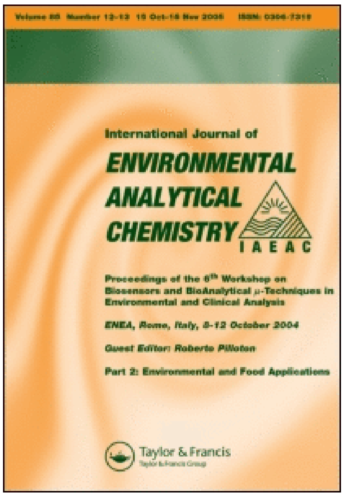

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Quantities and units in analytical chemistry

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Quantities and units in analytical chemistry

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Analytical chemistry is largely concerned with the determination of the composition of mixtures. The result of the analysis of a component in a mixture should comprise the product of a 'numerical value' and a 'unit' in order to express the value of the 'quantity' being measured (and an associated statement of uncertainty). The quantities and units which can be used to express these results are subtly different and can often be confused and misused. This article clarifies their meaning, presents a novel method of demonstrating the relationship between them, and discusses the advantages and drawbacks of their usage in analytical chemistry, particularly with respect to environmental analysis. Suggestions for best practice for use in analytical chemistry are also made.

Keywords: analytical chemistry; composition; units; quantities; symbols

1. Introduction

'Amount of substance' is the quantity used to characterise a number of entities [1]. Its use occurs largely, but not exclusively, in chemical studies. The name is sometimes shortened to 'amount' and, when the substance being measured is known, it can be made specific; for example 'amount of lead nitrate, $Pb(NO_3)_2$'. Amount of substance is an extensive quantity (because its magnitude is proportional to the size of the system it describes). It is usually related to a measurement of a mass, which is also an extensive quantity. For example, it is related to the mass of a pure substance by the relative molecular (or atomic) mass [2]. The symbol for the quantity amount of substance is n. The SI unit of amount of substance is called the *mole*, symbol: mol.

Analytical chemistry is largely concerned with the determination of the composition of mixtures containing two or more components [3]. (The term 'component' is used here to represent constituents of a non-reacting system.) The result of the analysis of a component in a mixture should comprise the product of a 'numerical value' and a 'unit' in order to express the value of the 'quantity' being measured (and an associated statement of uncertainty, of course) [4]. Amount of substance is rarely measured directly in analytical chemistry. In practical usage, the amount, mass or volume of a component (all extensive quantities) is usually combined with the amount, mass, or volume of the entire mixture (more extensive quantities), to derive quantities that express the composition of mixtures (all intensive quantities – those whose magnitude is independent of the size of the system described) [3,5] which can be used for expressing the results of analyses. These quantities

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are subtly different and can often be confused and misused, so it is helpful to clarify their meaning and the advantages and drawbacks of their usage in analytical chemistry. This is particularly relevant to environmental analysis where measurements are done on components at low levels, in a variety of matrices, and where there are numerous examples of non-standard quantities and units being used to express results, which can lead to confusion.

Measurements in environmental analytical chemistry are broadly performed on gaseous or liquid mixtures, or solids that have been digested or dissolved in liquids to form mixtures. Direct analysis of solid mixtures is rare, and often difficult, not least because of increased heterogeneity of the sample. The discussion presented here focuses on analytical measurements of composition performed on mixtures in the gaseous or liquid state. It is assumed in all cases that these mixtures are homogeneous.

Consideration of how to calculate and express the uncertainty of an analytical measurement is outside the scope of this paper, but guidance on this topic is available elsewhere [6].

2. Quantities

Table 1 lists and defines nine quantities that are commonly used to characterise composition. These quantities describe the relationship between a single component within the mixture (the analyte being measured) and the mixture as a whole (the sample being analysed). These quantities may be related by simple factors, such as density and relative

Table 1. Quantities used to characterise composition.

Quantity	Symbol	Definition	SI unit	Other common units
Mass fraction	W	$w_i = m_i/\Sigma m_j$	$\mathrm{kg\,kg^{-1}}$	$\mathrm{g\,g^{-1}}$, $\mathrm{\mu g\,g^{-1}}$, $\mathrm{ng\,g^{-1}}$, $\mathrm{mg\,kg^{-1}}$, $\mathrm{\mu g\,kg^{-1}}$, etc.
Volume fraction	φ	$\varphi_i = V_i/\Sigma V_j$	$\mathrm{m^3\,m^{-3}}$	
Amount fraction	x	$x_i = n_i/\Sigma n_j$	$\mathrm{mol\,mol^{-1}}$	$\mathrm{mmol\,mol^{-1}}$, $\mathrm{\mu mol\,mol^{-1}}$, $\mathrm{nmol\,mol^{-1}}$, etc.
Mass concentration	γ	$\gamma_\mathrm{i} = m_i/V$	$\mathrm{kg\,m^{-3}}$	$\mathrm{g\,dm^{-3}}$, $\mathrm{g\,L^{-1}}$, $\mathrm{mg\,dm^{-3}}$, $\mathrm{mg\,L^{-1}}$, etc.
Volume concentration	σ	$\sigma_\mathrm{i} = V_i/V$	$\mathrm{m^3\,m^{-3}}$	
Amount concentration (Molarity)	c	$c_i = n_i/V$	$\mathrm{mol\,m^{-3}}$	M, $\mathrm{mol\,dm^{-3}}$, $\mathrm{mol\,L^{-1}}$, mM, $\mathrm{mmol\,dm^{-3}}$, $\mathrm{mmol\,L^{1}}$, etc.
Molality	b	$b_i = n_i/m_\mathrm{sol}$	$\mathrm{mol\,kg^{-1}}$	
Volume content	κ	$\kappa_i = V_i/m$	$\mathrm{m^3\,kg^{-1}}$	
Amount content	k	$k_i = n_i/m$	$\mathrm{mol\,kg^{-1}}$	

Notes: The meaning of the symbols in the table is as follows: m_i, V_i, and n_i are the mass, volume (prior to mixing), and the amount, of component i; Σm_j, ΣV_j and Σn_j are the sums of the masses, volumes (prior to mixing), and the amounts, of all components; m_sol is the mass of the solvent only; m and V are the total mass, and total volume (after mixing), of the mixture. Fractions describe how much of the total property of a sample is contributed by one of its constituent substances; concentrations describe the ratio of one extensive quantity of a single substance to the total volume of the mixture; and contents describe the ratio of one extensive quantity of a substance to the total mass of the mixture. For gaseous mixtures, the symbol, y, is often used for amount fraction. Molality describes the amount of solute entities divided by the mass of the solvent.
Source: Adapted from references 3 and 8.

molecular mass, but there are important differences in precisely how they define composition.

The quantity mass fraction has the property that it can be used to describe the composition of a component in a mixture when only knowledge of the mass of the mixture and the mass of the component are available. Amount content and molality require the same information together with the identity of the component being described and its relative molecular (or atomic) mass. The use of these quantities does not require detailed knowledge of the composition of other components within the mixture, nor are they sensitive to temperature or pressure. Therefore, these quantities are the most suitable for routine use in the accurate description of the composition of mixtures. In contrast, quantities involving amount as a denominator require an exact knowledge of all components within the mixture. Amount fraction, often used in gas metrology, is often (wrongly) referred to as 'mole fraction' (this would be analogous to using 'kilogram fraction', rather than mass fraction). 'Content' quantities are used mostly in chemical metrology and clinical chemistry (the latter community often referring to 'substance content' rather than 'amount content').

It may be argued that quantities involving volumes are more limited in their application because their magnitude is dependent on temperature, and pressure (for gaseous mixtures), via the density of the mixture or individual components. Therefore for mass concentrations and amount concentrations it is strictly necessary to state at what temperature and pressure the value of the quantity is applicable. Such values can be quoted with respect to standard conditions, as in the case of measurements of chemical species in ambient air, where values are often corrected to standard conditions at 293 K and 101.3 kPa, or so-called 'normal air'. (This can result in the use of the 'unit' Nm^{-3} to express 'per cubic metre of normal air', which is to be strongly avoided as no additional labels on unit symbols are allowed (except for decimal multiples and submultiples)). The relationships between the quantities described in Table 1, and the properties of the mixture that link them, are displayed diagrammatically in Figure 1.

It should be noted that when high accuracy gravimetric preparation of solutions is involved, the expression of composition with these quantities also requires knowledge of the density of the component and/or mixture, in order to perform an accurate buoyancy correction when weighing in air. Additionally, the use of volume fraction and volume concentration is discouraged for accurate work without reiteration of the full description of the quantity, since definitions can vary as to whether the volume of the whole mixture is measured before or after the mixing of individual components. Moreover, only when there is no risk of any confusion should the term 'concentration' be used in isolation.

There are other quantities, not described in Table 1, which are sometimes used in analytical chemistry. Occasionally it is useful to refer to the ratio of two substances within a mixture. These quantities are not commonly used. Depending on which extensive quantity is used to express how much of each substance is present, mass, volume or amount ratios can be produced. It is also important to state which substance is being used as the denominator. In most cases where solutions are being considered, this will usually be the solvent. Very occasionally ratios are expressed using different extensive quantities – a practical example of this is molality – although some prefer to use the term ratio only to describe the ratios of quantities of the same dimension. Ratio quantities provide less information about the overall composition of mixtures, and for mixtures with three or more components are insufficient to describe the overall composition of a single component within the mixture. For these reasons molality is mostly used for expressing the

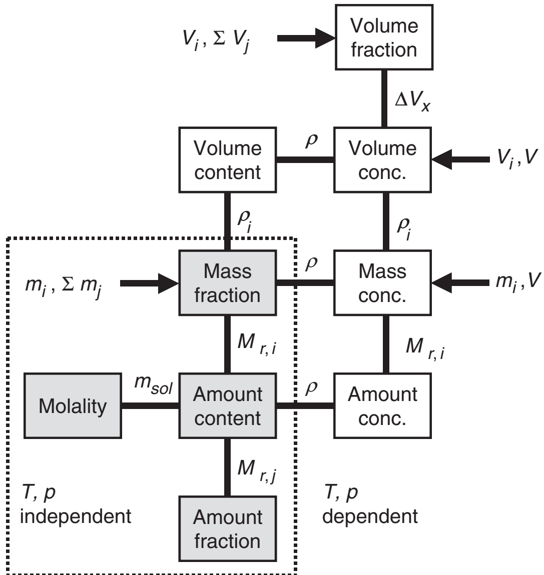

Figure 1. The relationship between the quantities described in Table 1, and the properties of the mixture that link them.
Note: The meaning of the symbols are the same as those in Table 1, with the addition that ρ is the density of the mixture after mixing, ρ_i is the density of component i (prior to mixing), $M_{r,i}$ is the relative molecular (or atomic) mass of component i, $M_{r,j}$ are the relative molecular (or atomic) masses of all other components in the mixture, and ΔV_x is the volume change on mixing ($\Delta V_x = V - \Sigma V_j$). There are four starting points on the diagram, indicated by arrows, relating to common (mass fraction, mass concentration) and less common (volume fraction, volume concentration) methods for preparing, and assigning compositional values to mixtures used for the calibration of analytical methods. The properties next to the arrows show what information is needed to describe the composition of component i in the mixture, in terms of the quantity indicated. The property on the lines joining the quantities shows what extra knowledge is required to convert from one quantity to another. The assigned values of the shaded quantities bound by the dashed border are independent of temperature and pressure; while the values of the unshaded quantities vary with temperature and pressure.

composition of binary mixtures. As an example of the lack of information provided by ratio quantities, consider an aqueous solution, equimolar in NaCl and KCl. The amount ratio of sodium to potassium ions in the solution is 1, however this gives no information on the overall amount concentration of NaCl or KCl in the mixture. Occasionally this information is more important than the absolute amount concentration; for example, the amount ratio of a radioactive isotope and its decay product can be a guide to the age and origin of the radioactivity in a sample. Ratios are quite often used for approximate measurements, such as the volume ratio of different solvents in chromatography.

Although not in common use in analytical chemistry, quantities involving 'number' as the numerator (number concentration and number content), or as the numerator and denominator (number fraction), can be used to describe composition in terms of the number of atoms, molecules or entities present in the mixture. Number concentrations are used to characterise size classified particle numbers in ambient air [7]. More details on quantities involving ratio and number are available from the seminal paper on this topic [3].

With the exception of some primary methods of measurement [8] analytical chemistry determines the composition of unknown mixtures using measurements that require calibration [9]. The preparation of standard materials to perform calibration requires decisions to be made about the quantities that should be used to label these materials. Generally the quantity used to express an analytical result will be the same as the quantity used in preparing and certifying the standards used for calibration. The driving force in this respect will be to minimise the uncertainty of the measurement in addition to the advantages and disadvantages of using the different quantities described above. Some exceptions exist for analytical techniques using the injection of a fixed volume of sample where the uncertainty may be minimised by using different quantities for the preparation of standards and the measurement of samples [10,11]. Calibration standards for analytical chemistry are usually prepared, initially at least, on either a mass fraction or mass concentration basis, and more rarely on a volume fraction or volume concentration basis, as indicated in Figure 1, and so the majority of analytical results will be expressed using these quantities.

3. Units

It is recommended that the quantities described above are always expressed using the SI units given in Table 1. Many other units are in common usage, although they are not necessarily recommended. Decimal sub-multiples may be used with all these SI units as per ISO 1000 [12] and some examples of these usages, along with other non-SI units are given in the 'other common units' column of Table 1.

Since the units used for some of these quantities such as amount fraction, mass fraction and volume fraction are $\mathrm{mol\,mol^{-1}}$, $\mathrm{kg\,kg^{-1}}$, and $\mathrm{m^3\,m^{-3}}$, respectively, they are often referred to as being 'dimensionless'. (More properly we should refer to these quantities as having the dimension 'one' since the expression for their units simplifies to unity (i.e. $\mathrm{mol\,mol^{-1}} = 1$) rather than to zero). The terms 'parts per million (ppm)', 'parts per billion (ppb)', 'per mille (‰)' and 'per cent (%)' are often used in place of units to express mass, volume or amount fractions; these terms are not units but simply represent the multipliers 10^{-6}, 10^{-9}, 10^{-3} and 10^{-2}, respectively [13]. Although amount, mass and volume fractions are quantities with the dimension one, units should always accompany them, since the use of the correct unit for a measurement result conveys useful information about the quantity actually measured. Ideally the quantity being expressed should also be stated in words as part of the expression of a result, for clarity, and to avoid confusion (especially between quantities such as molality and amount content, and between mass fraction and amount fraction). This is also necessary because the unit of the measurement does not itself define the quantity being measured, in the same way that a length expressed in metres gives no information about whether the measurement refers to a height, width, circumference or diameter. For example, when expressing a measurement result, it is best to state that:

The amount fraction of lead in aqueous solution, $x(\mathrm{Pb}) = 2.3 \times 10^{-6}\,\mathrm{mol\,mol^{-1}}$

or,

The amount fraction of lead in aqueous solution, $x(\mathrm{Pb}) = 2.3\ \mathrm{\mu mol\,mol^{-1}}$

It is less informative to state that:

$$\text{The amount fraction of lead in aqueous solution, } x(\text{Pb}) = 2.3 \times 10^{-6}$$

or,

$$\text{The amount fraction of lead in aqueous solution, } x(\text{Pb}) = 2.3 \text{ ppm}$$

Information about the measurand is not complete if it is stated that:

$$x(\text{Pb}) = 2.3 \times 10^{-6} \text{ mol mol}^{-1}$$

or,

$$x(\text{Pb}) = 2.3 \text{ µmol mol}^{-1}$$

And it is ambiguous to state that:

$$x(\text{Pb}) = 2.3 \text{ ppm}$$

or,

$$x(\text{Pb}) = 2.3 \times 10^{-6}$$

In the final example, the use of ‘ppm’ as a ‘unit’ does not unambiguously distinguish between quantities such as mass fraction, amount fraction, volume fraction and volume concentration – we are left to guess whether the symbol x has been correctly employed to represent amount fraction, or not. The equivalence of the final pair of examples emphasizes that ‘ppm’ is not a unit, but simply a replacement for the multiplier 10^{-6}. In general, terms such as ‘ppm’ and ‘ppb’ should be avoided if possible, but since these terms are still common in analytical chemistry it is vital that when they are used they are accompanied by a description of the quantity being measured. The term ‘ppt’ should also be avoided, not only for the reasons given above, but also because it is ambiguously used to represent both ‘parts per trillion’ (10^{-12}) and (less frequently) ‘parts per thousand’ (10^{-3}).

More importantly, the terms ‘ppm’ and ‘ppb’ are often wrongly, and confusingly, used as ‘units’ to express concentrations. By its definition (in Table 1), a concentration does not have the dimension one (except for the rather obscure quantity volume concentration). It is simply incorrect to use the descriptors ‘ppm’ and ‘ppb’ to describe quantities that are not dimensionless. Thus incorrect expressions such as:

The concentration of lead in aqueous solution is 2.3 ppm,

are often used, instead of the correct:

$$\text{The mass concentration of lead in aqueous solution, } \gamma(\text{Pb}) = 2.3 \text{ mg dm}^{-3}$$

The use of other similar notations such as ‘ppmv’, ‘wt%’, ‘w/w%’, ‘vol%’, ‘w/v%’, ‘atom%’, ‘mol%’ should also be avoided. These terms usually often arise from the perceived need to elaborate on what type of ‘fraction’ or ‘concentration’ quantity is being expressed, by adding additional symbols. Instead, the appropriate quantity from Table 1 should be used.

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