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CONCENTRATION UNITS IN WATER CHEMISTRY

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Concentration units in water chemistry

The concentration of a chemical in a water sample is commonly measured and reported in one of two dimensionally different ways, either as a mass concentration, often expressed in units of g l^{-1} or as an amount of substance concentration in units of mol l^{-1} . Traditionally water chemists have chosen to use mass concentration to represent the concentration of a given substance in a water sample. This choice and the consequent use of units such as g l^{-1} , or some multiple such as mg l^{-1} or pg l^{-1} is convenient but it has some disadvantages, namely:

- 1) Scientists in other disciplines are increasingly using amount of substance concentration to represent chemical concentration.
- 2) The use of mass concentration can be misleading as described below.

The object of this paper is to discuss some of the shortcomings of the use of mass concentration and thereby to encourage the more widespread use of amount concentration in water chemistry.

A very clear summary of the fundamentals of measurement, unit and the choice of unit has been given by McGlashan (1971) and the following quotes are useful:

"The only kind of physical quantity which we can measure, that is to say count, is one that is a number... For any other kind of physical quantity the best we can do is to count the number which is the ratio of two instances of the physical quantity." "For example we can measure the ratios l_1/l , l_2/l ... and the particular length l . We may then, if we so wish, treat l as a unit of length by giving it a name of its own." "The sole criterion for judging the usefulness of a unit should be its effectiveness as a means of making the results of measurements as immediately and unambiguously intelligible as possible with as little explanation as possible to all scientists in whatever fields and in whatever countries they may work."

1. QUANTITY AND UNITS OF CHOICE

While both mass concentration and amount concentration are recognised and approved quantities there is an increasing tendency in many scientific areas to use amount concentration as the quantity to represent the 'concentration' of a given chemical in a solution. In accord with this it is becoming increasingly common to identify the term 'concentration' with the quantity amount of substance concentration and therefore to use the recommended unit of mol l^{-1} or some appropriate multiple. This is happening increasingly in both the physical and the biological sciences and among chemists in general outside of the water chemistry area the use of mass concentration and the associated units such as g l^{-1} is fast disappearing in favour of amount concentration and units such as mol l^{-1} .

Some relevant recommendations from the current revision of the IUPAC Green Book, the Manual of Quantities, Units and Symbols in Physical Chemistry are:

<u>Name of Physical Quality</u>	<u>Symbol</u>	<u>Definition</u>	<u>SI base unit</u>
mass concentration	$\underline{g}, \underline{r}$	$\underline{g}_B = \underline{m}_B / \underline{V}$ ⁽¹⁾	kg m^{-3} ⁽²⁾
amount concentration ⁽³⁾	$\underline{c}$	$\underline{c}_B = \underline{n}_B / \underline{V}$ ⁽⁵⁾	mol m^{-3} ⁽⁴⁾

- (1) $\underline{m}_B$ denotes the mass of substance B, and $\underline{V}$ the volume of solution.
- (2) In practice g l^{-1} ($= \text{g dm}^{-3}$), mg l^{-1} , and 5g l^{-1} are more useful than kg m^{-3} , and are equally acceptable SI units.
- (3) 'Amount concentration' is an abbreviation for 'amount of substance concentration'. (When there is no risk of confusion the word 'concentration' may be used alone.) The symbol [B] is often used for amount concentration of entities B. A solution of (for example) 1 mol dm^{-3} is often called a 1 molar solution, denoted 1 M solution; however M should not be treated as a symbol for the unit: mol dm^{-3} .
- (4) In practice mol l^{-1} ($= \text{mol dm}^{-3}$), mmol l^{-1} , and $\mu\text{mol l}^{-1}$ are more useful than mol m^{-3} , and are equally acceptable SI units.
- (5) $\underline{n}_B$ denotes the amount of entities B, and $\underline{V}$ the volume of solution. Note that $\underline{n}_B = \underline{m}_B / \underline{M}_B$, where $\underline{M}_B$ is the molar mass of entity B; thus amount concentration is related to mass concentration by the equation
- $\underline{c}_B = \underline{g}_B / \underline{M}_B$. For example tribromomethane has a molar mass $\underline{M}_{\text{CHBr}_3} = 253 \text{ g mol}^{-1}$, and thus a solution of mass concentration $\underline{g} = 1 \text{ mg l}^{-1}$ has an amount concentration

$$\underline{c}_{\text{CHBr}_3} = \frac{1 \text{ mg l}^{-1}}{253 \text{ g mol}^{-1}} = 3.95 \mu\text{mol l}^{-1}$$

2. MASS CONCENTRATION IS MISLEADING?

Measurements of chemical concentrations in water are generally made to assess the likelihood or possible magnitude of biological or chemical effects for example the assessment of water quality for environmental or process control purposes. In general the interactions that cause the effects of concern are dependant on the number of molecules or moles of the chemicals concerned not their mass - for physico-chemical effects this is established in the early years of chemistry training for example for colligative properties and for biological/environmental effects is obvious when it is considered that some enzymic interaction is involved. It follows therefore that amount concentration is a more appropriate quantity than mass concentrations for these purposes. It could be argued that molecular weights in general do not range very widely so the differences between mass and amount are in fact of little importance. In most cases this is true but the atomic weights of the elements such as fluorine (19) and iodine (127) or aluminium (27) and lead (207) vary by a factor of nearly ten, as typically do the molecular weights of organic pollutants eg methyl chloride (50) and perchlorotriphenyl (855) or pp'DDT (354) so differences of at least an order of magnitude are to be expected and a factor of ten is not insignificant, particularly when it can be readily compensated for.

The use of terms such as parts per million usually expressed on a weight: weight basis for contaminants in water is often associated with the use of mass concentration since $1 \text{ mg l}^{-1} \approx 1 \text{ ppm}$. The use of parts per million has attractions because it provides a "feel" that non-scientists can appreciate. However in the case of water, because it has such a low molecular weight in comparison with most contaminants, the use of ppm on a weight : weight basis grossly overestimates the number of molecules or amount of contaminant to the number of

molecules or amount water, the extent of the overestimate is illustrated below:

Molecular weight of pollutant	parts per million	
	mass/mass	amount/amount
50	1	0.36
100	1	0.18
300	1	0.060
500	1	0.036
800	1	0.023

For example a solution of 1 mg l^{-1} of γ -hexachlorocyclohexane (γ -HCH) in water, ie 1 ppm in normal terminology is only 0.062 ppm or 62 ppb on a number of molecules or amount basis and $3.4 \text{ } \mu\text{mol l}^{-1}$ when expressed in molar concentration units.

If environmental quality standards or guideline values are available for comparison with a measured value, the selection of quantity and units is obviously not so important as long as the same ones are used in both cases. However, problems do occur when levels of concern or even standards are set. For example a decision could be made not to consider for certain purposes chemicals that occur at a mass concentration of less than $0.1 \text{ } \mu\text{g l}^{-1}$. Since biological effects are related to the number of molecules present and molecular weights vary by at least a factor of ten such a limit is likely to be either ten times too lax for compounds with low molecular weights or ten times too severe for compounds with high molecular weights. Thus even if it were possible scientifically to set such a limit of concern, which seems highly unlikely, it would be technically impossible to define it as a single concentration expressed on a mass basis (ie g l^{-1}).

There are a considerable number of problems with standards set for groups of chemicals and the assessment of compliance with such standards. One example of the problems is provided by Parameter 55 of the European Community Drinking Water Directive for which it is scientifically impossible to prove compliance because the set of 'pesticides' specified in the Directive is unbounded. Even with a bounded set of say trihalomethanes a number of problems can occur which are exacerbated if mass rather than amount concentration is used, as the following table shows for three different hypothetical water samples with the same total concentration when quoted on a mass basis.

Chemical	Concentration of chemical/(mg l^{-1})		
	Water 1	Water 2	Water 3
Chloroform	1	1	10
Bromodichloromethane	1	10	1
Dibromochloromethane	1	1	1
Tribromomethane	10	1	1
Total conc/(mg l^{-1})	13	13	13
Total conc/($\mu\text{mol l}^{-1}$)	58	78	98

The mass concentration clearly gives a misleading representation of the total amount of "trihalomethane" present.

Comparison of the 'toxicity' of chemicals can only be achieved if amount concentration is used whether the comparison is qualitative, X is more toxic than Y, or quantitative as for example in a quantitative structure activity relationship. The concentration of chemical that is lethal to 50% of fish in a given period of time quoted in mass concentration terms as say

0.1 mg l⁻¹ for X compared to 1 mg l⁻¹ for Y says nothing about the relative toxicities because if the molecular weight of Y is more than ten times that of X, Y is more toxic than X and if not the reverse is true.

A similar argument can be made if the sensitivity of analytical instrumentation is being compared. The following table gives detection limits for flame atomic absorption spectrometry for different elements:

Element	Detection limits	
	µg l ⁻¹	µmol l ⁻¹
Co	10	0.17
Pb	20	0.097
Al	30	1.1
Tl	30	0.17

From which it can be seen that the µg l⁻¹ detection limit gives a false picture of the relative sensitivity of flame AAS to the four different metals.

CONCLUSION: CONCENTRATION UNITS IN WATER CHEMISTRY

For well defined and identified organic and organometallic substances the contention of this paper is that a move towards amount concentration using units of mol l⁻¹ would be timely and desirable.

For well defined inorganic substances such as nitrate, phosphate, chloride and fluoride etc a move to amount concentration (units mol l⁻¹) is also desirable.

For other inorganic substances with more complex aqueous chemistries the case is less clear cut. The analytical procedures used for these elements often involve extensive digestion to convert different chemical forms that may be present in the sample into a single form for analysis. This implies that different forms are often present of unknown and probably variable molecular weights. However, this feature is well known and widely recognised and it is not felt that a move towards amount concentration in the presentation of results would prejudice this understanding, therefore such a move should not be discouraged for this reason.

The considerable problems involved in setting and monitoring compliance with composite standards covering groups of chemicals have been alluded to. In view of these and other difficulties single-compound standards are clearly preferable. However, if composite standards or analytical determinations are made, amount concentration is preferred to mass concentration and mol l⁻¹ preferred to g l⁻¹.

Several routine water chemistry measurements are effectively operationally defined, eg Biological Oxygen Demand (BOD) or alkalinity. The operational definition of a given measurement should not discourage the use of consistent units. If the determination, as in the case of BOD or alkalinity, involves the determination of the concentration of a single well characterised substance, for example oxygen or strong acid, amount concentration should be used. If the identity of the species involved is not well characterised, eg humic acid, the use of mass concentration is unavoidable, its continued use serves to emphasise that the identity of the species has still to be established.

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REFERENCE

McGLASHAN M L (1971) Physico-chemical quantities and units. Royal Institute of Chemistry, Monographs for Teachers 15.