Metrology for Climate Relevant VOCs

Static mixture preparation and uncertainty

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ISO 6142 – Part 1

Gas analysis — Preparation of calibration gas mixtures — Part 1: Gravimetric method for Class I mixtures

- Method for “Static Reference Gas Mixtures”
- Root of metrological traceability chain
- Class I type gas mixtures are individually verified
- Rigorous and comprehensive QA/QC for preparation and verification (e.g. accreditation ISO 17034)
- Uncertainties in general substantially smaller than by any other preparation method.
- ‘Stable’ components

Preparation: the route to traceability

1- Purity analysis of the gases (or liquids) that will be used for the gas mixture

2- Selection of the high-pressure gas cylinder and cleaning process

3- Evacuated cylinder is filled with the first gas by pressure difference

4- Cylinders are weighed using calibrated mass comparator (by difference against a reference cylinder)

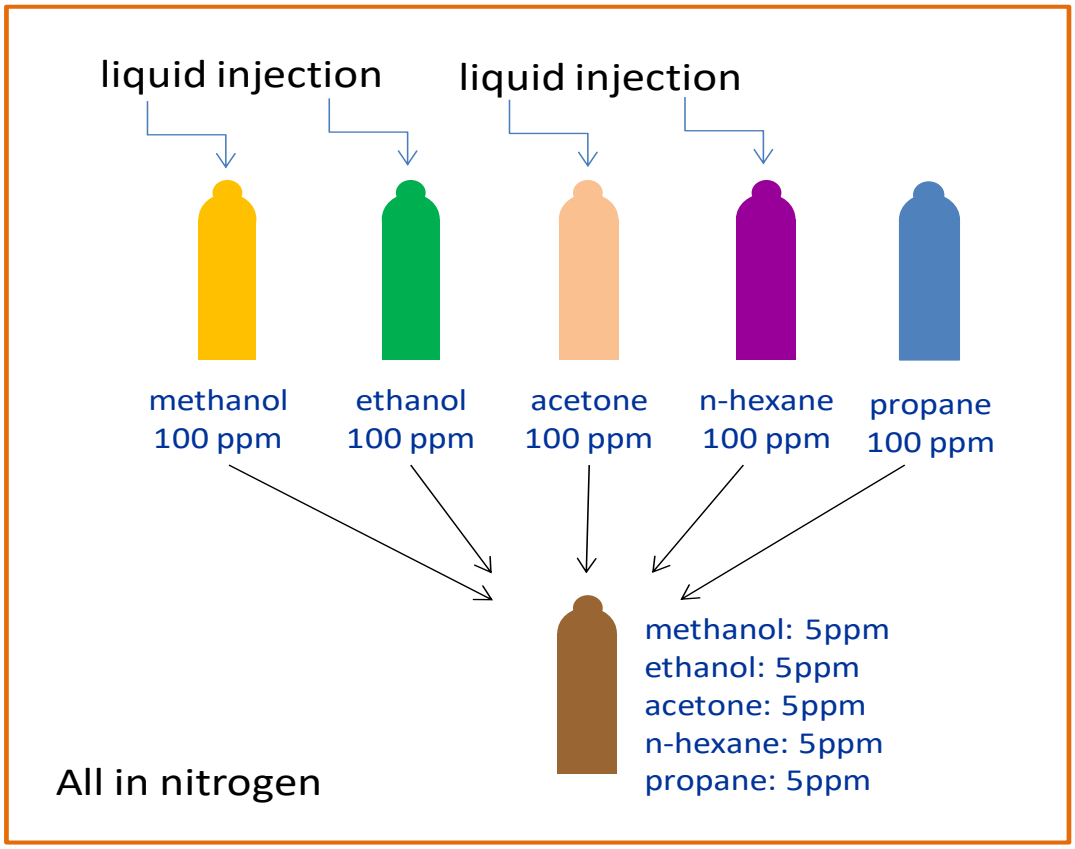
5- Steps 3 and 4 are repeated for multi-component gas mixtures

5- As last the matrix gas (e.g. nitrogen) is introduced to ca. 100-130 bar to achieve the target mole fraction

6- Calculation gas mixture purity (mass fractions converted into mole fractions)

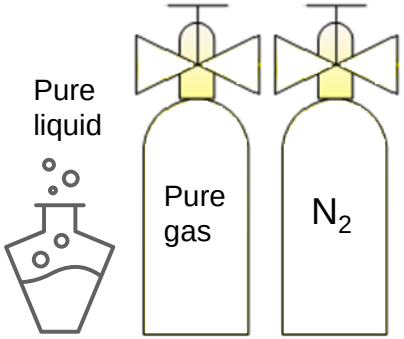
Preparation: the route to traceability (cont.)

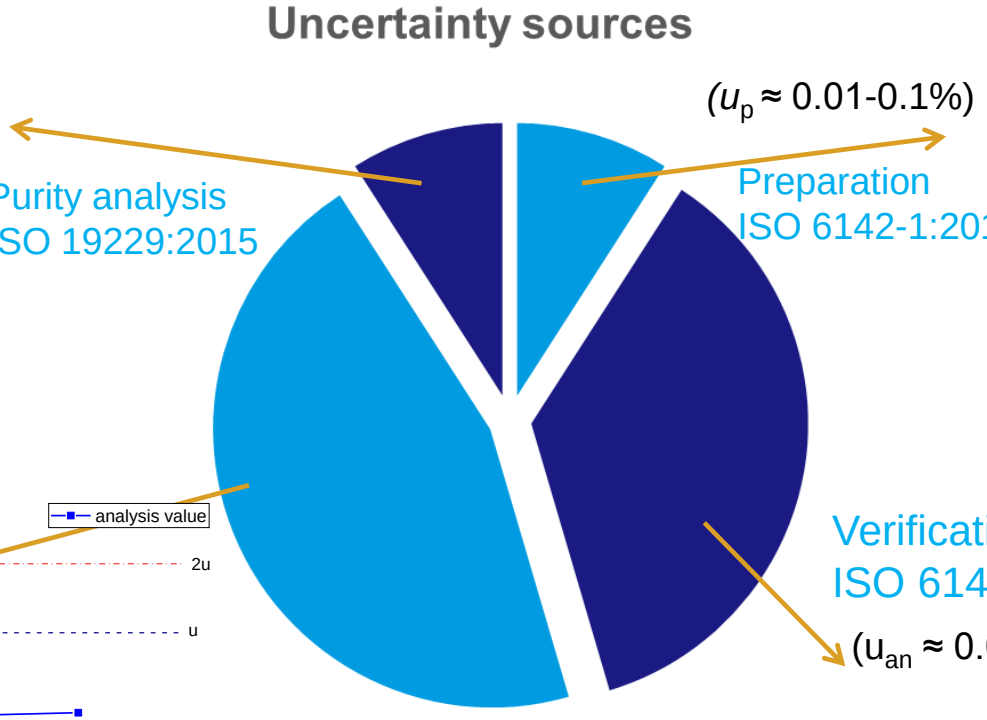
In case of liquid (e.g. VOCs), these are inserted in the gas cylinder as a single component or a liquid mixture by loop or syringe injection (gravimetrically)

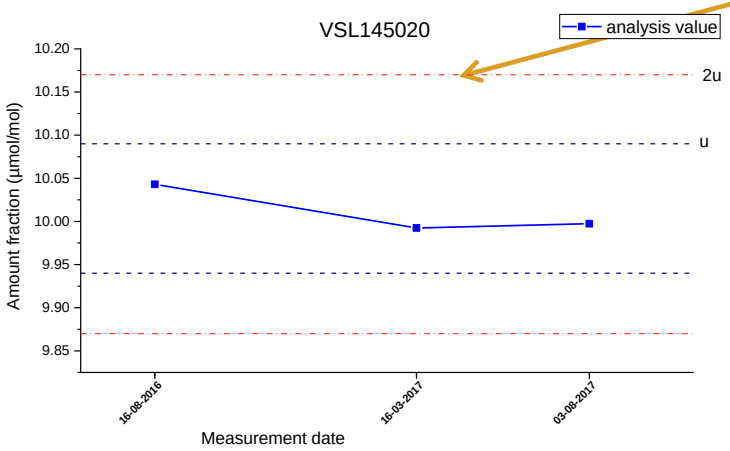


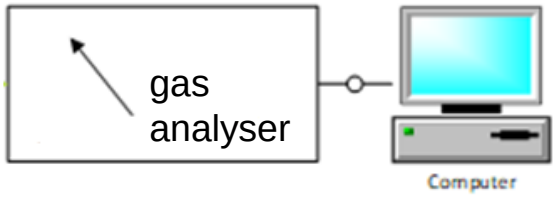
Primary realisation of Reference Gas Mixtures in mole fractions

$$u^2(x_{\mathrm{prep},i}) = u^2(x_{\mathrm{grav},i}) + u^2(\Delta x_{\mathrm{purity},i}) + u^2(\Delta x_{\mathrm{stab},i}) + u^2(\Delta x_{\mathrm{nr},i}).$$









Uncertainty of gravimetric preparation

Uncertainty sources:

- sensitivity
- linearity
- stability/drift
- repeatability
- influence of changing environmental conditions
- buoyancy effect
- calibration

Standard deviation weighing 2 mg.
At least 20 g of gas is inserted (0.01% repeatability)

VSL use a calibrated mass comparator under controlled environmental conditions

Compare weighing of sample cylinder (gas mixture in preparation) against another cylinder with same geometry and similar weight to reduce the uncertainty sources to sensitivity, stability/drift and repeatability

Purity of components

Purity of the main components (index s) is calculated as:

$$x_{sj} = 1 - \sum_{i=1}^{s-1} x_{ij} - \sum_{i=s+1}^{q} x_{ij}$$

The associated uncertainty is given by:

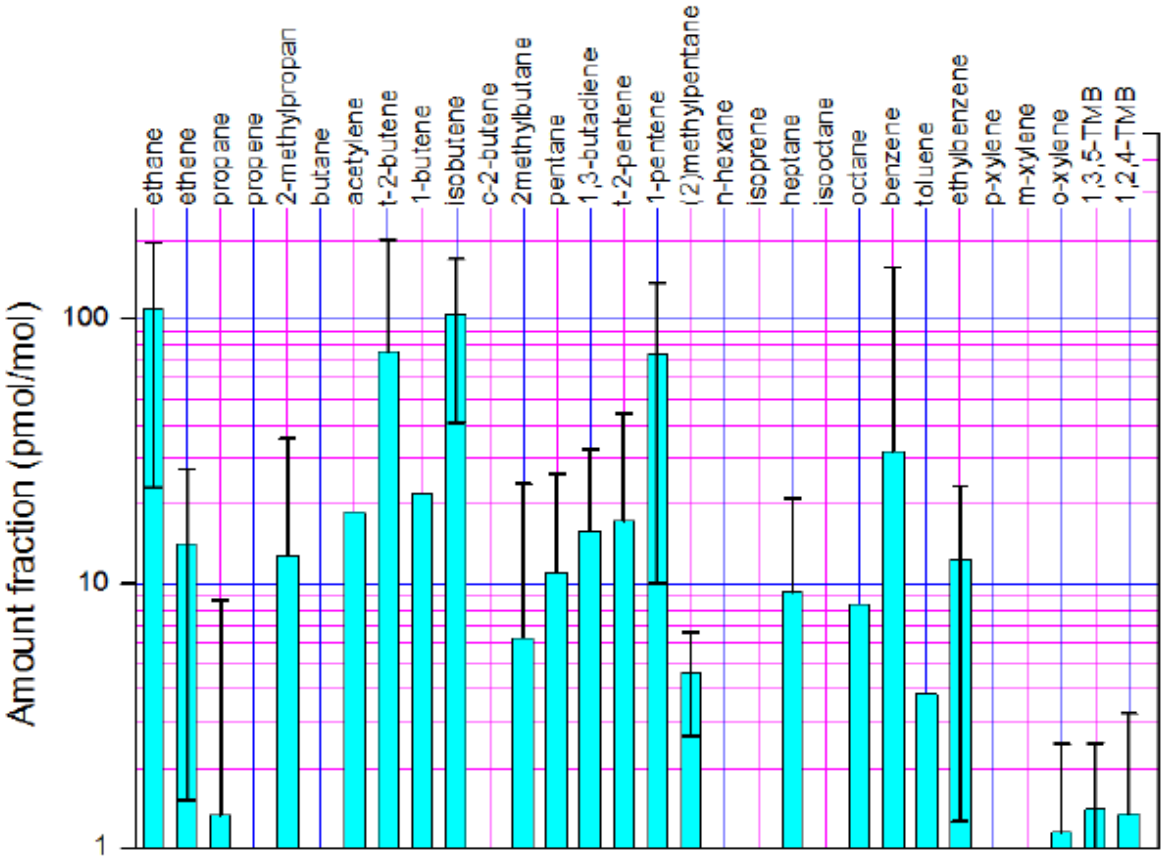
$$u^2(x_{sj}) = \sum_{i=1}^{s-1} u^2(x_{ij}) + \sum_{i=s+1}^{q} u^2(x_{ij})$$

Example: m-xylene purity table

component	Mass fraction (g/g)	Uncertainty (g/g)
o-xylene	0,001416	0,000271
m-xylene	0,997163	0,000321
p-xylene	0,000729	0,000067
ethylbenzene	0,000126	0,000026
toluene	0,000118	0,000026
water	0,000065	0,000001
1,3,5-Trimethylbenzene	0,000381	0,000153

Purity of matrix gas

Purity analysis of the matrix gas (in this case air from a cylinder)



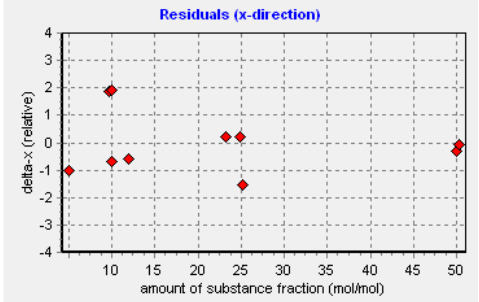
Verification (ISO 6143): comparison against traceable standards with proven accuracy & stability

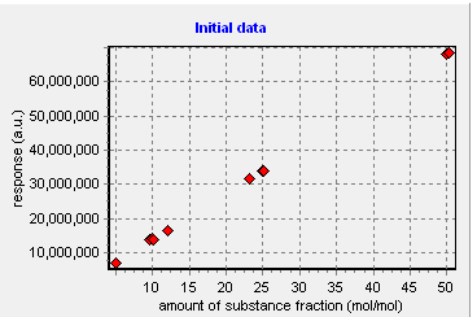
Example verification benzene gas standard against set of PSMs by TD-GC-FID with Generalised Distance Regression (GDR):

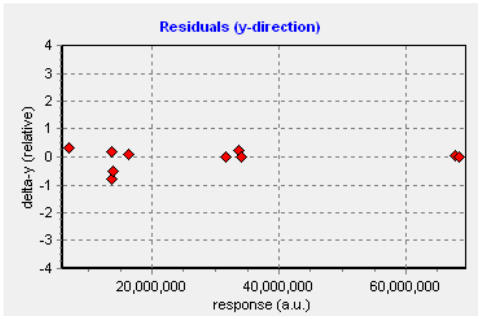
Regression model = straight line
Chi-squared = 12.6413
Probability = 0.1248
Goodness-of-fit (ISO 6143) = 1.8989

Coefficients regression model

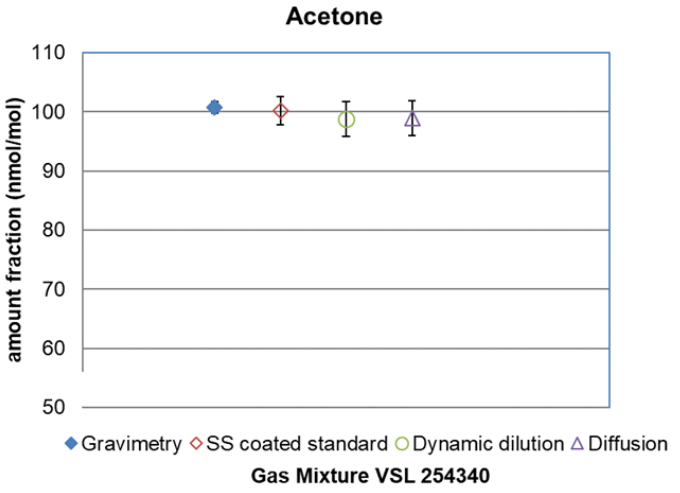
	value	uncertainty
a[0]	2.8666538E+05	8.5037227E+04
a[1]	1.3553822E+06	7.6018705E+03
a[2]		
a[3]		







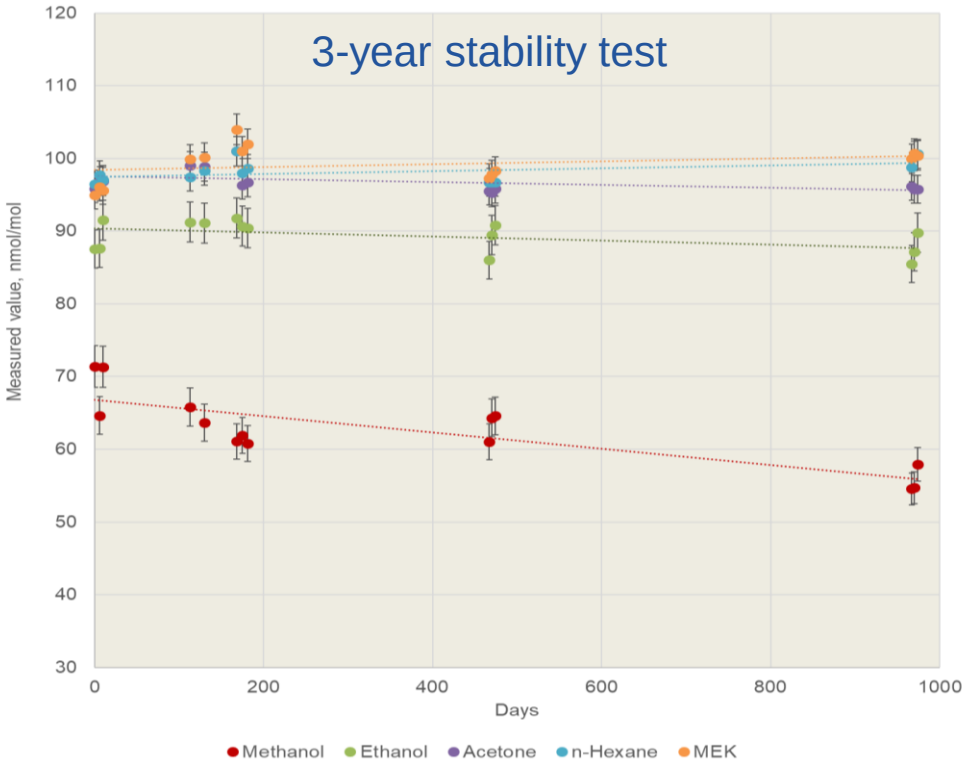
By cross-check against an independent refence method (dynamic)



Stability

A mixture is stable when the assigned value of the reference material and the measurement at certain time fulfil this criterium:

$$\left|x_{RM} - x_{meas}\right| \leq k \cdot \sqrt{u^2\left(x_{RM}\right) + u^2\left(x_{meas}\right)}$$



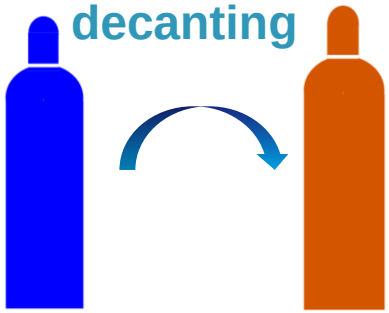
Stability of OVOCs

Gas mixtures	Age of the mixtures	Stability (against dynamic mixtures)		
		methanol	ethanol	acetone
Mix 1	1 month	<2.6%	<1.1%	<0.4%
Mix 2	5 years	<2.7%	<1.9%	<1.0%
Mix 3	6 years	<3.4 %	<0.3%	~0%

Gravimetric value 5 µmol/mol in N_2 for all 3 OVOCs

Quantifying adsorption loss in cylinders: decanting

Method: decanting (or cylinder-to-cylinder division).



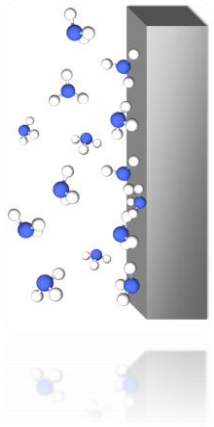
Both cylinders are analyzed and from the difference in analyzed value the adsorption is determined.

Metrologia 54 (2017) L26–L33 https://doi.org/10.1088/1681-7575/aa87b8

Short Communication

Determination of physical adsorption loss of primary standard gas mixtures in cylinders using cylinder-to-cylinder division

Sangil Lee[1,2], Mi Eon Kim[1,3], Sang Hyub Oh[1,2] and Jin Seog Kim[1,2]

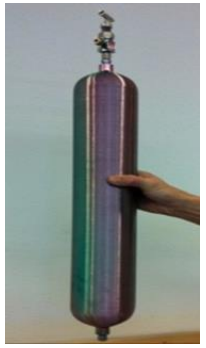


Oxy-VOC quantification of loss at 100 nmol/mol

Testing of different cylinders types

Cylinder types	methanol	ethanol	acetone	methacrolein	MVK	MEK	n-hexane
A	- 20 to - 30 %	- 5 to - 10 %	< 5 %	< 5 %	< 5 %	< 5 %	< 5 %
B	- 10 to - 20 %	- 5 to - 10 %	< 5 %	< 5 %	< 5 %	< 5 %	< 5 %
C	- 20 to - 55 %	-10 to - 40 %	< 5 %	< 5 %	< 5 %	< 5 %	< 7 %
D	- 50 to - 100 %	- 30 to - 55 %	< 5 %	< 5 %	< 5 %	< 5 %	-10 %
E	- 10 to - 30 %	- 5 to - 10 %	< 5 %	< 5 %	< 5 %	< 5 %	< 5 %
Coated SW	- 5 to - 10 %	- 3 to - 8 %	< 5 %	< 5 %	< 5 %	< 5 %	< 5 %

What goes in the cylinder does not per se come out!
Interaction with the cylinder surfaces and side reactions may occur, affecting the accuracy of preparation and stability
→ No universal cylinder treatment exists to fit all gases or fractions



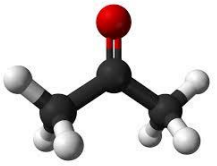
Uncertainty for an ‘easy’ oxy-VOC: acetone

Virtually no interaction with the cylinder surfaces or side reactions occur, affecting the accuracy of preparation and stability.

What goes into the cylinder = what comes out again.

Acetone at 5 µmol/mol

		Relative uncertainty	**remarks**
Gravimetry		0.03%	
Verification		0.5%	
Purity (mole fraction)	0.998 ± 0.001	0.1%	H_2O main impurity
Stability		stable	
‘Instant’ loss	no		



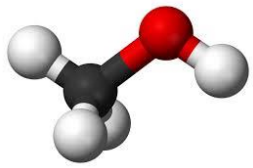
Uncertainty for a ‘difficult’ oxy-VOC’: methanol

Methanol interacts strongly with all kinds of surfaces including the cylinder wall, valve and pressure regulator. This strong interaction also affects the verification measurements. Loss at low µmol/mol level is a few % of the gravimetric value.

What goes into the cylinder ≠ what comes out again.

Methanol at 5 µmol/mol

		Relative uncertainty	remarks
Gravimetry		0.02%	
Verification		1%	
Purity (mole fraction)	0.99934 ± 0.00033	0.033%	H_2O main impurity
Stability		3%	
‘Instant’ loss	Yes (-2% to -5%)		



CMCs for OVOCs: acetone, methanol & ethanol

Component	Range of certified values (µmol/mol)	Range of expanded uncertainty	Mechanism for measurement service delivery
Acetone	**1-10**	**2%**	**PRM**
Methanol	**5-10**	**6% - 3%**	**CRM**
Ethanol	**1-10**	**5% - 3%**	**CRM**

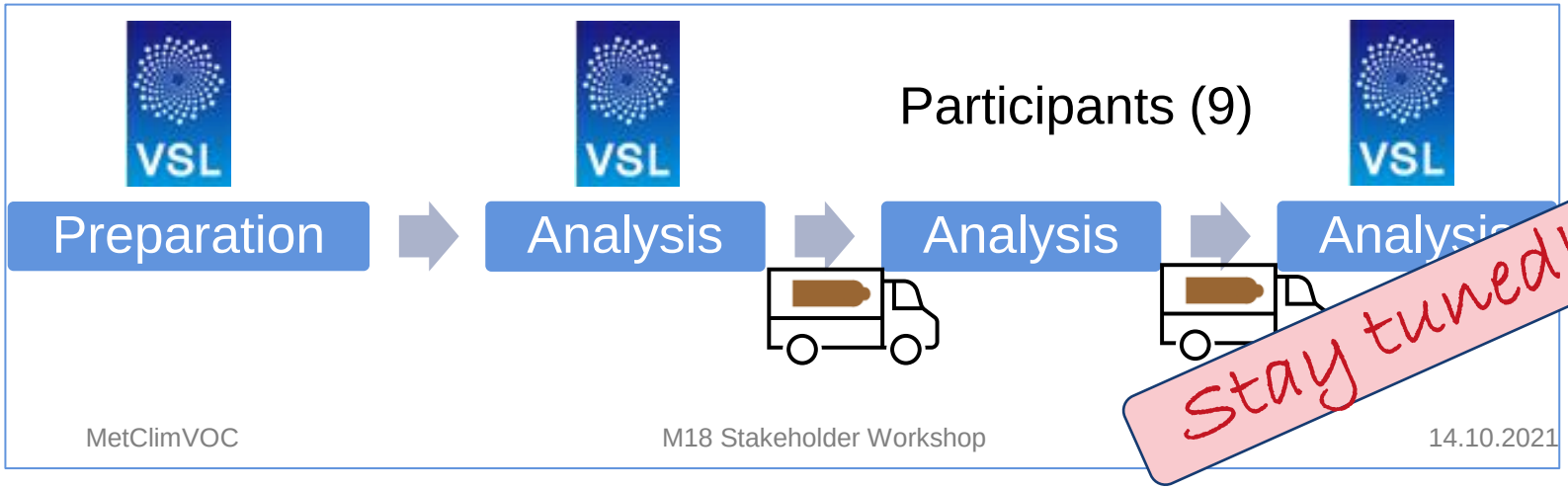
Matrix: N_2

Developments

In MetClimVOC project, VSL is working on Reference Gas Mixtures for oxy-VOCs at lower amount fractions (100 nmol/mol).

VSL also coordinates a new key comparison for NMIs: 'CCQM-K174 oxygenated VOCs' and prepares the mixtures.

Component	Amount fraction range (µmol/mol)
Acetone	0.1-1
Methanol	0.1-1
Ethanol	0.1-1
n-Hexane (internal standard)	0.1-1



Thank you for your attention!

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For more information, visit

www.metclimvoc.eu

EMPIR EURAMET

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