


Odorisation Interferences in Biomethane

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Summary

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- **Biomethane Odorisation in the EU (Marcogaz inquiry).**

- **Results from an Italian project (developed by Hera and Italgas Reti companies) to study the effects of some interfering substances on THT and TBM based odorants.**

Marcogaz inquiry on biomethane odorisation

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The Marcogaz Odorisation Working Group collects data on Odorisation in EU; a section of the "Natural Gas Odorisation practices in Europe" tables (available on the Marcogaz web site) deals on biomethane injections and odorisation.

Marcogaz inquiry on biomethane odorisation (updated to end 2018)

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Country	Number of biomethane injections on Transport (red if odorised)	Number of biomethane injections on Distribution (red if odorised)	Specific requirement for biomethane odorisation?
DE	~20	**~185**	No
ES	**1**	-	No
FR	**10**	**60**	No
IT	3	**3**	Before injection, both on TSO and DSO grids, biomethane must be proven to be odorisable, giving, after odorant addition, the same warning as odorized natural gas. Only when injected in DSO grid it must be odorised. Odorants and odorant concentrations are the same as for natural gas.
NL	**1**	**~40**	Before injection, both on odorized TSO (< 40 bar) and DSO grids, biomethane must be proven to be odorized giving the same warning as odorized natural gas. Odorants and odorant concentrations are the same as for natural gas
UK	**17** (local Transmission distribution, not connected to National Transmission System)	**77**	No

Marcogaz inquiry on biomethane odorisation

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- **The Netherlands and Italy foresee additional requirements for odorisation of biomethane, by means of periodical smell tests, with the aim to exclude possible interferences on odorisation.**

- **Anyway, biomethane composition can vary significantly and smell tests couldn't always be performed in time to avoid that some interfering odorous substances be injected into the gas grid, with possible odorisation problems.**

Hera/Italgas Reti project - Description

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- **A collaboration between the two companies *Hera* (multiutility leader in environmental, water and energy services in Italy) and *Italgas Reti* (the major DSO in Italy) launched a project (independent from Marcogaz, which doesn't perform R&D) with the aim to investigate the influence on odorisation of some compounds that can be found in biomethane.**

- **The project was performed from 2016 to 2018 by two laboratories: Italgas Reti and LOD.**

Hera/Italgas Reti project - Description

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- **This study is directed to help in performing a proper odorisation, which is the process that permits to warn gas leaks before they become dangerous.**
- **Knowing the limit concentrations of some odorous substances allows to perform instrumental checks finalized to reduce possible interferences on odorisation before a problem can be created.**
- **The substances to be tested were chosen among the known components of the biogas/biomethane produced in Italy at that time.**

Hera/Italgas Reti project – Method Description

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- **Method: derived from the one described in UNI 7133, using pure methane as matrix instead of actual samples of biomethane; the interfering substances and the odorants were added by evaporation on hot plate inside the testing room.**
- **Blank tests (without addition of odorant) were performed too, to prove the correctness of the results.**

Hera/Italgas Reti project – Tests Description

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- **Evaluation of the odour intensity of the sample added with the interfering substance and in presence of the odorant: the compliance of the result is reached if the value, to be summed to the uncertainty value, is at least equal to 2 olfactory degrees of the Sales scale.**

- **Evaluation of the odour character: at least 85% of the rhynologists must recognize the odour of the sample as the same of the odorised natural gas.**

Hera/Italgas Reti project – Olfactory laboratories

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- ***Italgas Reti Laboratory***: **located in Asti (Italy), works on olfactory measurements of combustible gases from the 50's; here is where Mr. Sales defined his Odour Intensity Scale.**

- ***LOD***: **Laboratory of Dynamic Olfactometry, specialized in measuring odours, is a spin-off of the University of Udine (Italy).**

Hera/Italgas Reti project – Italgas Reti Olfactory Lab

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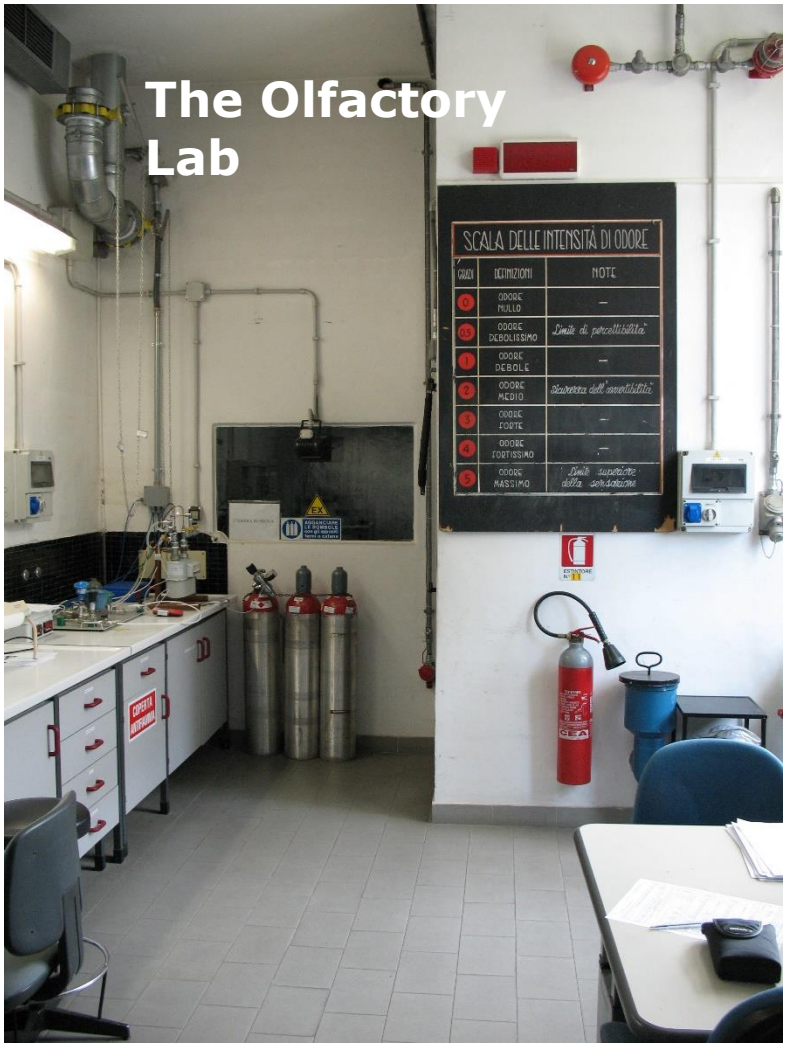

Hera/Italgas Reti project – Odorants chosen

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- **Odorants: THT and TBM (that is the major component – around 80% - of several odorants).**
- **Odorants concentrations:**
  - **THT: 20 and 32 mg/m³ (the second is the minimum concentration requested by the Italian standard).**
  - **TBM: 10 mg/m³ (near to the minimum concentration requested by the Italian standard for the mercaptan's mixture odorant – 9,3 mg/m³ as TBM).**

Hera/Italgas Reti project - Results

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- **The results were formerly presented (Italian language) during the workshop «Il biometano: una nuova opportunità di sviluppo in un contesto di economia circolare: l'esperienza del Gruppo HERA» (Bologna (Italy)– 21° September 2018).**
- **In the following slides a summary of the results is presented (green values are compliant to UNI 7133, red values are not compliant).**

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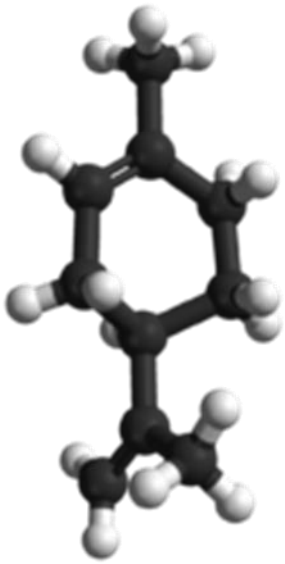
- **LIMONENE**



It is a cyclic monoterpene, and it is the major component in the oil of citrus fruit peels. It was tested at the following concentrations:

Concentrations of Limonene	THT 32 mg/m³	THT 20 mg/m³	TBM 10 mg/m³
17,3 mg/m³ (3 ppm)	X	X	X
34,6 mg/m³ (6 ppm)	X		
51,8 mg/m³ (9 ppm)	X	X	X
86,4 mg/m³ (15 ppm)	X	X	X
103,7 mg/m³ (18 ppm)	X	X	X
120,9 mg/m³ (21 ppm)	X		
172,8 mg/m³ (30 ppm)		X	X

In The Netherlands, in 2010 an incident occurred at a biomethane injection plant; litres of oil substance (mainly composed of Limonene) were found in the grid: the gas smelled like oranges, because of the digestion of tons of waste oranges.

Hera/Italgas Reti project - Results

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- **LIMONENE: effect on odour intensity**

Concentrations of Limonene	THT 32 mg/m³	THT 20 mg/m³	TBM 10 mg/m³
17,3 mg/m³ (3 ppm)	1,9 ± 0,2	1,5 ± 0,2	2,2 ± 0,2
34,6 mg/m³ (6 ppm)	1,9 ± 0,2		
51,8 mg/m³ (9 ppm)	1,9 ± 0,2	1,6 ± 0,3	2,1 ± 0,3
86,4 mg/m³ (15 ppm)	1,9 ± 0,3	1,4 ± 0,4	1,9 ± 0,2
103,7 mg/m³ (18 ppm)	1,8 ± 0,3	1,7 ± 0,4	1,9 ± 0,3
120,9 mg/m³ (21 ppm)	1,7 ± 0,3		
172,8 mg/m³ (30 ppm)		1,7 ± 0,1	2,0 ± 0,2

With 10 mg/m³ TBM and with 32 mg/m³ THT, the odour intensity wasn't affected by the presence of Limonene, inside the tested range of concentrations.
At the THT concentration of 20 mg/m³ there was an effect at all the tested concentrations of Limonene, probably related to modification in the odour character, which could weaken the odour intensity, too.

Hera/Italgas Reti project - Results

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- **LIMONENE: effect on odour character**

Concentrations of Limonene	THT 32 mg/m³	THT 20 mg/m³	TBM 10 mg/m³
17,3 mg/m³ (3 ppm)	96%	89%	89%
34,6 mg/m³ (6 ppm)	92%		
51,8 mg/m³ (9 ppm)	83%	72%	72%
86,4 mg/m³ (15 ppm)	92%	67%	78%
103,7 mg/m³ (18 ppm)	73%	56%	75%
120,9 mg/m³ (21 ppm)	72%		
172,8 mg/m³ (30 ppm)		28%	50%

Using linear interpolation were evaluated the limit values for interference on odour character :

- **For 32 mg/m³ of THT the limit is 65 mg/m³ of Limonene (about 11,3 ppm);**
- **For 20 mg/m³ of THT the limit is 25 mg/m³ of Limonene (about 4,3 ppm);**
- **For 10 mg/m³ of TBM a significant interference is obtained already at about 22 mg/m³ (3,8 ppm).**

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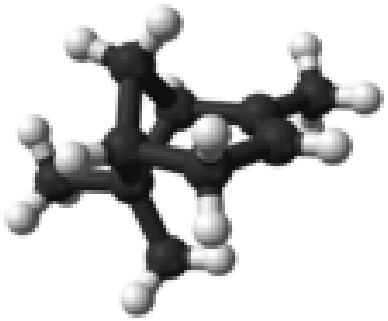
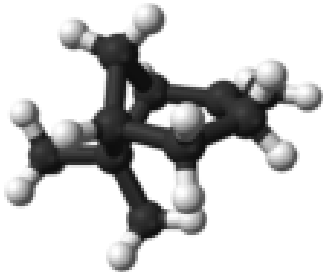
- **PINENE**





It is a bicyclic monoterpene, with two structural isomers found in nature; both forms are important constituents of pine resin. It was tested at the following concentrations:

Concentrations of Pinene	THT 32 mg/m³	THT 20 mg/m³	TBM 10 mg/m³
17,3 mg/m³ (3 ppm)	X		
34,6 mg/m³ (6 ppm)	X		
51,8 mg/m³ (9 ppm)	X		
86,4 mg/m³ (15 ppm)	X		
120,9 mg/m³ (21 ppm)	X		

Hera/Italgas Reti project - Results

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- **PINENE: effect on odour intensity**

Concentrations of Pinene	THT 32 mg/m³	THT 20 mg/m³	TBM 10 mg/m³
17,3 mg/m³ (3 ppm)	2,0 ± 0,2		
34,6 mg/m³ (6 ppm)	1,9 ± 0,2		
51,8 mg/m³ (9 ppm)	1,8 ± 0,2		
86,4 mg/m³ (15 ppm)	1,9 ± 0,4		
120,9 mg/m³ (21 ppm)	1,9 ± 0,3		

At a concentration of 32 mg/m³ of THT odour intensity seems not being affected by the presence of Pinene, inside the tested range of concentrations.

Hera/Italgas Reti project - Results

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- **PINENE: effect on odour character**

Concentrations of Pinene	THT 32 mg/m³	THT 20 mg/m³	TBM 10 mg/m³
17,3 mg/m³ (3 ppm)	92%		
34,6 mg/m³ (6 ppm)	100%		
51,8 mg/m³ (9 ppm)	100%		
86,4 mg/m³ (15 ppm)	92%		
120,9 mg/m³ (21 ppm)	92%		

With the tested concentrations of Pinene, in presence of a concentration of 32 mg/m³ of THT as gas odorant, no effect on odour character was found.

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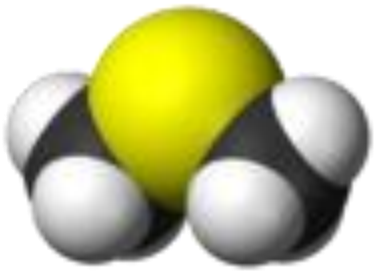
- **DMS (DiMethyl Sulphide)**



Also known as methyl thiomethane is an organosulfur compound with the formula $(CH_3)_2S$. Has a characteristic disagreeable odour and it is a component of the smell produced from cooking of certain vegetables, like maize, cabbage, beetroot and seafoods. It was tested at the following concentrations:

Concentrations of DMS	THT 32 mg/m³	THT 20 mg/m³	TBM 10 mg/m³
7,9 mg/m³ (3 ppm)		X	X
15,8 mg/m³ (6 ppm)		X	X
26,3 mg/m³ (10 ppm)		X	X
52,5 mg/m³ (20 ppm)		X	X

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- **DMS: effect on odour intensity**

Concentrations of DMS	THT 32 mg/m³	THT 20 mg/m³	TBM 10 mg/m³
7,9 mg/m³ (3 ppm)		1,7 ± 0,3	1,9 ± 0,2
15,8 mg/m³ (6 ppm)		1,8 ± 0,3	2,0 ± 0,3
26,3 mg/m³ (10 ppm)		1,7 ± 0,3	2,2 ± 0,5
52,5 mg/m³ (20 ppm)		1,9 ± 0,3	2,1 ± 0,3

THT: odour intensity seems not being strongly affected by the presence of DMS, inside the tested range of concentrations.

TBM: the results confirms what is known from literature: mixtures of mercaptans and sulphides produce a synergistic effect that can enhance the olfactory sensation.

Hera/Italgas Reti project - Results

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- **DMS: effect on odour character**

Concentrations of DMS	THT 32 mg/m³	THT 20 mg/m³	TBM 10 mg/m³
7,9 mg/m³ (3 ppm)		94%	94%
15,8 mg/m³ (6 ppm)		83%	83%
26,3 mg/m³ (10 ppm)		74%	62%
52,5 mg/m³ (20 ppm)		61%	100%

THT: when gas is odorized with 20 mg/m³ of THT, linear interpolation gives a concentration limit of 14 mg/m³ (5,3 ppm) for DMS. Previous tests, carried out to update UNI 7133, established that 32 mg/m³ THT guarantee the correct odorisation even in presence of a concentration of DMS up to 60 mg/m³ (about 23 ppm).

TBM: interferences were found at average concentrations; mixtures of TBM and DMS are used as odorants for gas odorisation in Europe, so interferences were unexpected. More tests would be useful.

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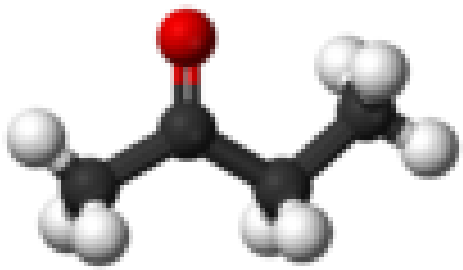
- **METHYL ETHYL KETONE (MEK)**



Also known as Butanone, is an organic compound with the formula $CH_3C(O)CH_2CH_3$. It has a sharp, sweet odour reminiscent of butterscotch and acetone. It was tested at the following concentrations:

Concentrations of MEK	THT 32 mg/m³	THT 20 mg/m³	TBM 10 mg/m³
9,1 mg/m³ (3 ppm)	X		
18,3 mg/m³ (6 ppm)	X		
27,4 mg/m³ (9 ppm)	X		
45,7 mg/m³ (15 ppm)		X	X
54,9 mg/m³ (18 ppm)	X	X	X
64,0 mg/m³ (21 ppm)		X	X
82,3 mg/m³ (27 ppm)	X	X	X

Hera/Italgas Reti project - Results

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- **MEK: effect on odour intensity**

Concentrations of MEK	THT 32 mg/m³	THT 20 mg/m³	TBM 10 mg/m³
9,1 mg/m³ (3 ppm)	1,9 ± 0,2		
18,3 mg/m³ (6 ppm)	1,9 ± 0,2		
27,4 mg/m³ (9 ppm)	2,0 ± 0,2		
45,7 mg/m³ (15 ppm)		1,8 ± 0,4	1,9 ± 0,2
54,9 mg/m³ (18 ppm)	1,6 ± 0,2	1,7 ± 0,4	2,0 ± 0,4
64,0 mg/m³ (21 ppm)		1,9 ± 0,3	1,8 ± 0,3
82,3 mg/m³ (27 ppm)	1,7 ± 0,4	1,8 ± 0,2	1,8 ± 0,3

The THT results on odour intensity are questionable: interpolating the results at 32 mg/m³ an interference was found at about 45 mg/m³ (14,8 ppm); however, this result wasn't confirmed by the tests with 20 mg/m³ of THT, where, despite the presence of a lower odorant content, a minor interference was observed: the limit was estimated at about 94 mg/m³ (30 ppm). Further investigation could be necessary.
No significant interference with TBM.

Hera/Italgas Reti project - Results

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- **MEK: effect on odour character**

Concentrations of MEK	THT 32 mg/m³	THT 20 mg/m³	TBM 10 mg/m³
9,1 mg/m³ (3 ppm)	96%		
18,3 mg/m³ (6 ppm)	100%		
27,4 mg/m³ (9 ppm)	100%		
45,7 mg/m³ (15 ppm)		83%	78%
54,9 mg/m³ (18 ppm)	100%	94%	67%
64,0 mg/m³ (21 ppm)		86%	78%
82,3 mg/m³ (27 ppm)	100%	67%	89%

No interferences were found at the concentration of 32 mg/m³ of THT, while for 20 mg/m³ of THT a limit value of about 59 mg/m3 (19,4 ppm) of MEK was evaluated. At 10 mg/m³ of TBM the slope of the extrapolation line is increasing, so the interference would be positive; this behavior is unexpected: further tests should be carried out to verify this result.

Hera/Italgas Reti project - Conclusions

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Generally speaking, the interfering substances taken into account haven't had a detected strong effect on the odour intensity, although in some cases the results haven't been conclusive: Methyl Ethyl Ketone and DMS in particular have caused somewhat incoherent results, so it will be appropriate to further their study.

Limonene is confirmed to have a strong impact on odour character; this determines the necessity of limiting its concentration in biomethane injected in natural gas grids.

On the other hand, no significant impact on odour has been found, at the tested concentrations, for Pinene (which belongs to the same group of substances as limonene - the Terpenes), both for odour intensity and character.

Hera/Italgas Reti project - Conclusions

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DMS has a strong odour; the value of 14 mg/m³ as maximum concentration in natural gas odorized with THT at 20 mg/m³ is not far from what expected, to avoid changes in odour character. However, DMS mixed with TBM is used as a natural gas odorant, so in this case the results regarding odour character interferences are unexpected. More investigation is needed.

Methyl Ethyl Ketone seems not have a significant impact on odour character, at the tested concentrations, but some results must be checked.

Investigations on these aspects are of fundamental importance to ensure the safety in gas distribution and utilisation, both for customers and gas workers.

Thank you !

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