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TECH FORUM

Gas Odorisation

Presentations

MARCOGAZ documents:

“Natural gas odorisation practices in Europe” and “Odorization for natural gas/hydrogen mixtures and pure hydrogen”

Eugenio Salati

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Technical Association of the European Gas Industry

MARCOGAZ Tech Forum on Gas Odorisation

WG ODORISATION report

Eugenio Salati

30 May 2024

MARCOGAZ – WG Odorisation

26 members from 15 countries:

Odorisation of the gas

ISO/TS 16922(2022) "Natural gas — Odorization"

Processed natural gas normally has little or no odour. ***For safety reasons distributed natural gas is therefore odorised, to permit the detection of the gas by smell.***

The odorisation is predominantly a safety measure for the user of natural gas. Odorised natural gas needs to be recognized by the characteristic smell.

ISO 13734(2013) "Natural gas — Organic components used as odorants — Requirements and test methods"

Odorisation is the addition of odorants, normally intensely smelling organic sulfur compounds, to natural gas *(normally odourless) to allow the recognition of gas leaks by smell at very low concentration (before a build up to a dangerous gas in air concentration can occur).*

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Odour of natural gas and odorisation

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Odorisation practices in Marcogaz Countries

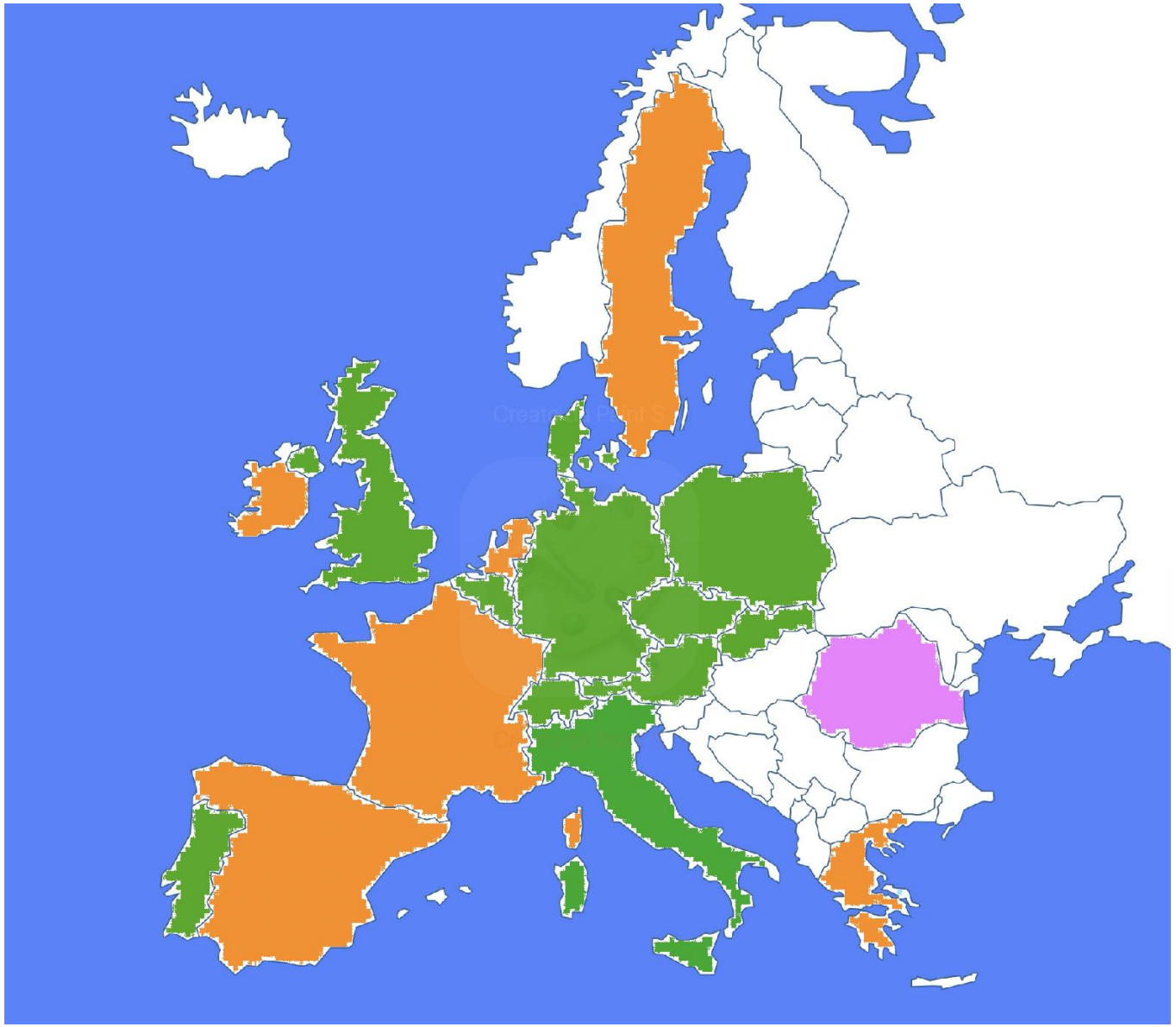
Odorisation is required in all Countries, by national laws or technical rules or regulations.

Odorisation is usually required only for domestic users. However, some high-pressure grids in Europe are also odorised, due to national regulations. Leaks in HP grids are usually detected by other systems, rather than smelling.

The requirements usually specify a minimum level of odorant concentration or olfactory sensation to be fulfilled; in some cases, the requirement is qualitative and the quantitative requirement is obtained from technical documents or national regulations.

Some industrial users (glass, ceramics, chemical, petrochemical, etc.) need gas with a low content of sulphur. In some cases, they might need to desulphur the gas if the content is above the required limit.

Where odorisation is performed



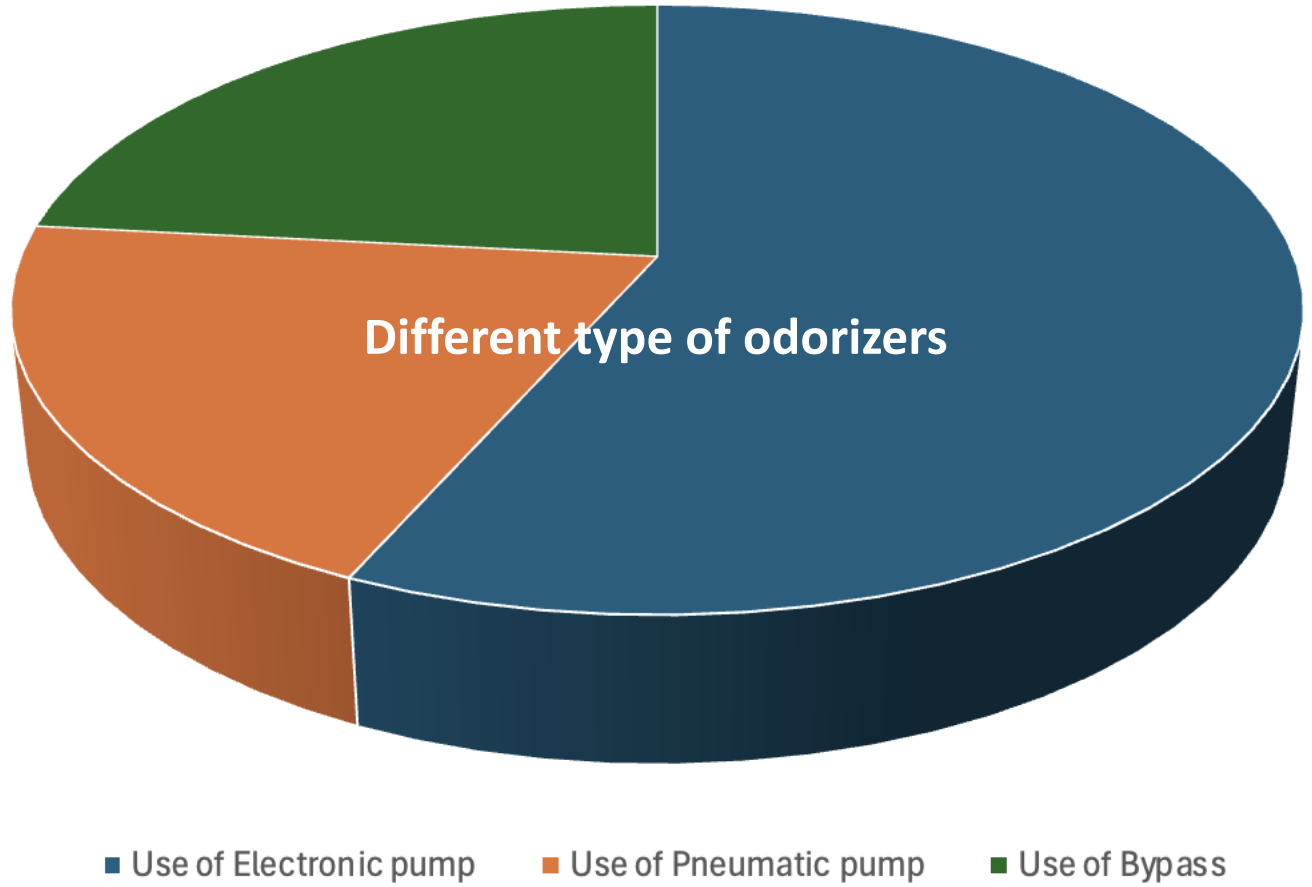
Odorisation performed by DSO.

Odorisation performed by TSO.

Odorisation performed both by TSO and DSO.

Odorisation plants

- **Distribution grids:** odorisation plants are usually located at **city gates and biomethane injections**.
- **Transmission grids:** **entry points** like interconnection points, LNG terminals, underground storages, gas fields and biomethane injection points.



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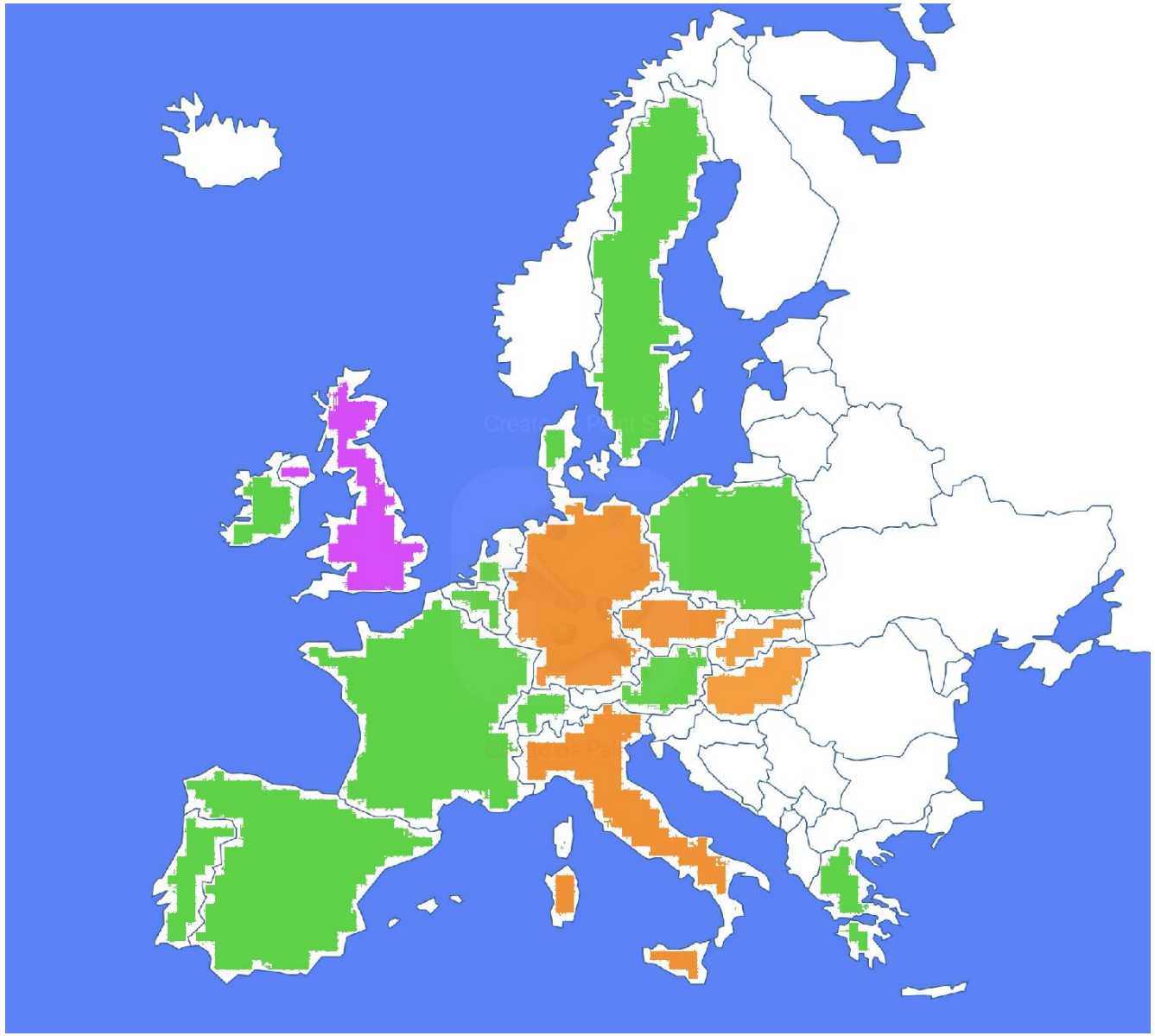
Controls

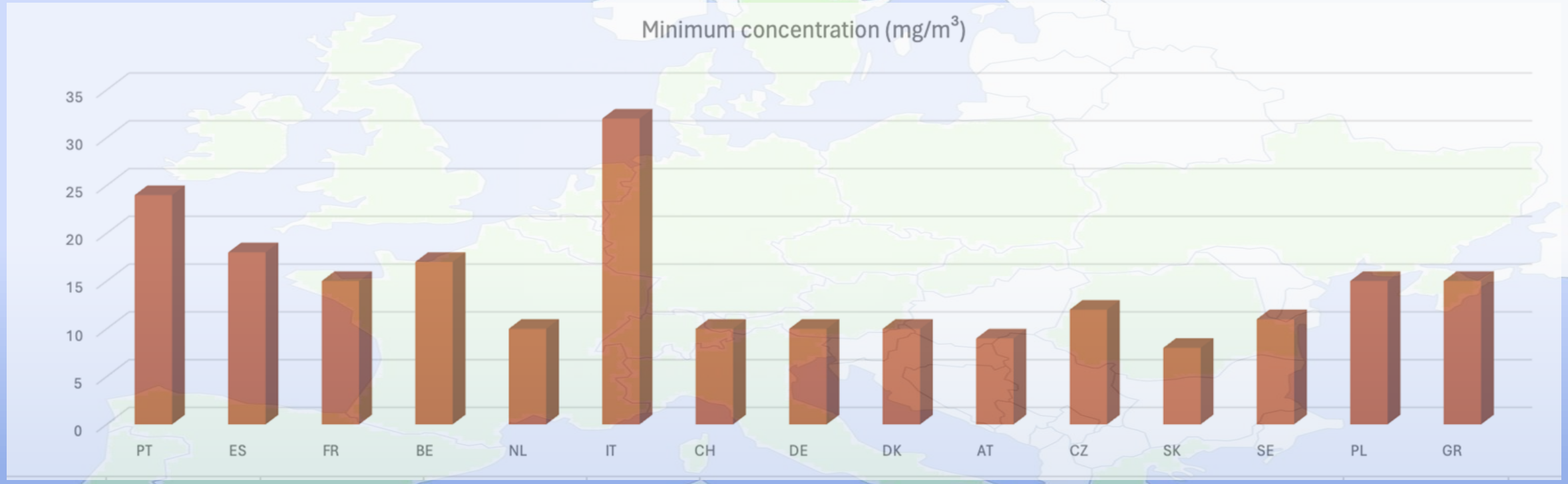


Odorant concentration.

Smell.

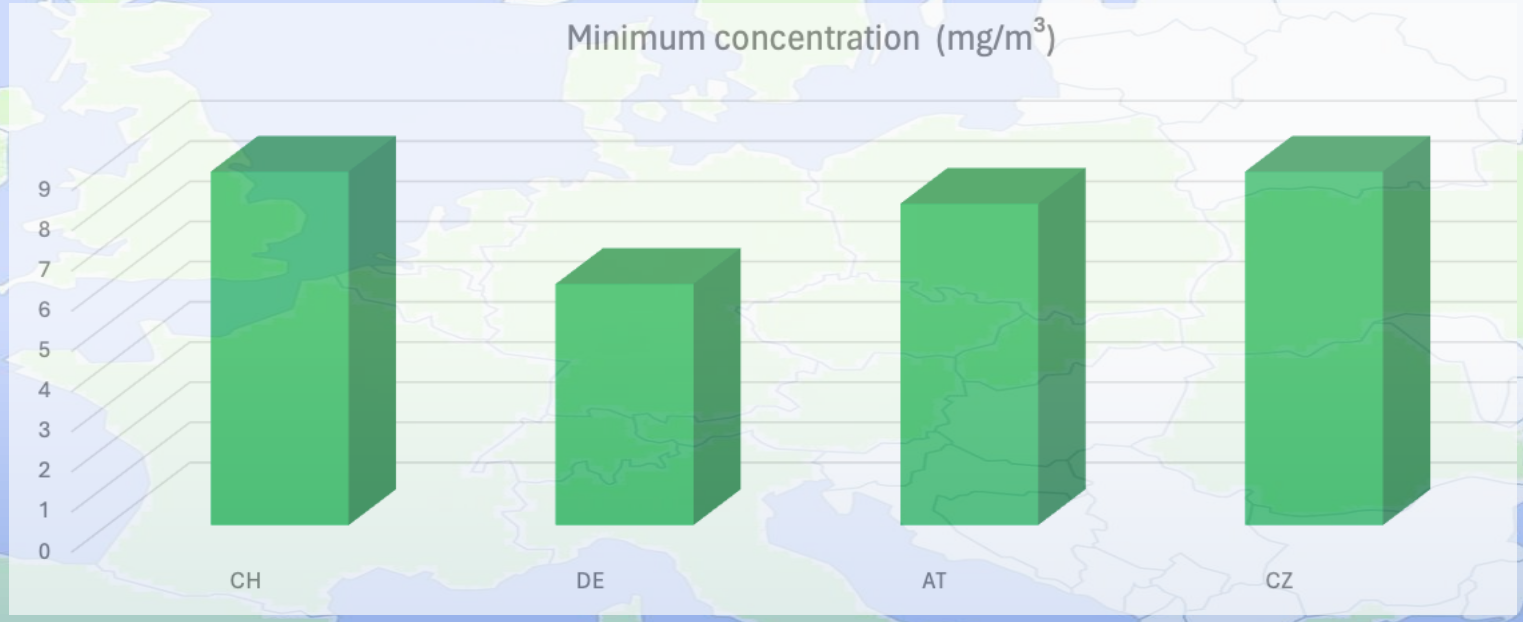
Both.

Odorants: THT



15 Countries	PT	ES	FR	BE	NL	IT	CH	DE	DK	AT	CZ	SK	SE	PL	GR
Minimum concentration (mg/m^3)	24	18	15	17	10	32	10	10	10	9	12	8	11	15	15

Odorants: Sulfur free



4 Countries	CH	DE	AT	CZ
Minimum concentration (mg/m³)	8,8	6	8	8,8

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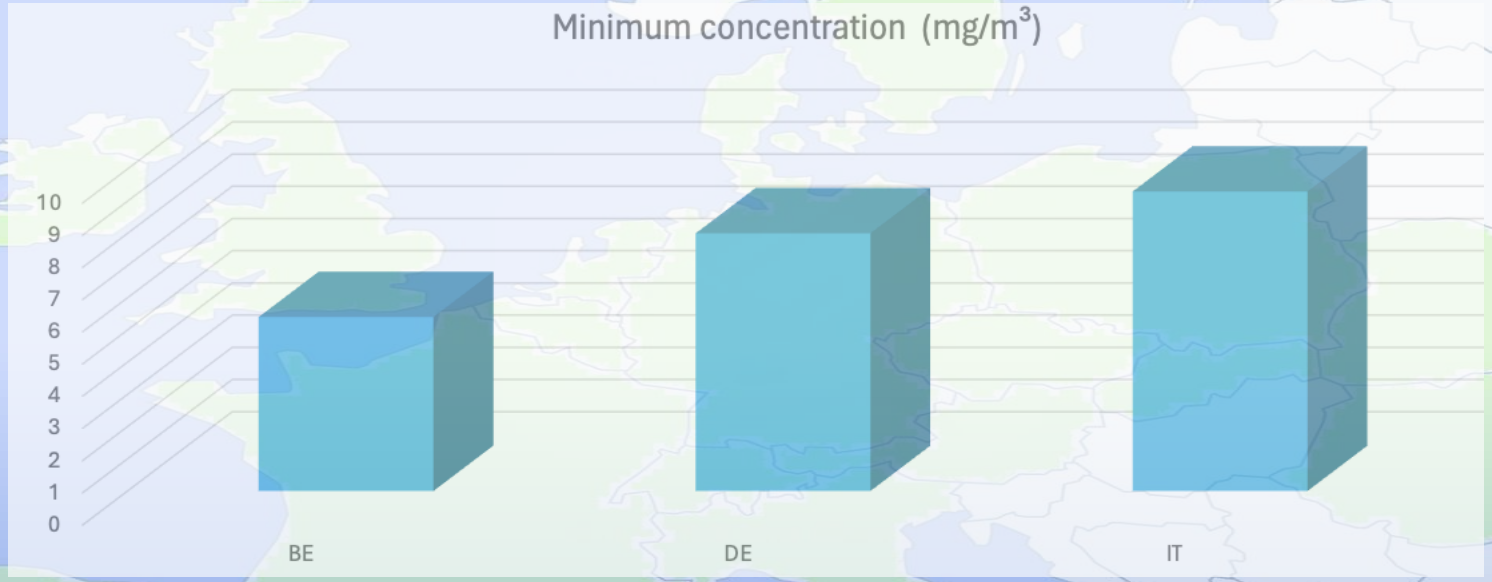
Odorants: mercaptans (TBM+IPM+NPM)



3 Countries	BE	DE	IT
Minimum concentration (mg/m³)	5,4	8	9,3

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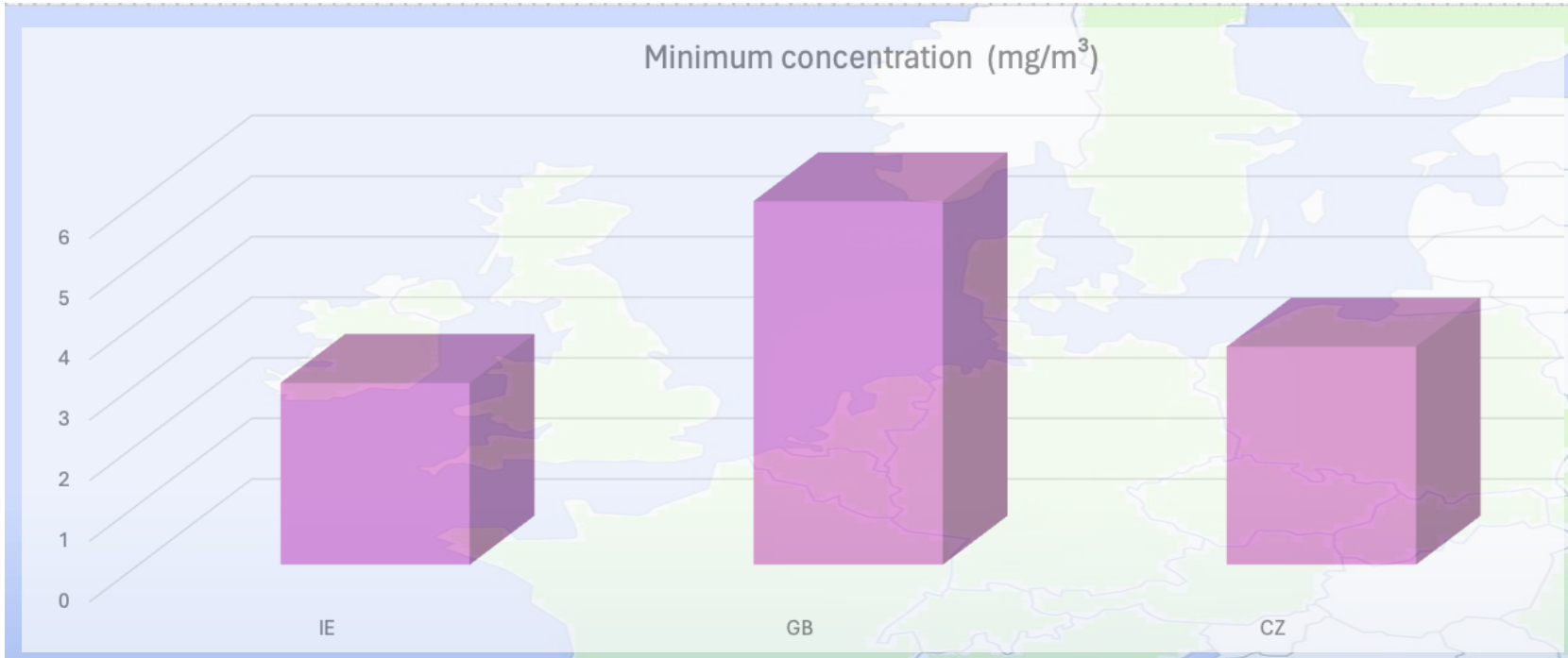
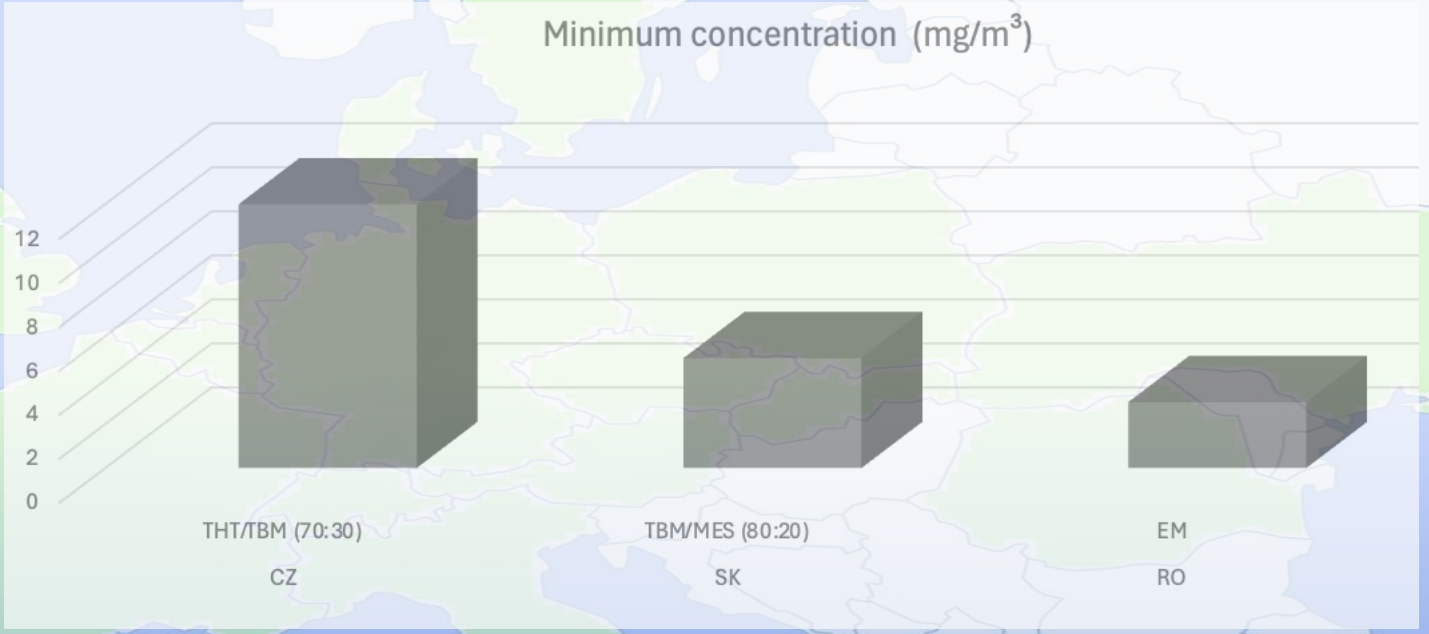
Odorants: TBM+DMS



3 Countries	IE	GB	CZ
Minimum concentration (mg/m³)	3	6	3,6

Odorants: other odorants



3 Countries	CZ	SK	RO
Odorant	THT/TBM (70:30)	TBM/MES (80:20)	EM
Minimum concentration (mg/m³)	12	5	3

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Odorants: composition

ODORANTS TABLE															
Odorant	Composition %										%S	Density at 273K (kg/m3)	Vapour Pressure at 273K (mbar)	Density (kg/m^3 at 15°C)	Vapour Pressure bara at 15°C)
	THT Tetrahydro thiophene	TBM Tertiary Butyl Mercaptan	IPM Isopropyl Mercaptan	NPM Normal Propyl Mercaptan	MES Methyl Ethyl sulphide	DMS DiMethyl sulphide	EM Ethyl Mercaptan	Ethyl Acrylate	Methyl Acrylate	2-Ethyl-3-Methylpyrazin					
Formula	C_4H_8S	$C_4H_{10}S$	C_3H_8S	C_3H_8S	C_3H_8S	C_2H_6S	C_2H_6S	$C_5H_8O_2$	$C_4H_6O_2$	$C_7H_{10}N_2$					
Molecular weight	88,2	90,2	76,2	76,2	76,2	62,1	62,1	100,1	86,1	122,2					
Sulphur Free								66%	32%	2%	0,0%				
THT + EA (Ethyl Acrylate)	12%							88%			4,4%	950	11		
THT + TBM	70%	30%									36,1%			893,1	0,084
THT	100%										36,4%	1016	5,8	1002,8	0,014
TBM + IPM + NPM		76%	16%	8%							37,1%	825	82	810,8	0,17
TBM + MES		80%			20%						36,9%	828	71		
TBM + DMS (UK+IE)		80%				20%					38,8%	830	114	814,4	0,23
TBM + DMS (CZ)		65%				35%					41,2%	837	140		
EM							100%				51,6%	861	246	844,3	0,474

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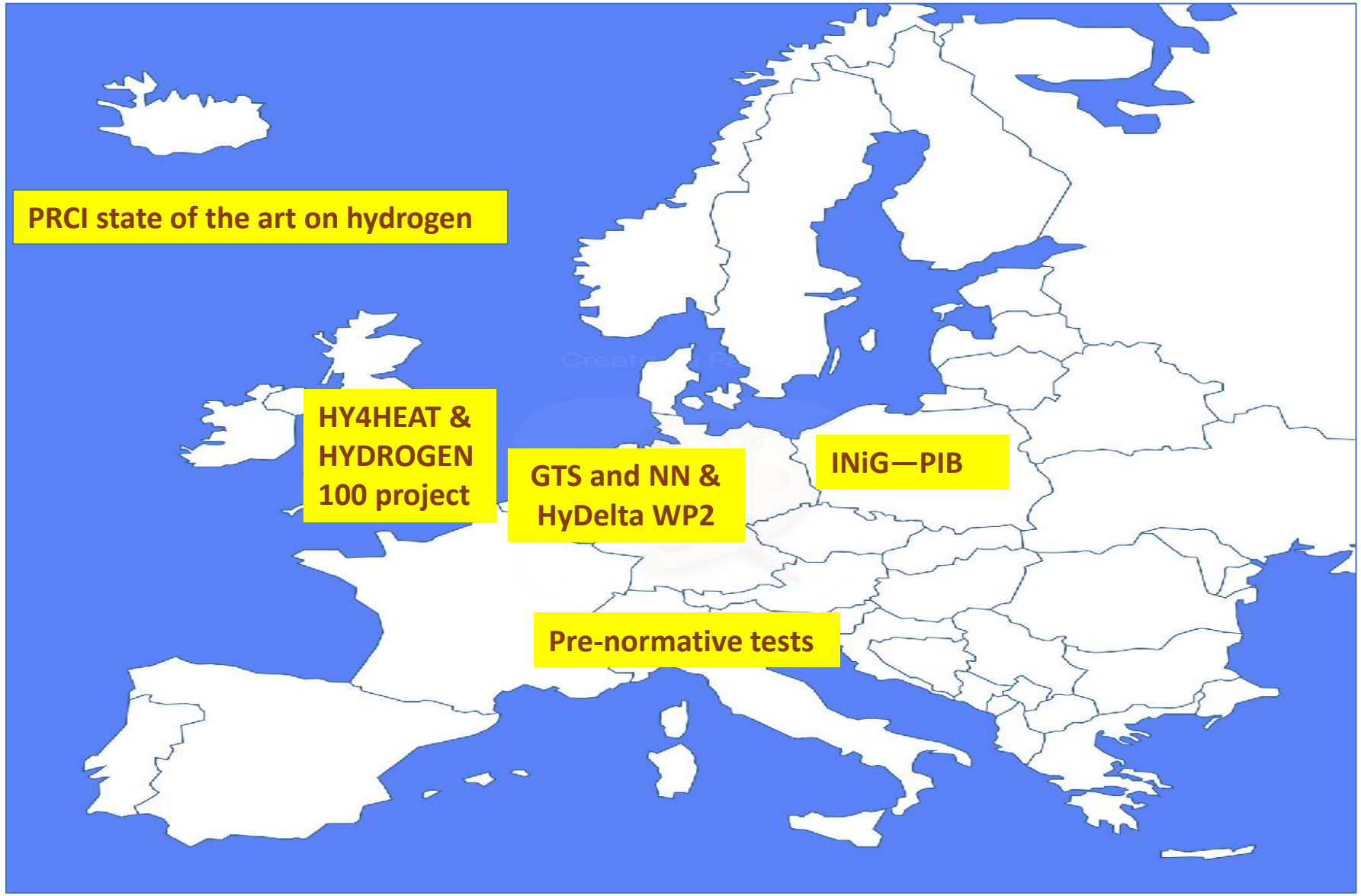
Biomethane odorisation

- Usually, the **same requirements as for natural gas** are applied for biomethane.
- Italy and The Netherlands have **specific tests**, to prove that biomethane can be odorized with the same odorants and the same concentrations of natural gas; these tests are based on olfactive trials.
- A study on some **interferences in biomethane** was presented in 2019, at the Egatec conference in Groningen.

Hydrogen blends odorisation: experimental tests



- GTS and NN - The Netherlands
- HY4HEAT - UK
- PRCI state of the art on hydrogen - USA
- HYDROGEN 100 project – UK.
- INiG—PIB - Poland
- HyDelta WP2 - The Netherlands
- Pre-normative tests - Italy

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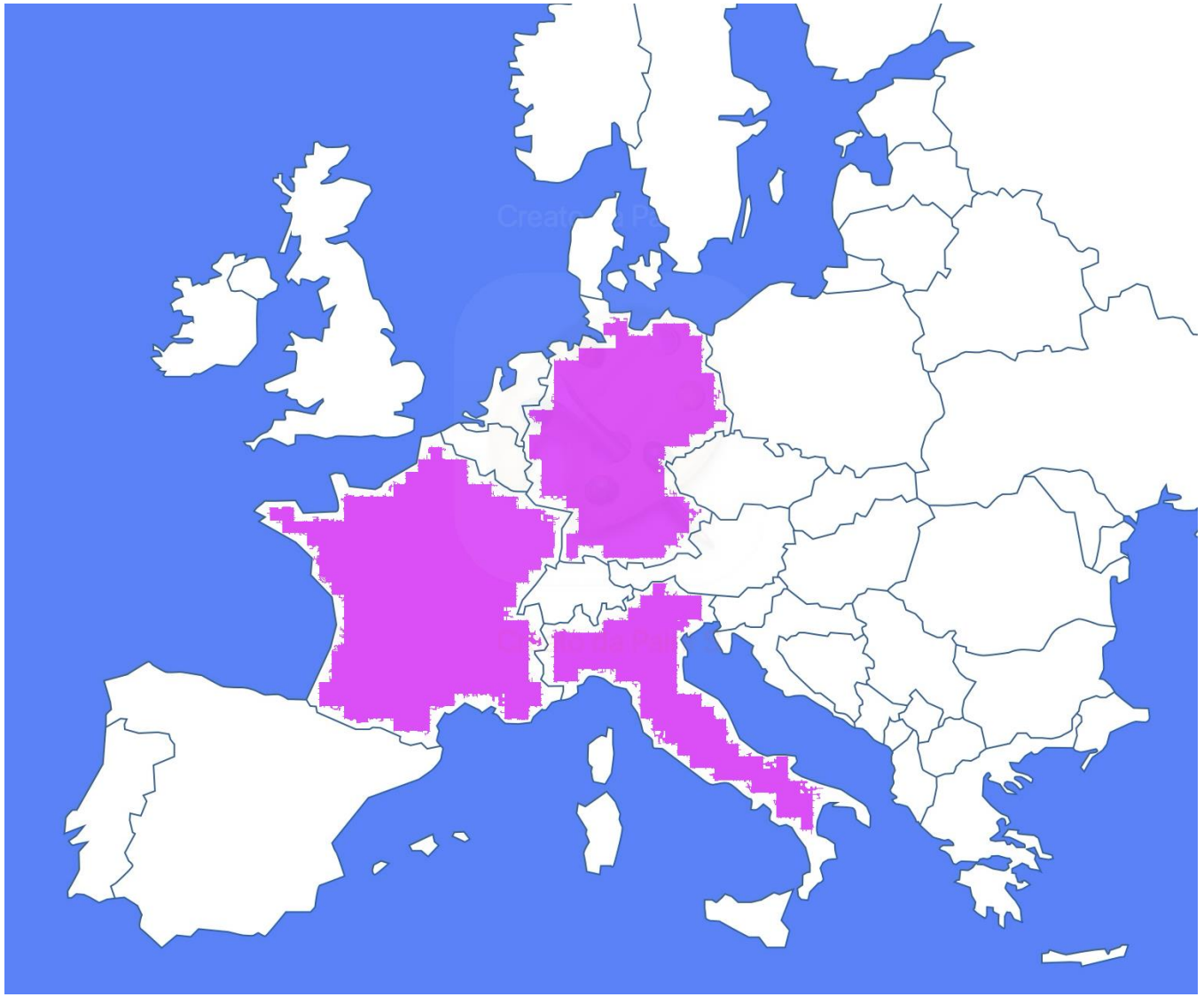
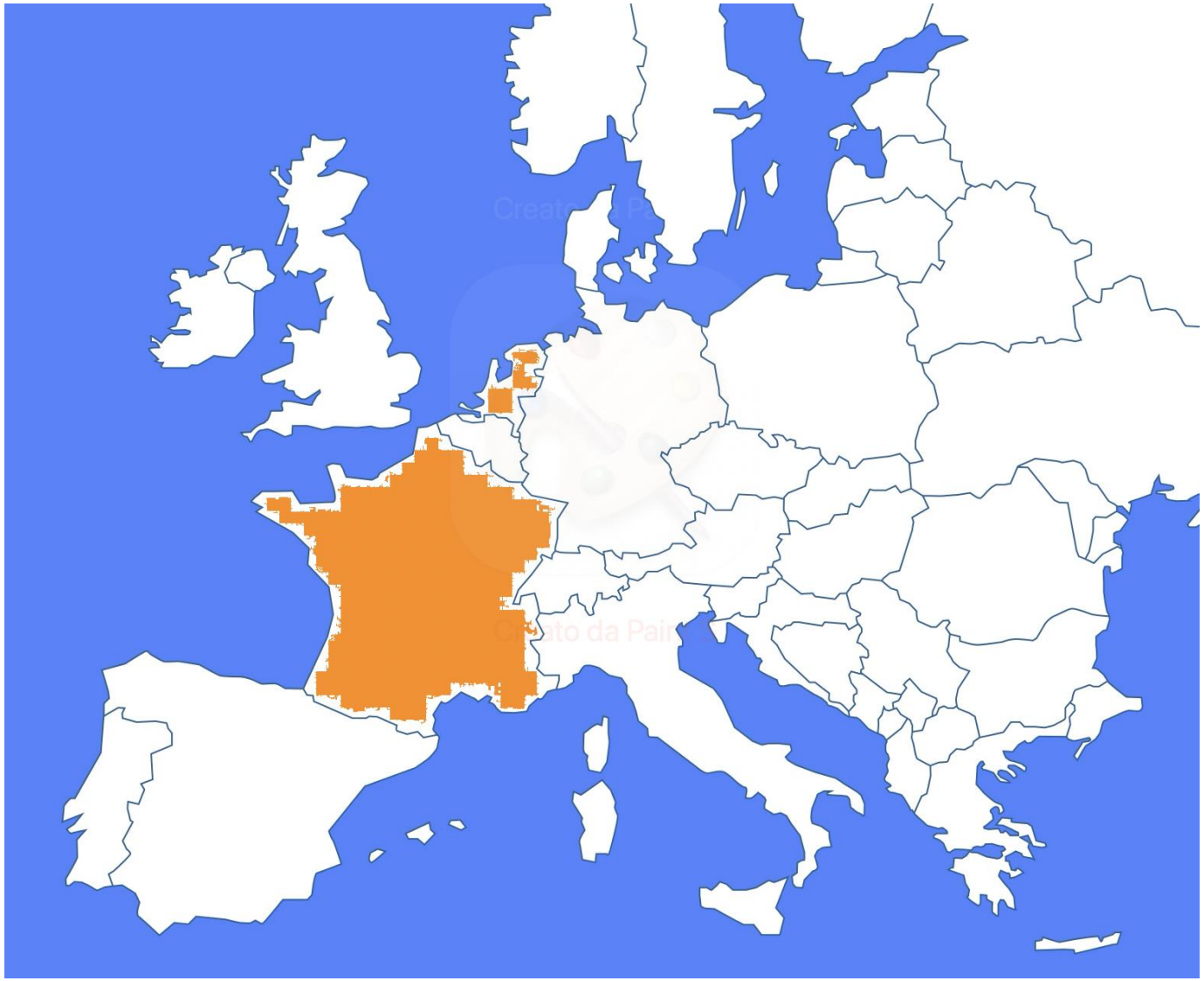
Hydrogen blends odorisation: field tests with Hydrogen injection into natural gas at Maximum Operating Pressure (MOP) ≤ 16 bar



- Tests from France, Germany, Italy

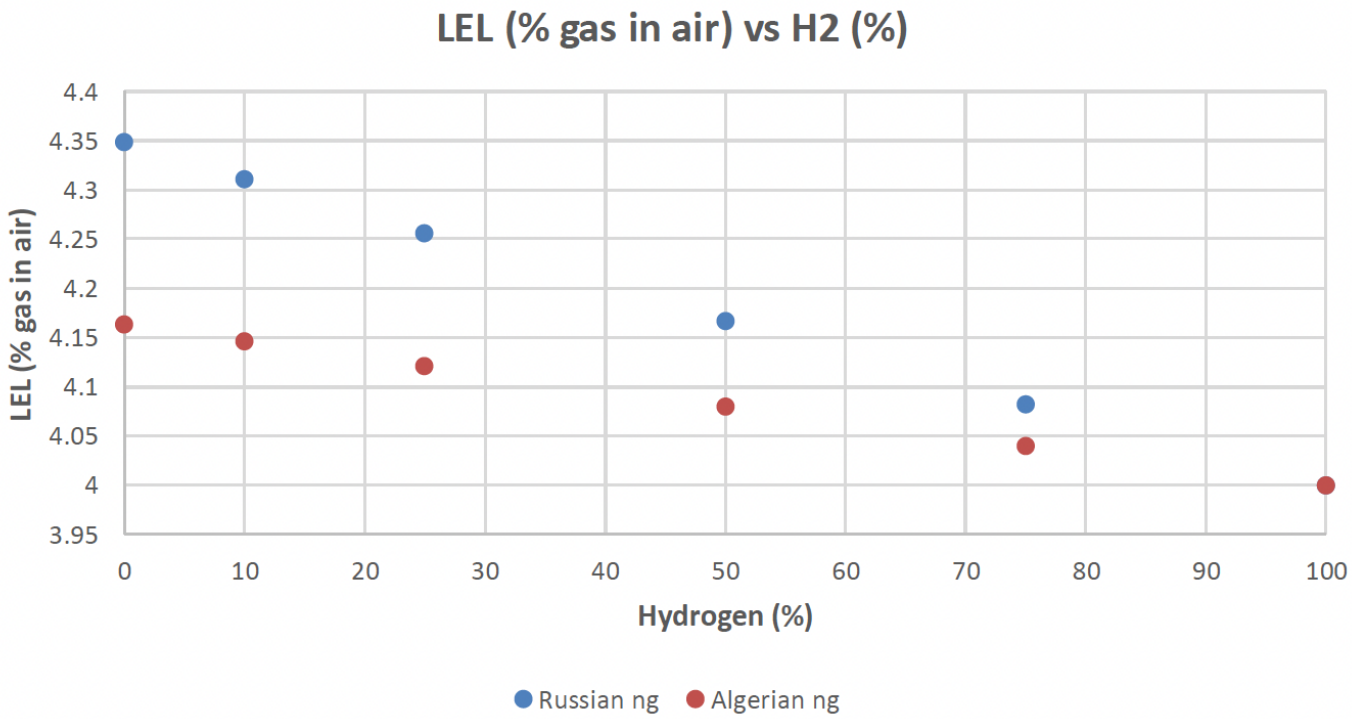
Hydrogen blends odorisation: field tests with Hydrogen injection into natural gas at Maximum Operating Pressure (MOP) > 16 bar



- Tests from France, The Netherlands

Hydrogen blends odorisation

- Information has been collected about:
  - *Possible **chemical reactions** between hydrogen and odorants*
  - ***Physical effect** of hydrogen addition in natural gas: due to density and vapour pressure, lower Explosion Limits (LEL) of H_2–NG mixtures*
  - ***Odorant masking** by hydrogen in H2–NG mixtures*
  - ***Measurement of odorant** in H_2–NG mixtures*



Hydrogen blends odorisation: considerations

Up to **20% of hydrogen** in blends with natural gas can be considered safe for traditional odorisation processes:

No evidence of problems in odorisation after addition of hydrogen to natural gas were found yet, although experiences are small, up to now. The available olfactory results show that the odorisation of natural gas - hydrogen mixtures could be performed with the same odorants and concentrations as for natural gas.

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Hydrogen blends odorisation: more considerations

Available data is usually referred to the **conditions of the distribution grids**: it could be not easy to extend the information to higher pressurized transmission grids (when odorised).

New data will be welcomed on the following topics:

- Possible effects on odorisation due to the actual condition of the distribution and transmission grids.
- Possible chemical reaction between hydrogen and odorant at high pressure condition.
- Influences of possible impurities from hydrogen production.

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Pure Hydrogen odorisation: considerations

Pilot projects demonstrate that odorisation of blends up to **pure hydrogen** with natural gas odorants give promising results, but more evidence is needed, i.e. taking into account the differences in flow speed of the pure hydrogen.

In the case of distribution of pure hydrogen, some uses can be more widespread, for instance fuel cells, and due to the high purity hydrogen that is needed for this kind of usage, the presence of the **odorants may have a negative effect**.

Proposed solutions:

- Removal by filtration of the sulfur (and/or other poisoning agents) for the sensitive users.
- Use of sulfur free odorants, already available or under development, to be tested for the effectiveness in avoiding the issues with the final utilization by the customers.

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Available standards on odorisation

- **ISO TC193 WG5** is well active, producing:
  - ISO/TS 16922 “Natural gas – Odorization”.
  - ISO 13734 “Natural gas – Organic components used as odorant – Requirements and test methods”.
  - ISO/DTS 18222 “Natural gas — Correlation between odorant concentration in air and odour intensity”.
  - ISO/DTR 5268 “Natural gas — Odorants and Odor character”.
- At a **CEN** level no standards were produced, but there was the adoption of the EN ISO 13734 standard.
- At a **national level** several standards are published.

Reports (https://www.marcogaz.org/technical-work/infrastructure/odorisation/)

Natural gas odorisation practices in Europe

20.12.2023

PUBLICATIONS

Odorisation of natural gas/hydrogen mixtures and pure hydrogen

20.12.2023

PUBLICATIONS

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Technical Association of the European Gas Industry

Thank you!

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Metrology of odorants

Adriaan van der Veen

Chief Scientist at VSL Dutch Metrology Institute

VSL

National Metrology Institute

Metrology for odorisation

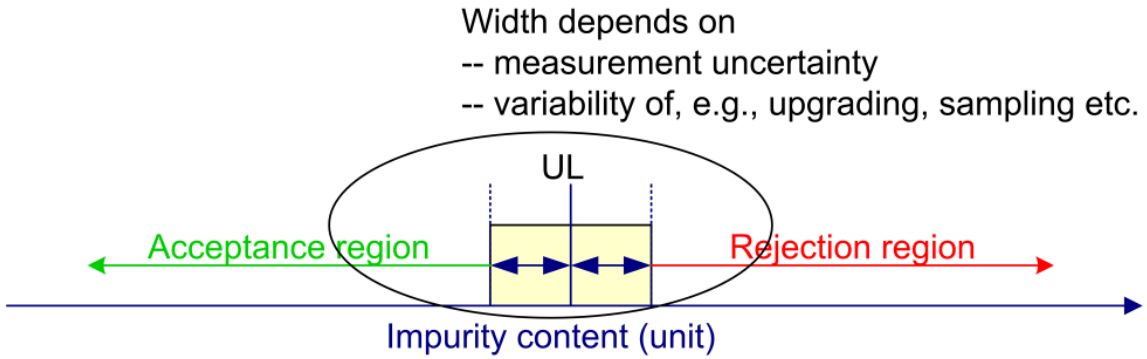
Adriaan M H van der Veen

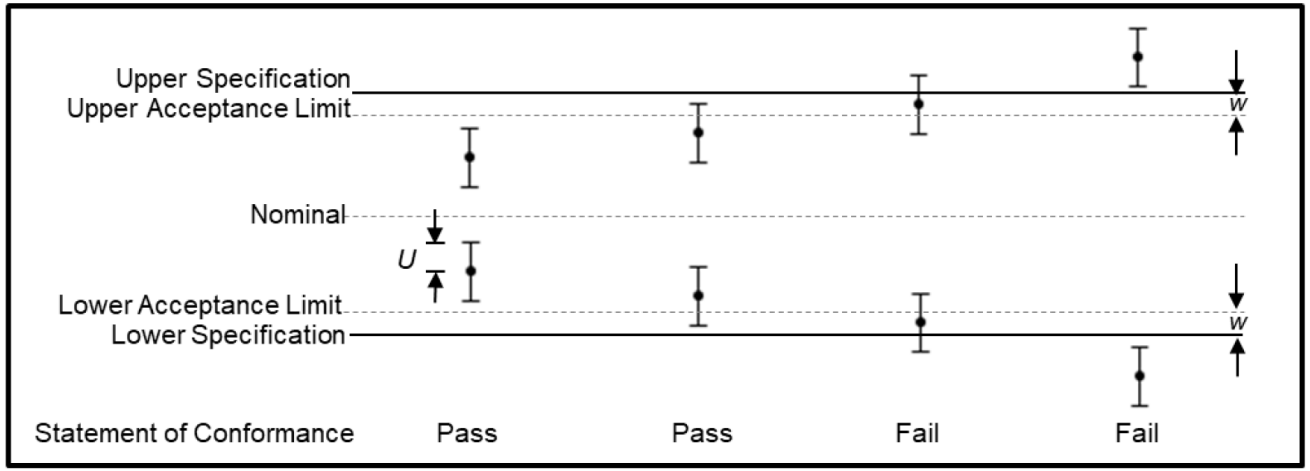
MARCOGAZ TechForum

30 May 2024

Why metrology?

- Odorisation of natural gas and related gases is regulated
- To assess compliance with regulations, the concentration measurement shall be metrologically traceable to the SI (International System of Units)
- Thereby, the result can be traced back to the SI unit
- For industry and laboratories, traceability is achieved by calibration of instruments
- For this calibration, a calibration gas mixture is needed with appropriate metrological traceability



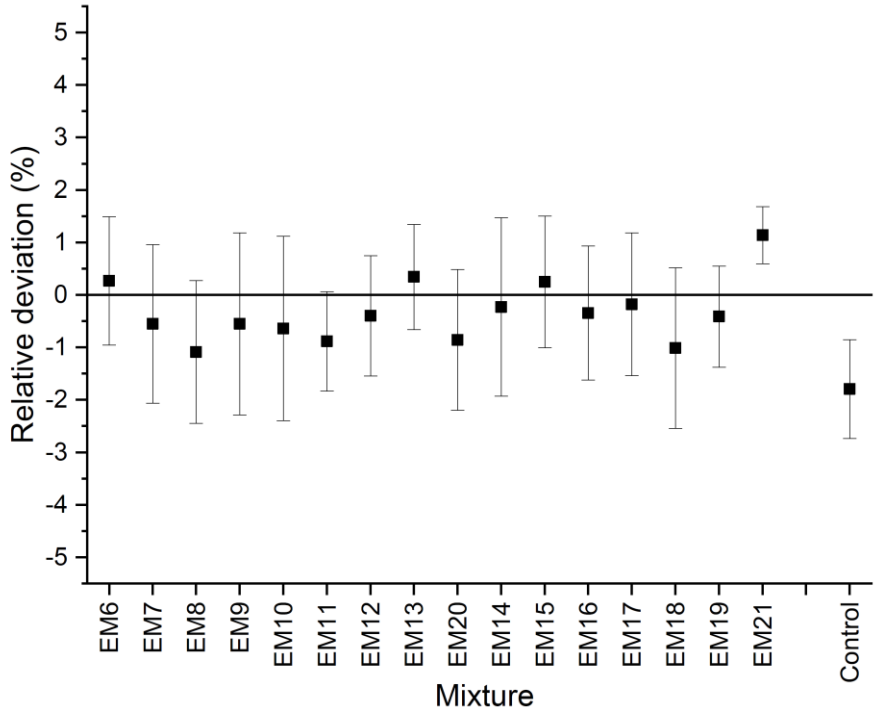


U = 95% expanded measurement uncertainty [ILAC G8:2019]

Sulfurous odorants

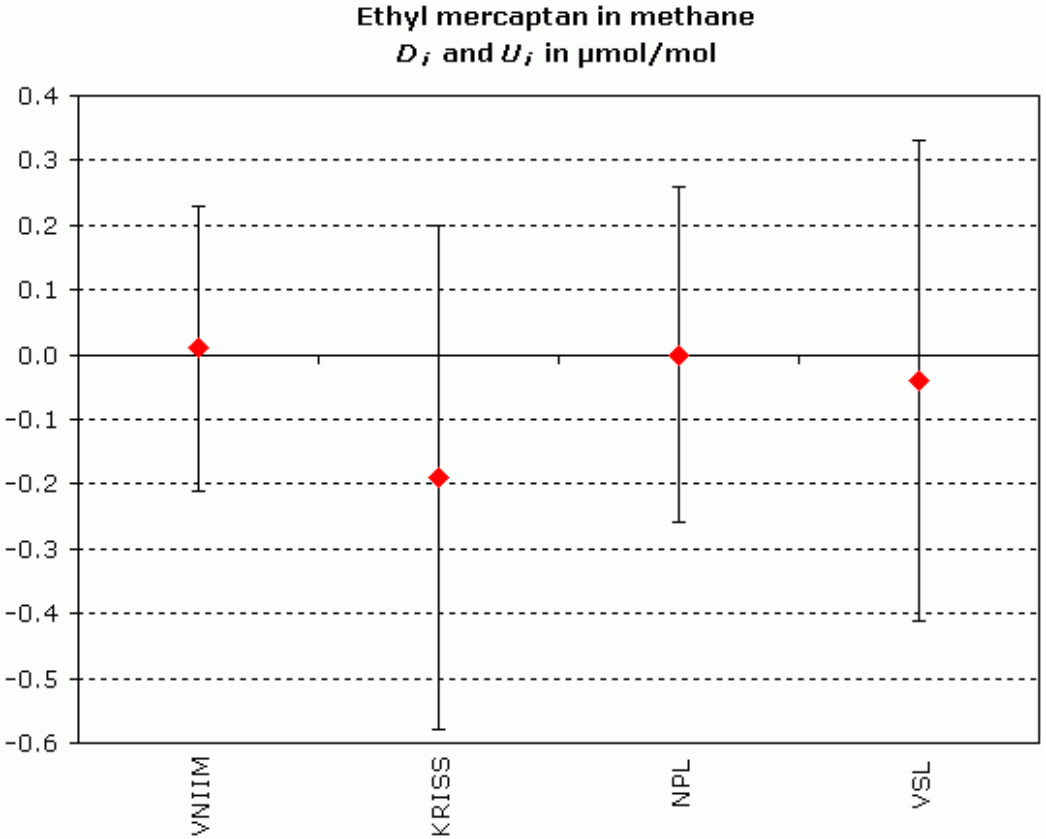
- Standards and calibration gas mixtures prepared by static gravimetry (ISO 6142-1)
- Purity analysis of all materials used
- Compounds introduced as vapour (H_2S, COS, …) or liquid (EtSH, THT, …) in the cylinder
- Analysis needed to assess consistency
- Analysis methods used based on GC/SCD, GS/MS, GC/FID, …

Compound	Formula	x	$u(x)$
Hydrogen sulfide	H_2S	0.999914	0.000005
Carbonyl sulfide	COS	0.98781	0.00278
Methyl mercaptan	CH_3SH	0.99920	0.00010
Ethyl mercaptan	C_2H_5SH	0.99767	0.00020
Dimethyl sulfide	$(CH_3)_2S$	0.99839	0.00010
Dimethyl disulfide	$(CH_3)_2S_2$	0.99619	0.00034
Diethyl disulfide	$(C_2H_5)_2S$	0.99909	0.00010
Tetrahydrothiophene	C_4H_8S	0.99307	0.00015



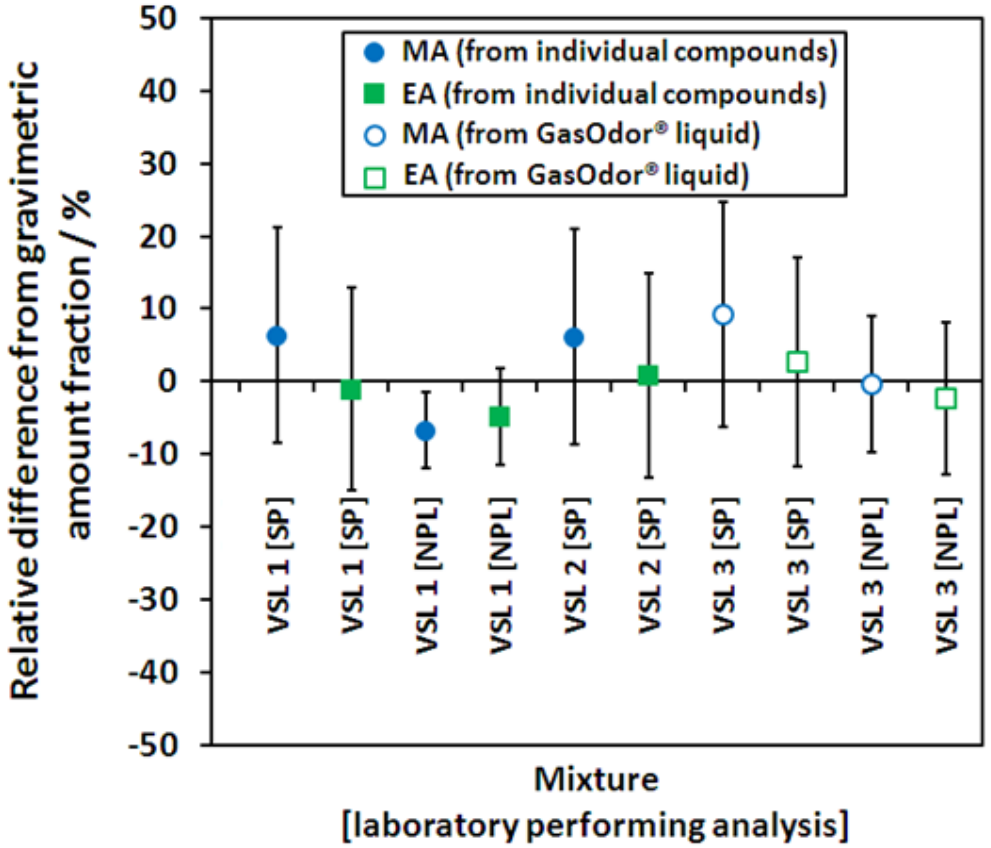
Equivalence of measurement standards

- At the level of national metrology institutes, assessed in key comparisons
- At the level of industry, assessed in proficiency testing
- Results of key comparisons are published
- Acceptance of NMI certificates regulated in CIPM-MRA
- Acceptance of certificates from industry through ILAC-MRA
- Prerequisite: conformity with ISO/IEC 17025



Sulfur-free odorants

- Methyl- and ethylacrylate blend
- Standards prepared in methane using ISO 6142-1
- Analysis using GC/FID or GC/MS
- Equivalence assessed between VSL, NPL and RISE (then SP)
- Work pivotal for
  - providing standards to the industry
  - Standardisation of an analytical method



Hydrogen and hydrogen-enriched natural gas

- Stability of odorising compounds
- Looks no different for several sulfurous compounds and acrylates
- Seems to be different for 2-hexyn
- Gas matrix may influence performance analytical method
- For sulfurous odorants, deviations up to 1.5 % observed

Concluding remarks

- Dealing with metrological aspects essential for implementing regulations with respect to odorisation
- National metrology institutes in Europe support the specialty gas industry and the gas industry by providing calibration gas mixtures
- NMIs collaborate in standardisation (e.g., ISO/TC193 Natural gas)
  - in specifying analytical methods,
  - providing tools for instrument calibration
  - Providing proficiency testing
- Calibration gas mixtures should come with a proper certificate in accordance with ISO/IEC 17025

For more information, please have a look at
https://www.vsl.nl

Questions?

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ISO Standardisation on odorisation

Amelie Louvat

Odorisation expert and R&D
Project Manager at GRTGaz

MARCOGAZ TECH FORUM ON GAS ODORIZATION

ISO standardization on Odorization

Amélie LOUVAT, GRTgaz, Convenor of the ISO TC 193 / WG5

ISO / TC 193 - Overview

Secretariat: NEN

Chairman
Adriaan van der Veen

Committee Manager
Nicolet Baas

29 participating countries

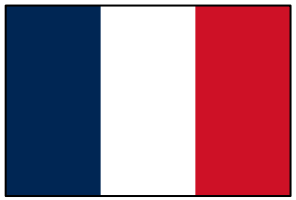
28 observating countries

8 **W**orking **G**roups

2 **S**ub-**C**ommittees:
- Analysis of Natural Gas
- Upstream area

ISO TC 193 / WG 5 - Overview

Convenor
AFNOR
(Amélie Louvat)



WG Secretariat
AFNOR
(Thierry Monat)

10 participating countries

30 members

Germany, Belgium, China, South Korea, Spain, USA, France, Italy, the Netherlands, UK

ISO TC 193 / WG 5

SCOPE: topics related to odorization for natural gas, biomethane, blends with hydrogen (up to 20%)

4 international standards

3 under revision

ISO/CD TR 5268
ISO/AWI 13734
ISO/DTS 18222

1 publication

ISO/TS 16922:2022

Focus on the odorization standards

ISO/TS 16922:2022 – Natural gas odorization

→ gives the specifications and guidelines for the methods to be used in the odorization of natural gas and other methane rich gases delivered through natural gas networks to gas applications under a safety point of view.

→ specifies the principles for the odorization technique (including handling and storage of odorants) and the control of odorization of natural gas and other methane rich gases

→ also includes the Requirements and parameters for consideration when selecting an odorant

Publication in 2022

Focus on the odorization standards

ISO/AWI 13734 Natural gas — Organic components used as odorants — Requirements and test

→ specifies requirements and test methods for organic compounds suitable for odorization of fuel gases hereafter referred to as odorants

→ includes Requirements for an effective odorant

→ Annexes provide information on properties of odorants

Call for experts done in 2023

Revision of the 2013 version (update of the document, include H2 blends)

Draft will be finalized during the next meeting and motion for a ballot will be decided

Focus on the odorization standards

ISO/CD TR 5268 - Odorants and Odour character

→ collects and gives information regarding the determination of fuel gases odour character and related odorants.

The olfactory methods described can be utilized as a basis for the judgment of the compliance of the odour character of a gas or odorant sample.

Ballot to be launched in 2024 (final work on the figures by the ISO)

Focus on the odorization standards

ISO/DTS 18222 - Natural gas — Olfactory method for the evaluation of odour intensity

→ describes how to establish the correlation between odorant concentration in air and odour intensity, usually presented in the form of odour intensity curves, following the odour intensity scale

→ does not fix a required level of odour intensity in the natural gas: this prescription is specified by local/national regulation

→ contains the training scale for smellers with a possibility to compare results obtained from different ways

3rd ballot to be launched in 2024
(technical errors found in the last ballot)

Future of odorization standardization

→ Inputs for the revision of the standard on the vocabulary (ISO 14532)

→ Discussion on the odorization of « pure » hydrogen (Pure hydrogen is in the scope of ISO TC197)

Thank you for your attention. Any questions?

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Panel discussion and Q&A Session are available in the full video of the webinar, published on the Communications Hub/Videos section of our website