GASODOR®
S-FREE

NATURAL GAS - THE ENERGY OF THE FUTURE

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REGARDING ODORANT BEHAVIOR:
Extremely low odorant loss is among its excellent properties.

ADSORPTION AND STABILITY:
This sulfur-free odorant remains extremely stable in gas lines with very little adsorption taking place.

COMPATIBILITY BONUS:
Compatibility of GASODOR® S-FREE with a wide variety of gas line materials is excellent.

THE ADVANTAGE OF VERSATILITY:
No need for new facilities. GASODOR® S-FREE can theoretically be used in any existing odorizing systems.

AND YET ANOTHER ADVANTAGE:
The new odorant can also conceivably be used in applications such as fuel cells, which would be sensitive to sulfur.

GASODOR®
S-FREE

SAFE
ECOLOGICAL
INNOVATIVE

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History

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History

GASODOR®
S-FREE

- 1993: First meeting with E.ON Ruhrgas AG
- 1998: Patent of Gasodor® S-Free filed
- 1998: Involvement of the DVGW
- 2001: Start of field test, Philippsburg
- 2002: Certification according to DIN EN ISO 13734
- 2003: Inclusion in Technical Standard G 280 by the DVGW
- 2004: Start of field test (high pressure), Eifel/ Trier/ Bitburg
- 2015: 30% market share in Germany
  - approved and used in Austria, China, Turkey, Scandinavia,
  - Israel pilot projects in Russia, Italy and Poland

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GASODOR®
S-FREE

R&D

TARGET

SICHER
ÖKOLOGISCH
INNOVATIV

- reduction of sulphur content in odorants

=

- reduction of sulphur emission in the atmosphere
- use of natural gas in applications where the sulphur content causes technical problems so far
- excellent solubility/distribution in natural gas mains
- clear warning odour characteristic
- low minimum odorizing rate
- high stability / long shelf-life
- commercial benefit

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Product Data

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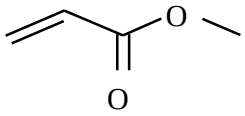
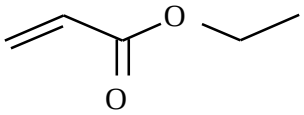
Composition

GASODOR®
S-FREE

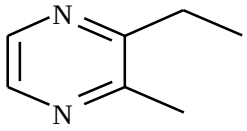
Methylacrylate



Ethylacrylate



Methylethylpyrazine-2,3



Physical-Chemical Product Data

GASODOR® S-FREE

State:	Liquid
Color:	Colorless
Odor:	Strong, Warning
Density (+25° C):	0,933 kg/l
Flash Point:	+5° C
Lower Explosion Limit:	1,6%
Upper Explosion Limit:	23,0%
Water Solubility (+20° C):	1%
Water Contamination Class:	2

Hazard Symbols:

Physical Product Data

GASODOR®
S-FREE

Melting Point:	-80° C to -110° C
Flammability Point as per DIN 51794:	395 ° C
Valor Density:	
Methylacrylate	3,00 (air = 1)
Ethylacrylate	3,45 (air = 1)
Methylethylpyrazin-2,3	4,21 (air = 1)
Relative Density of Air-Gas Mixture (20 ° C):	
Methylacrylate	1,18 (air = 1)
Ethylacrylate	1,09 (air = 1)
Methylethylpyrazin-2,3	0,987 g/ ml
Vapor Pressure (25° C):	83 hPa

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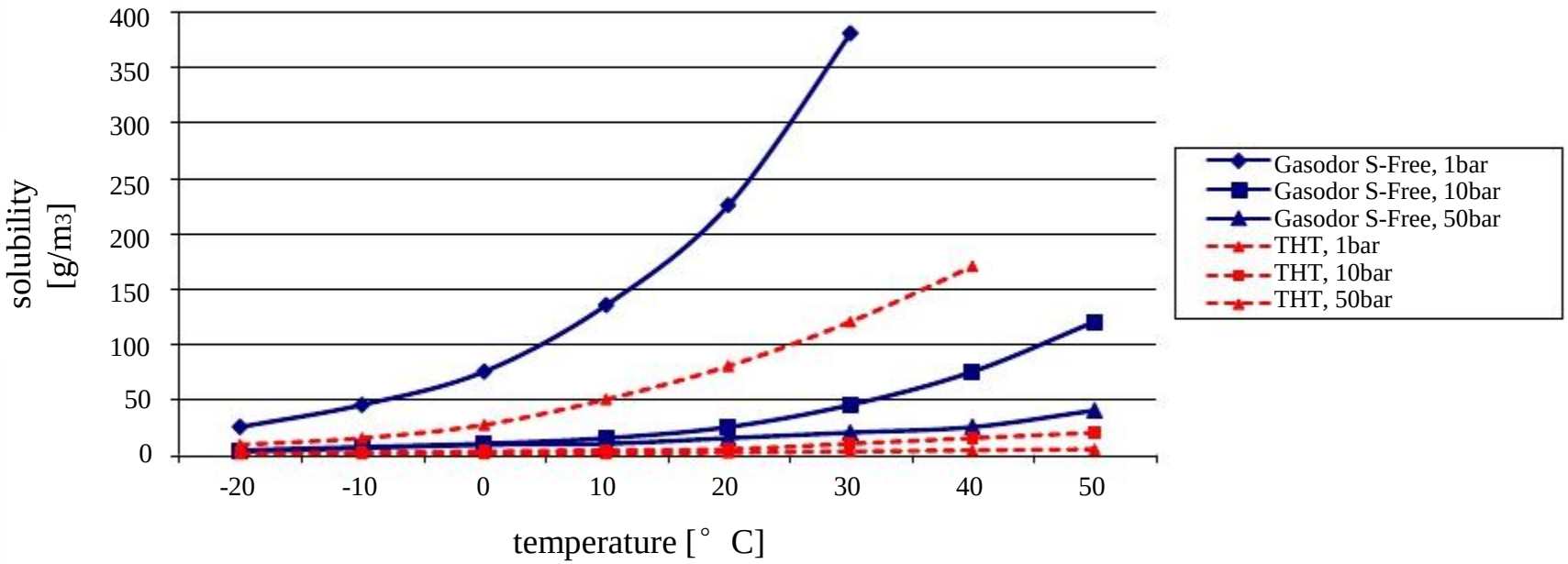
Solubility in Natural Gas



Source: Engler-Bunte-Institute of the University Karlsruhe (TH) 2002

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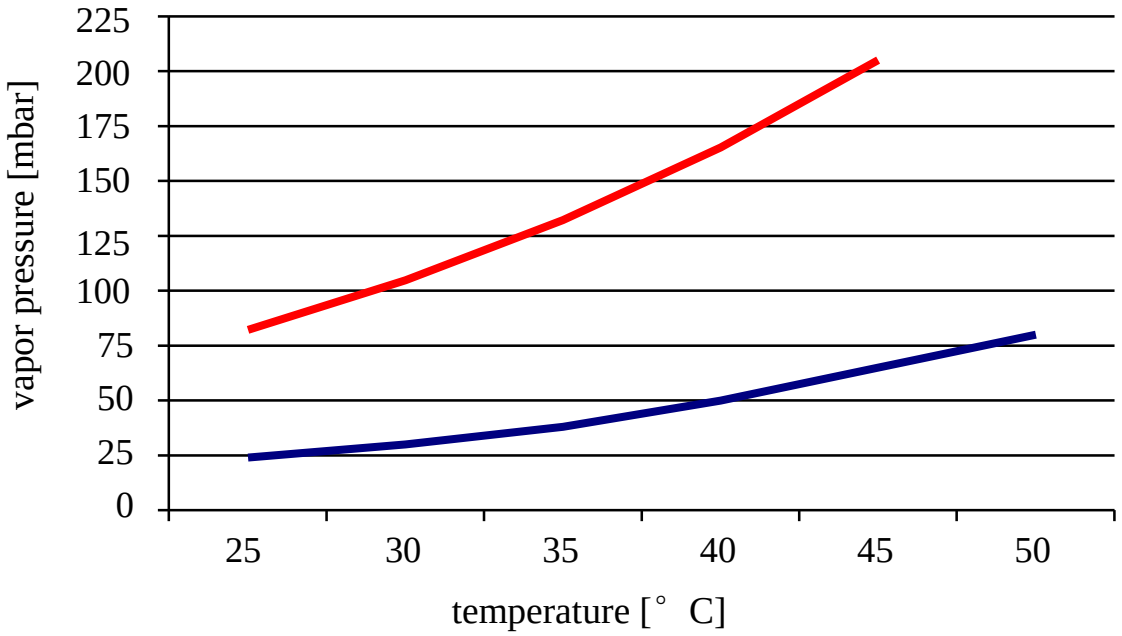
Vapor Pressure Against Temperature



Gasodor® S-Free

Tetrahydrothiophen

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Technical Excelleny

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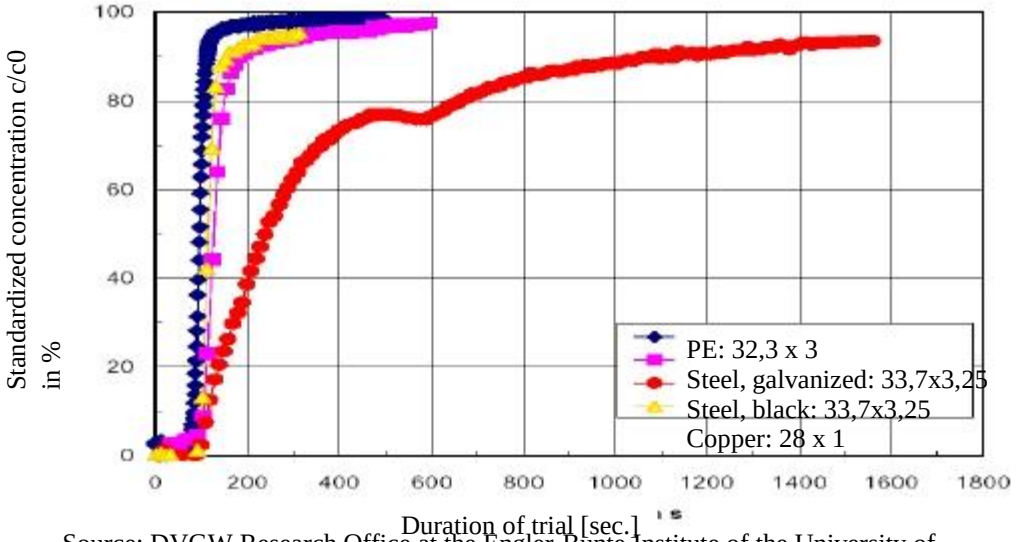
Stability

GASODOR®
S-FREE

- long stability
  - at least 18 months
- no crystallization at low temperatures for a period of 12 months
- high performance stability at higher temperatures (+50 ° C)
- no corrosion evidenced in piping or systems
- no chemical reactions evidenced in natural gas mains
- no decomposition identified in natural gas mains
- low adsorption in gas mains



Source: DVGW Research Office at the Engler-Bunte Institute of the University of Karlsruhe

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Packing/ Odorizer

GASODOR®
S-FREE

- can be employed in essentially all injection systems with a quantity control pump odorizer: type of LEWA, DMT, RMG,…
- has normal intervals in odorizer maintenance.
- can be shipped and stored in essentially all existing containers.

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Cross Sensitivity

GASODOR®
S-FREE

Reaction properties with other S-odorants (liquid phase):

• Ethyl Mercaptan:	Decomposition:	Yes
• Propyl Mercaptan:	Decomposition :	Yes
• Sec.-Butyl Mercaptan:	Decomposition :	Yes
• Tert.-Butylmercaptan:	Decomposition :	Marginal
• Dimethylsulfide:	Decomposition:	No
• Tetrahydrothiophene:	Decomposition:	No

Test conditions: 4 weeks at room temperature and +40° C

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FOCUS COMPATIBILITY

Interaction with sealing materials

GASODOR® S-FREE

Suitable sealing materials for contact with gaseous Gasodor® S-Free:

Conditions	suitable	unsuitable
liquidphase(odorizationstation)	Kalrez	Viton
	VitonExtreme	Fluor-silicone
	Isolast	NBR
	Teflon	Perbunan
	FFKM	HNBR
		Silicone
gaseousphase(lowpressurenetwork)	Viton	none
	Fluor-silicone	
	NBR	
	Perbunan	
	HNBR	
	Silicone	

FOCUS COMPATIBILITY

Time life in pipelines

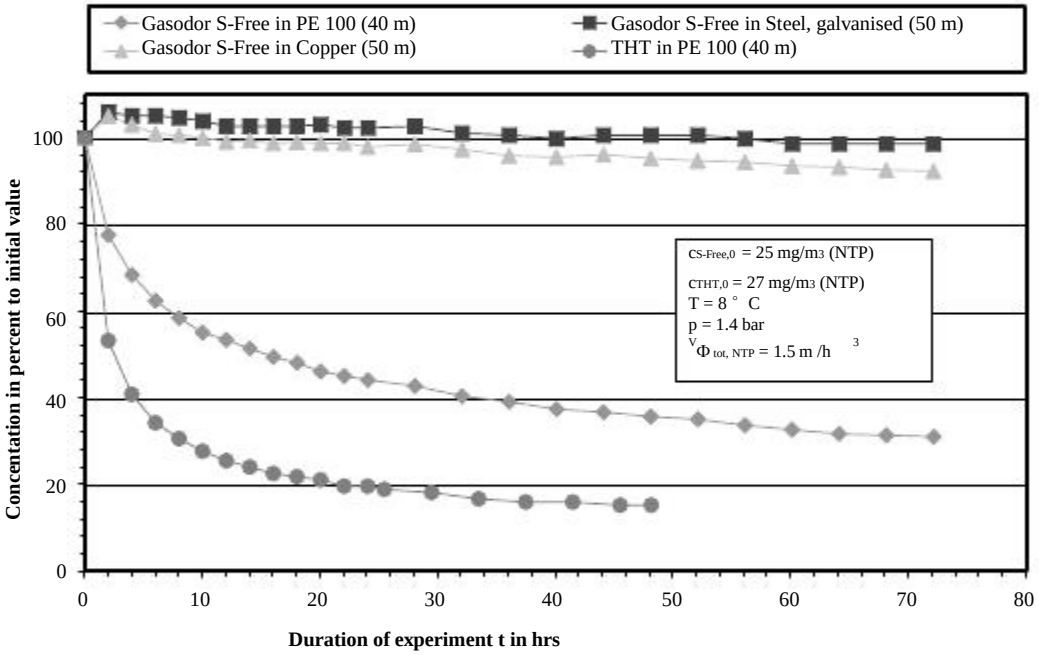
GASODOR® S-FREE

TEST SET-UP

- **Pipe lenght: 10 m**
- **Odorized gas was circulated in the pipes**
- **Gas chromatographic analysis**

CONCLUSION

- **Slight decrease of Gasodor® S-Free concentration in metallic pipes (copper, galvanized steel)**
- **Clear reduction of odorant concentration in PE**
- **The diffusion of THT in PE material is more distinctive as for Gasodor® S-Free**



Source: Graf, F.; Kröger, K.; Reimert, R.; Energy & Fuels 21, 3322-3333 (2007)

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Compatibility with new Technologies

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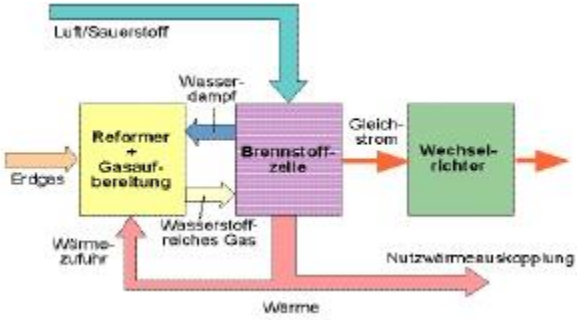
Fuel Cell

For the moment natural gas is the preferred energy source for fuel cells.

To start running fuel cells natural gas has to guarantee a maximum size of no sulphur content.

CFC Solutions GmbH intends to build a fuel cell plant of type HotModule at Friedrichshafen which applies natural gas odorized with Gasodor® S-Free.

- Because of the missing supply of sulphur of the odorant the durability of the activated carbon filter will be extended and so the operation of the fuel cell plant will be much more economic.



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Natural gas fuel station

GASODOR®
S-FREE

Gasodor® S-Free is already in use in numerous supply areas which carry on a fuel station for natural gas.

The future-oriented Gasodor® S-Free fulfils all expectations and therefore provide an essential contribution for compliance with legal requirements concerning fuels in the present and in future.

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Ecology

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SO_2- emission

GASODOR®
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The Message:

- X tons of Gasodor® S-Free produce ZERO tons of sulphur dioxide emission

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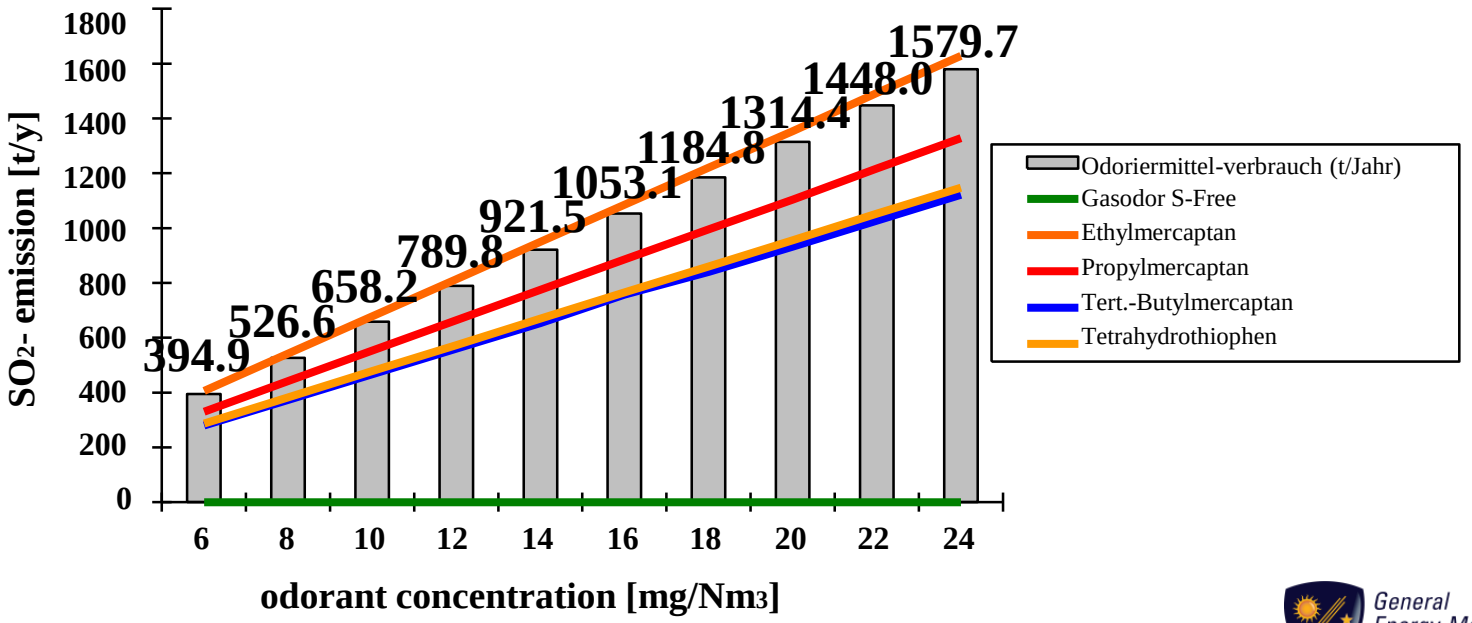
SO_2- emission



(calculated on the German natural gas consumption (year 2000): 63,82 Mrd. Nm^3)

Smelling Character and Minimum Odorizing Rate

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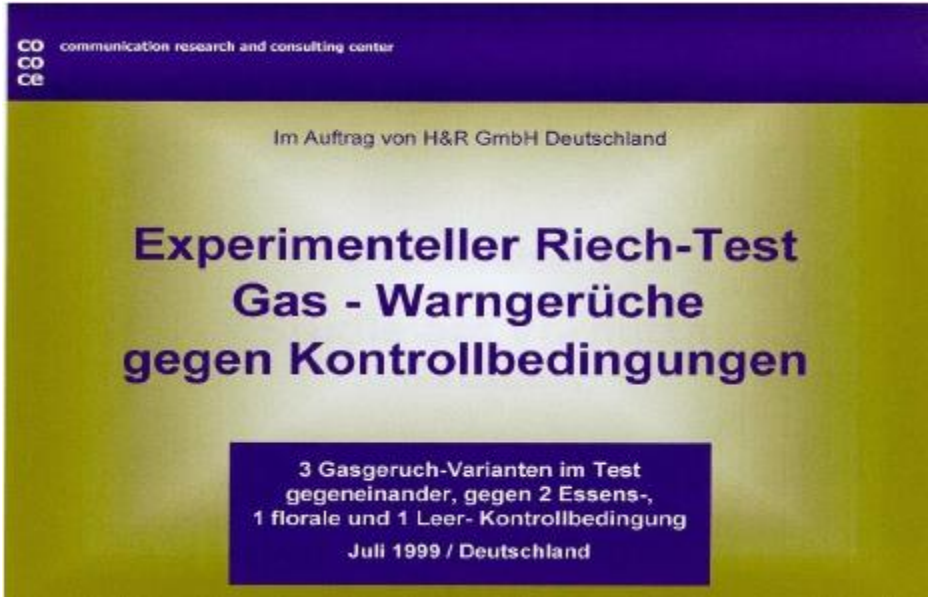
Smelling Character



GASODOR®
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Odors employed:

- Gasodor® S-Free
- THT, TBM
- Fish, Roast
- Jasmin
- Ambient Air

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Assessment Criteria

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S-FREE

(1) How would you assess the intensity of the smell you just perceived?

(2) Which of the following statements can you best associate with the smell you have just perceived?

- Fine, Tasty Food
- Aromatic
- Aggressive
- Burned
- Fresh
- Bitter
- Spoiled Food
- Fruity
- Strange, Irritating
- Sweet
- Stuffy
- Pleasant
- Floral
- Musty
- Chemical

(3) Please now describe precisely and in detail: What do you think it smells like in the container? What do you associate with it?

(4) Please now describe precisely and in detail your feelings and the reaction the smell evoked in you:

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Odor Description

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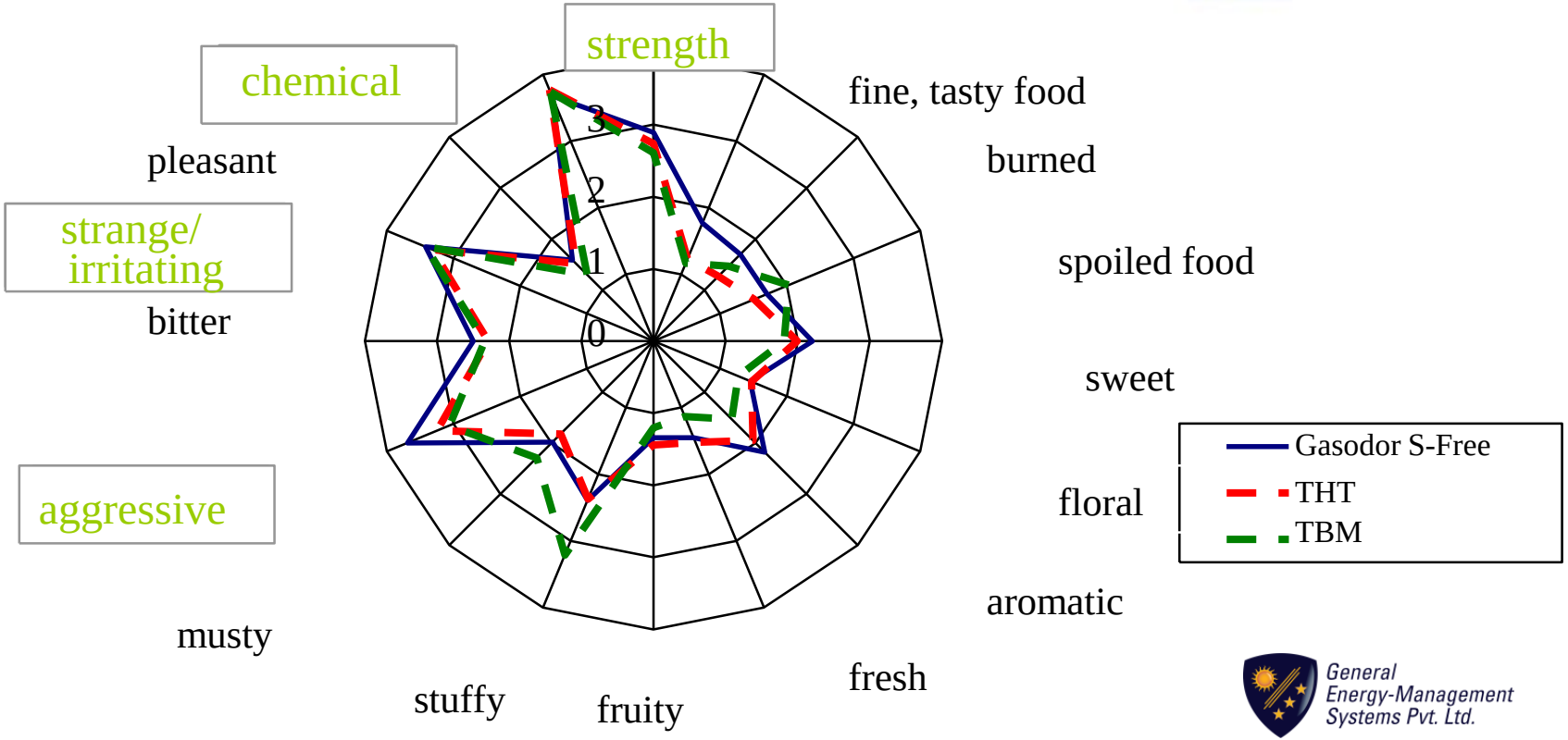

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ODOUR STATISTICS

Conclusion

GASODOR®
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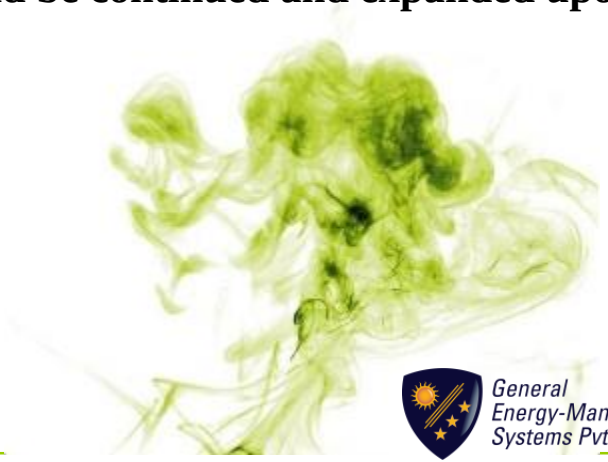
- **Gasodor® S-Free is perceived as a warning smell**
- **There is no perceived changed in people's behavious after the switch to Gasodor® S-Free**
- **Odour statistics should be continued and expanded upon further odourants**



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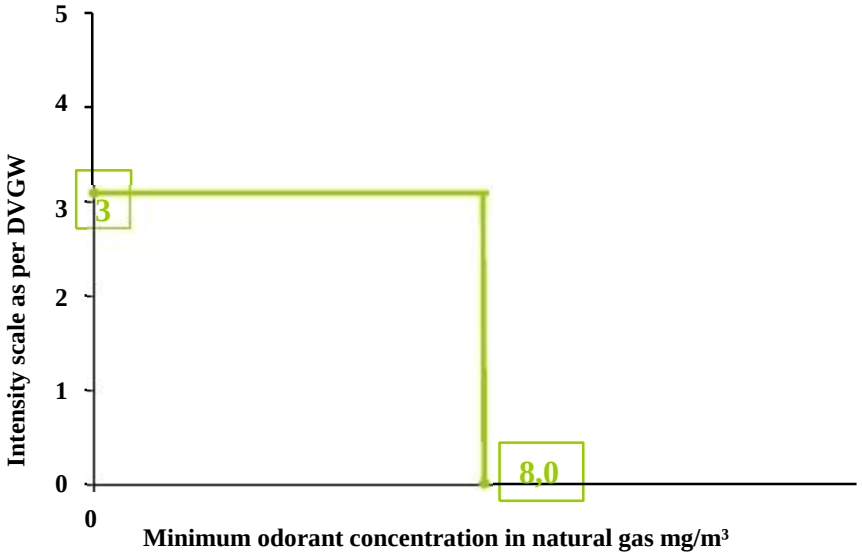
GASODOR® S-FREE has a minimum odorant concentration in natural gas of

8,0 mg/m3



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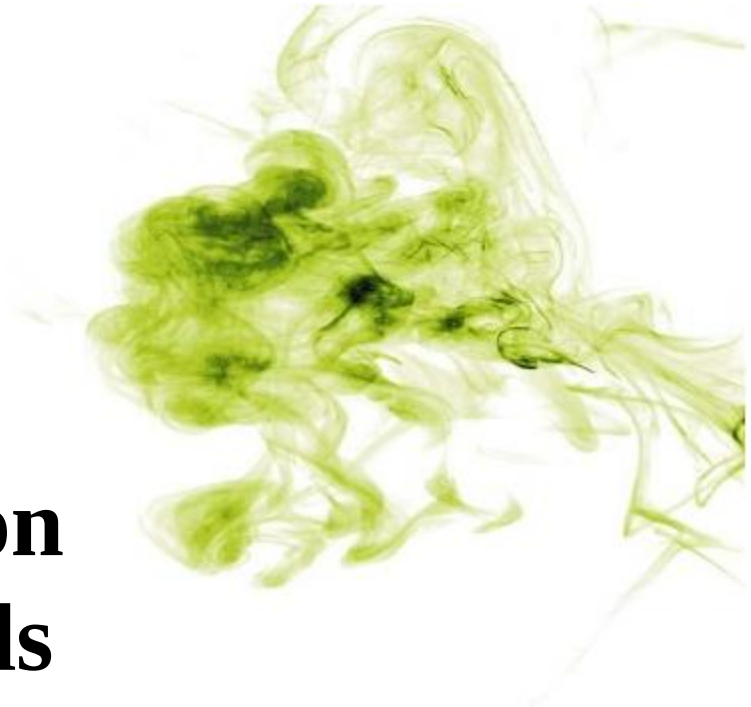
Detection Methods



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Stationary Measurements

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S-FREE

Mikro-GC

Varian Deutschland GmbH
Alsfelder Strasse 6
D-64289 Darmstadt

Compact GC

Axel Semrau GmbH & Co. KG
Stefansbecke 42
D-45549 Sprockhövel

IMS-Odor

G.A.S. Gesellschaft für analytische Sensorsysteme mbH
BioMedizinZentrumDortmund
Otto-Hahn-Str. 15
D-44227 Dortmund

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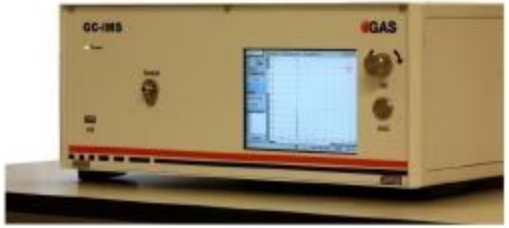
Mobile Measuring Instruments

GASODOR®
S-FREE

GC-MS-ODOR

G.A.S. Gesellschaft für analytische Sensorsysteme mbH
BioMedizinZentrumDortmund
Otto-Hahn-Str. 15
D-44227 Dortmund



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Practical Experiences

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Ferngas Nordbayern

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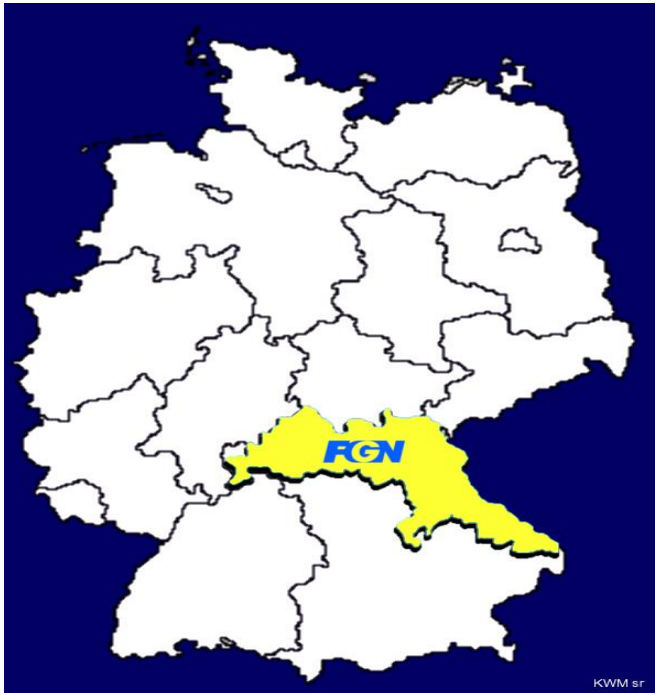
S-FREE

Changeover to sulphur-free centralized odorization with Gasodor® S-Free by January 2004 (Schwanenkirchen) and April 2007 (Hub und Ragenhof)

Benefits of changeover:

- Fast and equal distribution within the network at adequate discharge rate
- No mutual interference at mixture with other odorants
- Environmentally sound and reduced emission of combustion
- Minimization of error sources
- Reduction of specific odorant costs
- Decrease of required operating expenditure



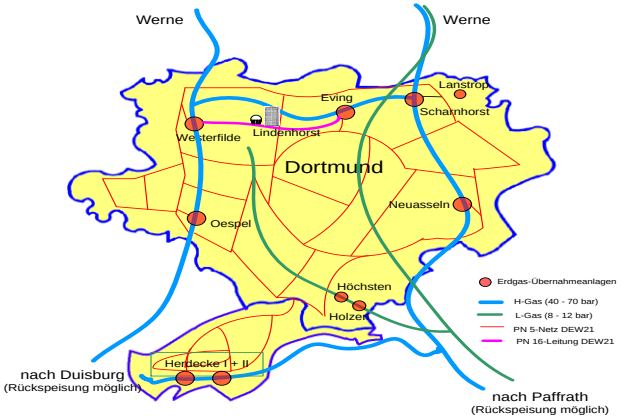
DEW 21

GASODOR® S-FREE

Changeover by December 2006

Benefits of changeover:

- Dosage rate THT ~ 25 mg/m_N^3 with up to 70 % leakage of THT in the distribution system because of the network topology.
- Current dosage rate of Gasodor® S-Free ~ 17 mg/m_N^3 only with up to 35 % leakage of Gasodor® S-Free in the distribution network.
- Odorant savings of > 30%!
- No shift of the number of warning odor signals detected.



e·on | Hanse

GASODOR® S-FREE

Changeover of Western Pomerania in springtime 2007, Schleswig-Holstein changes over in autumn 2007 and Hamburg will change over to Gasodor® S-Free in the beginning of 2008.

Benefits of changeover:

- Reduction of odorizing facilities from 149 to 59 after completion of the whole changeover to Gasodor® S-Free.
- Well improved odorizing behaviour of Gasodor® S-Free in comparison to THT.
- More stable concentrations in pipelines with low flow rate.
- Very good recovering rates in general.

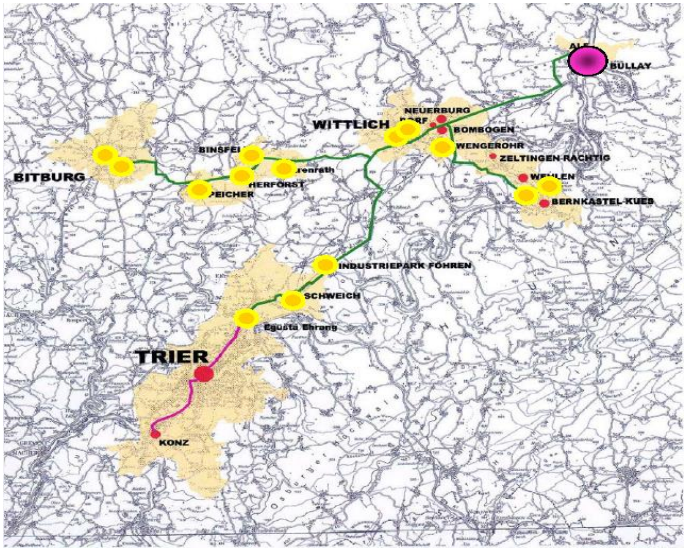
Saar Ferngas & SWT

GASODOR®
S-FREE

Changeover by February 2004

Benefits of changeover:

- Reduction from 14 decentralized to 1 centralized odorizer.
- The calculated saving potential is >17.000 €/ y.
- Very good and fast spreading of Gasodor® S-Free in the high-pressure network (max. 65 bar).
- The medium recovering rate of Gasodor® S-Free is at very good 74% over all networks (high-pressure and local networks).



Sources

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Sources

GASODOR® S-FREE

Gasodor® S-Freewill be distributed by:

Symrise AG

(Mühlenfeldstrasse 1, D-37603 Holzminden)

Actor Gesellschaft für Anlagenbau mbH

(Mittelweg 9, D-01454 Wachau)

Bohlen & Doyen Bauunternehmung GmbH

(Hauptstrasse 248, D-26633 Wiesmoor)

Brenntag GmbH

(Am Röhrenwerk 46, D-47259 Duisburg)

LF Service GmbH & Co. KG

(Ammerländer Heerstrasse 368, D-26129 Oldenburg)

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List of Literature (1)

DVGW Research Center at the Engler-Bunte-Institute of University of Karlsruhe
Gas Technology

Literature of EBI concerning the sulfur-free odorant

Bernhart, M.; Reimert, R.: Voruntersuchungen an einem schwefelfreien Odoriermittel. gwf Gas Erdgas 140 (1999) no. 2, p. 92 - 96.

Schunk, C.; Bernhart, M.; Reimert, R.: Schwefelfreies Odoriermittel – Steigerung der Umweltfreundlichkeit unter Wahrung des Sicherheitsniveaus. gwf Gas Erdgas 140 (1999) no. 10, p. 716 - 721.

Kröger, K.; Bernhart, M.; Reimert, R.: Ergebnisse eines Feldversuches mit dem schwefelfreien Odoriermittel „Gasodor® S-Free“. gwf Gas Erdgas 142 (2001) no. 11, p. 779 - 784.

Schmeer, F.; Reimert, R.: Entwicklung eines schwefelfreien Odoriermittels - Aktueller Stand. gwf Gas Erdgas 144 (2003) no. 1, p. 524 - 528.

Schmeer, F.; Reimert, R.; Kaesler, H.: Schwefelfreie Odorierung - Erfahrungsberichte. gwf Gas Erdgas 145 (2004) no. 10, p. 584 - 585.

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List of Literature (2)

GASODOR® S-FREE

Literature of EBI concerning the sulfur-free odorant

Kröger, K.; Henrich, T.; Bajohr, S.; Graf, F.; Reimert, R.: Aktuelle Forschungsaktivitäten auf dem Gebiet der schwefelfreien Odorierung. Energie|Wasser Praxis (2005) no. 12, p. 118 - 121.

Graf, F.; Kröger, K.; Reimert, R.: Sulfur-Free Odorization with Gasodor® S-Free - A Review of the Accompanying Research and Development Activities, Energy & Fuels (2007) 21, p. 3322 - 3333.

Graf, F.; Kröger, K.: Current developments in the odorization of natural gas in Germany. Abstract IGRC, Paris 2008.

Graf, F.; Kröger, K.: Ändert sich die Geruchswahrnehmung der Bevölkerung nach Umstellung auf schwefelfreie Odorierung? Energie|Wasser Praxis 59 (2008) no. 9, p. 56 - 60.

Graf, F.; Kröger, K.: Olfaktorische und analysetechnische Untersuchungen von Odoriermitteln und Odoriermittelmischungen. gwf Gas Erdgas 150 (2009) no. 1 - 2, p. 58 - 67.

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Please visit our website: www.gasodor-s-free.com

GASODOR® S-FREE …

the worldwide first and only sulphur-free odorant for natural gas

- **has a warning odor**
- **has a minimum odorant concentration of 8,0 mg/m³**
- **is economical**
- **is compatible with modern technologies**
- **saves the environment**

conclusion:

satisfies utilities in daily use

General Energy-Management Systems Pvt. Ltd.

GASODOR®
S-FREE

……. green odorant

for

green natural gas!

Thank you very much
For your attention !

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