Metrology for Climate Relevant VOCs

Metrological vocabulary and traceability – terminology in chemical analysis

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Examples

WMO

Greenhouse Gas Bulletin

The State of Greenhouse Gases in the Atmosphere Based on Global Observations through 2009

Table 1. Global abundances of and changes in key greenhouse gases from the GAW global greenhouse gas monitoring network. Global abundances for 2009 are calculated as an average over twelve months.

	CO_2 (ppm)	CH_4 (ppb)	N_2O (ppb)
Global abundance in 2009	386.8	1803	322.5
Increase since 1750[1]	38 %	158 %	19 %
2008–09 absolute increase	1.6	5	0.6
2008–09 relative increase	0.42 %	0.28 %	0.19 %
Mean annual absolute increase during last 10 years	1.88	2.2	0.77

[1] Assuming a pre-industrial mixing ratio of 280 ppm for CO_2, 700 ppb for CH_4 and 270 ppb for N_2O.

741.13

Verordnung der Bundesversammlung über Alkoholgrenzwerte im Strassenverkehr

vom 15. Juni 2012 (Stand am 1. Oktober 2016)

Die Bundesversammlung der Schweizerischen Eidgenossenschaft,

gestützt auf Artikel 55 Absatz 6 des Strassenverkehrsgesetzes vom 19. Dezember 1958[1],
nach Einsicht in die Botschaft des Bundesrates vom 20. Oktober 2010[2],

beschliesst:

Art. 1 Angetrunkenheit

Fahrunfähigkeit wegen Alkoholeinwirkung (Angetrunkenheit) gilt als erwiesen, wenn der Fahrzeugführer oder die Fahrzeugführerin:

a. eine Blutalkoholkonzentration von 0,5 Gewichtspromille oder mehr aufweist;

b. eine Atemalkoholkonzentration von 0,25 mg Alkohol oder mehr pro Liter Atemluft aufweist; oder

c. eine Alkoholmenge im Körper hat, die zu einer Blutalkoholkonzentration nach Buchstabe a führt.

Art. 1 Etat d'ébriété

Un conducteur est réputé incapable de conduire pour cause d'alcool (état d'ébriété) lorsqu'il présente:

a. un taux d'alcool dans le sang de 0,5 gramme pour mille ou plus;

b. un taux d'alcool dans l'haleine de 0,25 milligramme ou plus par litre d'air expiré;

c. une quantité d'alcool dans l'organisme entraînant le taux d'alcool dans le sang fixé à la let. a.

Purpose of Terminology

Definition: Technical vocabulary for standardising the terms of a field of knowledge.

Purpose: **Preventing** professional **communication problems**

Metrology: VIM (Vocabulaire International de Metrologie)

Chemical Analysis as a sub-discipline of metrology has an extended vocabulary:

IUPAC colour books:
z.B. Green book: Quantities, Units and Symbols in Physical Chemistry
Gold book: Compendium of Chemical Terminology
Orange book: Compendium of Analytical Nomenclature

EURACHEM Guide: Terminology in Analytical Measurement

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

Quantities, Units, Dimensions

Quantity	Quantity symbol	Unit	Unit symbol	Dimen-sion
Length	*ℓ, h, r, x*	meter	m	L
Mass	*m*	kilogramm	kg	M
Time	*t*	second	s	T
Electric current	*I, i*	ampere	A	I
Thermodynamic temperature	*T*	kelvin	K	Θ
Amount of substance	*n*	mole	mol	N
Luminous intensity	I_V	candela	cd	J
Catalytic activity	*a*	katal	kat	$N\ T^{-1}$
Energy	*E*	joule	J	$L^2 \cdot M \cdot T^{-2}$
Amount of substance concentration	c_B	mole / litre	mol/L	$N \cdot L^{-3}$

Quantities, Units, Dimensions
Compositions of mixtures by Cvitaš

Ratios:

Name	Symbol	Definition
Mass ratio	$\zeta_{i,j}$	$\zeta_{i,j} = m_i/m_j$
Volume ratio	$\psi_{i,j}$	$\psi_{i,j} = V_i/V_j$
(Chemical) amount ratio, mole ratio, number ratio	$r_{\mathrm{B,A}}$	$r_{\mathrm{B,A}} = n_{\mathrm{B}}/n_{\mathrm{A}} = N_{\mathrm{B}}/N_{\mathrm{A}}$

Ratios are not commonly used. Neither the IUPAC nor the IUPAP explicitly recommends symbols for these quantities. The ISO [4.i] recommends only the amount

Quantities, Units, Dimensions
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Fractions:

Name	Symbol	Definition
Mass fraction	w	$w_i = m_i / \sum m_j$
Volume fraction	φ	$\varphi_i = V_i / \sum V_j$
(Chemical) amount fraction, mole fraction, number fraction	x	$x_B = n_B / \sum n_j = N_B / \sum N_j$

The denominator in all these definitions refers to the sum over all the composite parts including the one in the numerator. Since the number of entities is proportional to the chemical amount of entities and the proportionality constant is equal for all substances, the amount fraction is identical with the number fraction.

Quantities, Units, Dimensions
Compositions of mixtures by Cvitaš

Concentrations:

Name	Symbol	Definition	SI unit	Common units
Mass concentration	γ, ρ	$\gamma_i = m_i / V$	$\mathrm{kg\,m^{-3}}$	$\mathrm{g/L = g\,dm^{-3}}$
Volume concentration	σ	$\sigma_i = V_i / V$	1	1
Amount concentration	c	$c_\mathrm{B} = n_\mathrm{B} / V$	$\mathrm{mol\,m^{-3}}$	$\mathrm{mol/L = mol\,dm^{-3}}$
Number concentration	C	$C_\mathrm{B} = N_\mathrm{B} / V$	$\mathrm{m^{-3}}$	$\mathrm{cm^{-3}}$

Quantities, Units, Dimensions
Compositions of mixtures by Cvitaš

Contents:

Name	Symbol	Definition	SI unit
Volume content	κ	$\kappa_i = V_i/m$	$m^3\ kg^{-1}$
Amount content	k	$k_B = n_B/m$	$mol\ kg^{-1}$
Number content	K	$K_B = N_B/m$	kg^{-1}

Exotic Quantity:

Molality *b* oder *m* $b_B = n_B/m_{solv}$ mol kg^{-1}

Quantities, Units, Dimensions
Compositions of mixtures by Cvitaš

Example:

70 mL EtOH in

30 mL H_2O bei

20 °C

Ratios	
Volume ratio	$\psi(\text{EtOH}, \text{H}_2\text{O}) = 7:3$
Mass ratio	$\zeta(\text{EtOH}, \text{H}_2\text{O}) = 1{,}84:1 \approx 11:6$
Amount ratio	$r(\text{EtOH}, \text{H}_2\text{O}) = 0{,}721:1 \approx 3:4$
Fractions	
Volume fraction	$\varphi(\text{EtOH}) = 70\,\%$
Mass fraction	$w(\text{EtOH}) = 64{,}8\,\%$
Amount fraction	$x(\text{EtOH}) = 41{,}9\,\%$
Concentrations	
Mass concentration	$\gamma(\text{EtOH}) = 571\ \text{g/L}$
Volume concentration	$\sigma(\text{EtOH}) = 0{,}723$
Amount concentration	$c(\text{EtOH}) = 12{,}4\ \text{mol/L}$
Number concentration	$C(\text{EtOH}) = 7{,}47 \times 10^{21}\ \text{cm}^{-3}$
Molality	
Molality	$b(\text{EtOH}) = 40\ \text{mol kg}^{-1}$
Contents	
Volume content	$\kappa(\text{EtOH}) = 822\ \text{mL kg}^{-1}$
Amount content	$k(\text{EtOH}) = 14{,}1\ \text{mol kg}^{-1}$
Number content	$K(\text{EtOH}) = 8{,}49 \times 10^{21}\ \text{g}^{-1}$

Examples improved?

WORLD METEOROLOGICAL ORGANIZATION | GLOBAL ATMOSPHERE WATCH

WMO GREENHOUSE GAS BULLETIN

The State of Greenhouse Gases in the Atmosphere Based on Global Observations through 2018

Table 1. Global annual surface mean abundances (2018) and trends of key greenhouse gases from the GAW global GHG monitoring network. Units are dry-air mole fractions, and uncertainties are 68% confidence limits [12]. The averaging method is described in the GAW Report No. 184 [11]. A number of stations are used for the analyses: 129 for CO_2, 127 for CH_4 and 96 for N_2O.

	CO_2	CH_4	N_2O
2018 global mean abundance	407.8±0.1 ppm	1869±2 ppb	331.1±0.1 ppb
2018 abundance relative to year 1750*	147%	259%	123%
2017–2018 absolute increase	2.3 ppm	10 ppb	1.2 ppb
2017–2018 relative increase	0.57%	0.54%	0.36%
Mean annual absolute increase over the last 10 years	2.26 ppm yr^{-1}	7.1 ppb yr^{-1}	0.95 ppb yr^{-1}

* Assuming a pre-industrial mole fraction of 278 ppm for CO_2, 722 ppb for CH_4 and 270 ppb for N_2O.

Anhang 1
(Art. 4 und 7)

Spezifische Anforderungen an Atemalkoholtestgeräte

1 Anforderungen an den Aufbau und die messtechnischen Eigenschaften

Atemalkoholtestgeräte müssen die Anforderungen der Norm SN EN 15964[14] und dieses Anhangs an den Aufbau und die messtechnischen Eigenschaften erfüllen.

2 Messbereiche

2.1 Der Mindestmessbereich für Atemalkoholtestgeräte ist in Tabelle 1 angegeben.

Tabelle 1

Messgrösse	Messbereich
Atemalkoholkonzentration	(0,025 … 1,50) mg/l bei 34 °C und Umgebungsdruck
umgerechneter Blutalkoholmassengehalt	(0,05 … 3,00) g/kg oder ‰

2.2 Der Blutalkoholmassengehalt wird über den Umrechnungsfaktor von 2000 l/kg nach Artikel 11 Absatz 2 der Strassenverkehrskontrollverordnung vom 28. März 2007[15] aus der Atemalkoholkonzentration errechnet und in g/kg oder ‰ (Promille) angegeben.

Version of 30.1.2015 of the Swiss ordinance on breath alcohol devices: Blood alcohol concentration --- Blood alcohol mass content

Examples improved?

ERRATA
(2015-07-10)

OIML R 126
Edition 2012 (E)

Evidential breath analyzers

This should be corrected to read:

11.4.4.14 Influence of mass concentration of CO_2

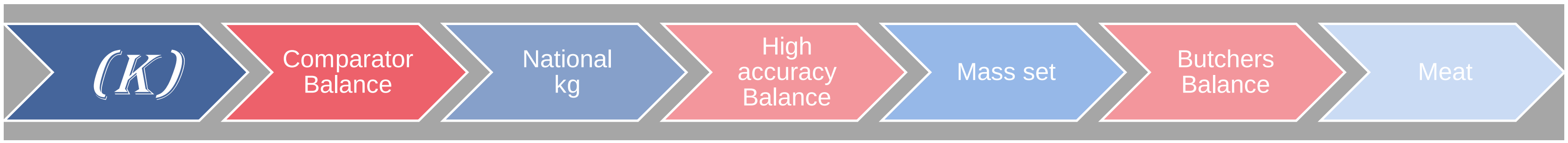
This test is applied to verify compliance with the provisions in 5.8.1 k) under conditions of CO_2 in the test gas.

The following shortened test procedure shall be applied:

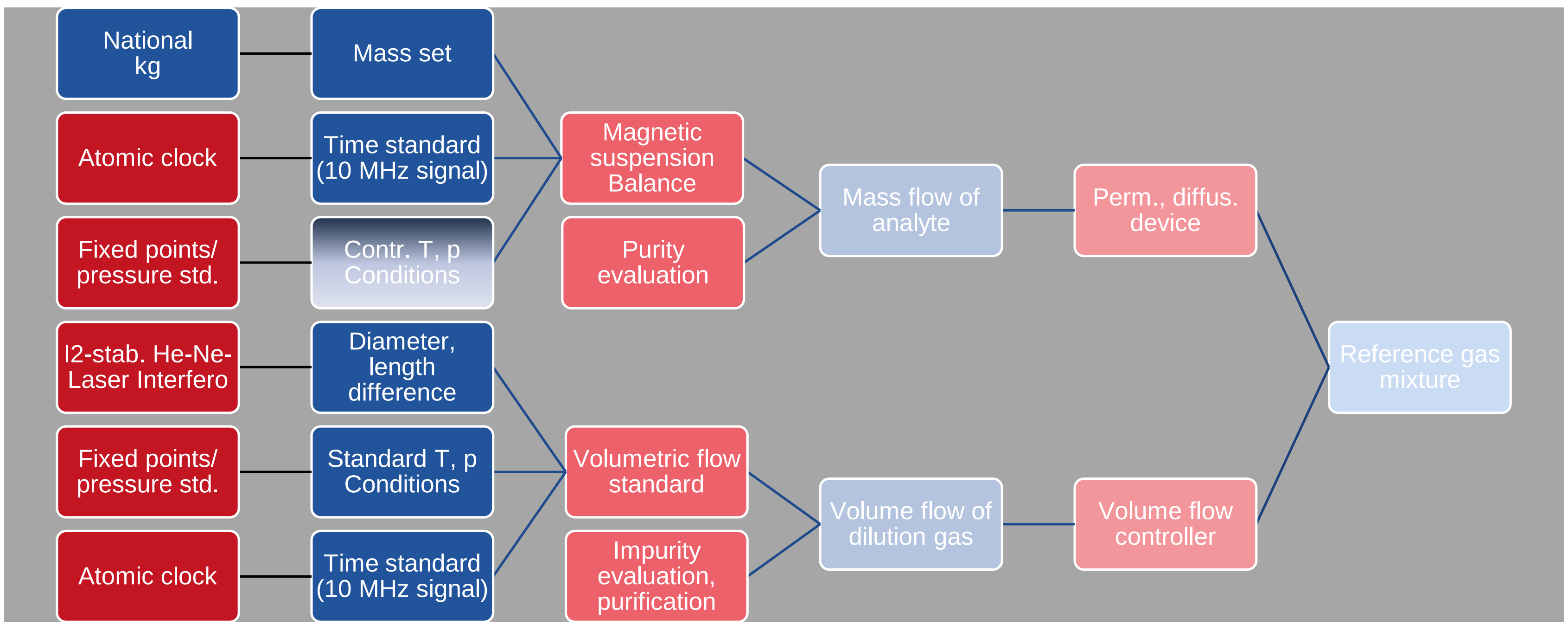
Precondition	Normal electric power supplied and "on" for a time period equal to or greater than the warm-up time specified by the manufacturer.
Condition of the EUT	Power is to be "on" for the duration of the test.
Test	The EUT shall not be readjusted at any time during the test. Perform 5 measurements using test gas No. 4 defined in 11.4.4.1 with 10 % (mass concentration) of CO_2 and record: a) date and time, b) temperature, c) relative humidity

The Traceability Issue

Traceability chain for physical (base) quantities (example):



For dynamic RM (mixtures) realisations of derived quantities:



What is primary?

Definition of the CCQM (1995):

A primary method of measurement is a method having the highest metrological qualities, whose operation can be completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units, and whose results are, therefore, accepted without reference to a standard of the quantity being measured.

3 criteria:

- Lowest uncertainty (= highest qualities)
- Transparent (no empirical corrections)
- Independent (no relation to other method measuring the same Q)

Take-home messages

1. Most chemical quantities are **quotients**.
2. (Total) **volume-related quantities** are called **concentrations** (FR: concentrations, DE: Konzentrationen).
   (Total) **mass-related quantities** are called **contents** (FR: teneurs, DE: Gehalte).
3. The quantity designates the **analyte** and the **matrix**. They should not be abbreviated or only abbreviated in an internationally harmonised way (BrAC?).
4. Units (symbols) are often not suitable for assigning the corresponding quantity.
5. **Quantities** can**not** be defined **as a function of units** (‘mole fraction’ of B in X).

Literature

- Cvitaš T.: Quantities describing compositions of mixtures; *Metrologia*, 1996, **33**, 35-39
- ISO 80000-1:2009(E): Quantities and units - Part 1: General
- ISO 80000-9:2009(E): Quantities and units - Part 9: Physical chemistry and molecular physics
- M J T Milton and T J Quinn: Primary methods for the measurement of amount of substance, *Metrologia,* 2001, **38** 289

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For more information, visit

www.metclimvoc.eu

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