instrumental analysis, a 2.35  $\mu\text{g/L}$  Ni concentration was obtained in the 20  $\mu\text{L}$  analyzed aliquot. What is the concentration of Ni in the fuel oil sample?

Solution: 47 ng/g (*Hint*: remember the meaning of ‘aliquot’).

31. Calcium hypochlorite is used widely for drinking water disinfection. Commercial products are available as bleaching powder or tablet forms. The disinfection ‘power’ of the various forms of presentation of calcium hypochlorite was expressed as its available chlorine, which ranged between 25 % (for bleaching powder) and 70 % (for HTH, high test hypochlorite). How would you prepare 10 L of a solution containing 50 g/L of available chlorine from bleaching powder and from HTH?

Solution: 2 kg of bleaching powder, 0.7 kg for HTH.

## EXERCISE REFERENCES

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- [3] Marthaler, T. M.; Petersen, P. E. (2005). Salt fluoridation — an alternative in automatic prevention of dental caries, *International Dental Journal*, 55: 351–358.