



State of the art in the utilization of odorants for hydrogen and hydrogen-enriched natural gas

A1.4.1 - LITERATURE SURVEY ON THE CURRENT STATE-OF-ART ABOUT THE UTILIZATION OF ODORANTS

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<p>Abstract</p> <p>The state of the art about the utilization of odorants used in the natural gas industry for the hydrogen supply chain was reviewed. Purpose of the review was to obtain a list of odorants that are considered for hydrogen and hydrogen-enriched natural gas in supply lines, to identify the best practices in establishing metrological traceability in the development of measurement standards and certified reference materials (CRMs) and the analysis methods employed.</p> <p>Odorants that are currently contemplated for hydrogen-enriched natural gas and hydrogen can be subdivided into two groups, sulfur-containing and sulfur-free odorants. The latter group of odorants has the advantage that these do not contribute to sulfur dioxide emissions when the gas is used in combustion processes.</p> <p>Research in the use of odorants in hydrogen is focussed on the specific properties of hydrogen, such as its potential to react with odorants. To support this work, measurement standards and CRMs are required to ensure that measurement results are metrologically traceable, and that conformity with legislative and operational requirements can be duly assessed. The methods currently used for preparing such measurement standards and CRMs are also suitable for producing the required standards in hydrogen-enriched natural gas or hydrogen.</p>		
Key words Odourisation, natural gas, gas grids, hydrogen, hydrogen-enriched natural gas, odorant, olfactometry		
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Contents

1	Introduction.....	4
2	Odorants used in the natural gas industry.....	5
3	Suitability of odorants used in natural gas for hydrogen	6
4	State of the art on certified reference materials for odorant concentration measurements.....	8
5	Analysis methods that have been developed for odorants – offline and online.....	10
5.1	Sulfur containing odorants	11
5.2	Sulfur-free odorants	12
6	New types of odorants.....	12
7	Conclusions	13
	Bibliography.....	13



1 Introduction

Hydrogen is the simplest and most abundant element on earth. Hydrogen can store and deliver energy, but it must be produced from compounds that contain it. Hydrogen can be produced from diverse resources. Currently, most hydrogen is produced from fossil fuels, specifically natural gas [1]. Electricity surplus from the grid or from renewable sources such as biomass, geothermal, solar, or wind is also currently used to produce hydrogen. Even solar energy and biomass can be used to generate hydrogen. To reduce greenhouse gas emissions, hydrogen can be used in replacement of fossil fuels in electrical power generation, transport, industry and the built environment. However, to apply hydrogen safely, traceable measurements for leak testing, material compatibility, sensors for monitoring processes and odorization are required to demonstrate compliances with legislation.

Hydrogen is colourless and odourless and therefore undetectable by normal human senses [2]. Because hydrogen is a small and light molecule, very small leaks are common. Normally, these very small leaks do not present a problem as the small amount of hydrogen released will not be enough to cause its self-ignition in the air. However, if hydrogen gas can accumulate over time in a confined area, a risk of a flammable mixture or asphyxiation arise. For characterization of leakage, several techniques are established both on a general technical level as well as by standardization: tracer (sniffer) techniques that use the sensitivity of a sensor to the gas under investigation or hydrostatic testing analysing the (partial) gas pressure drop across the component to be tested (and the related steady state gas flow). Odorants allow the detection of leakages by humans without use of any special equipment. Odorants are especially useful in in places where it may be difficult to position detectors/sensors. While significant research has been undertaken on the odorization of natural gas in pipelines, there is a lack of information regarding odorization of hydrogen.

The use of odorants in hydrogen and hydrogen-enriched natural gas is essential in the built environment. It is viewed as the only means to ensure that citizens timely detect leaks from gas lines and can take prompt action to prevent accidents or a dangerous situation. At the same time, the use of odorants is incompatible with other uses, such as hydrogen for fuel cells. The scope of this work is therefore on those applications where odorization is currently applied and where in the foreseeable future it still will be used in view of health, safety and environment requirements.

In this report, we review the different aspects that contribute to a safe and metrological use of odorants (accurate injection of the odorant, proper monitoring technique) such as what are the odorants used in the natural gas industry, are they also usable for hydrogen, are there new odorants specific for hydrogen, the state-of-the-art on certified reference materials (CRM) for the identified odorants incl. material compatibility (cylinders) and stability along the hydrogen supply chain (in hydrogen when available and other matrices otherwise), and finally the analysis methods that have been developed for odorants – offline and online.



2 Odorants used in the natural gas industry

There are different national safety requirements for odorization. E.g, the national fire protection association (USA) and certain pipeline safety regulations require that the combustible gases in pipelines be detectable at one fifth of the lower explosive limit by a person with a normal sense of smell, either by the natural odor of the gas or by means of artificial odorization [3]. The lower explosive limits for natural gas (NG) and hydrogen (H₂) are 3.9 % and 4 %, respectively [4]. Therefore, the proper odorization and odorants are integral parts of the safety.

The selection of an (artificial) odorant to be injected into the gas grid requires knowledge of the chemical composition of the gas, the physical and chemical characteristics of available odorants, the physical layout of the pipeline system and local storage tanks, ambient conditions, the desired odorant level, and the current recognition of smell that the local population has [5]. The characteristics to consider when selecting an odorant or odorant blend include vapor pressure, gassy odor, soil penetrability and resistance to oxidation and reactions with impurities (odorant-fading). Other requirements include freezing point, boiling point and stability.

Several standardization documents deal with the odorization of natural gas. Standard ISO 13734:2013 [6] sets requirements and test methods for organic compounds suitable for odorization of natural gas. ISO/TS 16922:2022 [7] 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. The odorants shall meet several recommendations [6].

Among other, the gas odorant shall have a strong, unpleasant, distinctive (universally associated with gas) odor at very low concentration, be stable during storage and when it is mixed with the natural gas, the resulting blend shall not be harmful. Experience in many countries has shown that these requirements are best met by *organic sulfur compounds* - sulfides (thioethers) and secondary and tertiary mercaptans (thiols) - with boiling points below 130 °C.

Odorants which are commonly used today are typically a blend made of the following components:

- Tertiary Butyl Mercaptan (TBM)
- Isopropyl Mercaptan (IPM)
- Normal Propyl Mercaptan (NPM)
- Secondary Butyl Mercaptan (SBM)
- Dimethyl Sulfide (DMS)
- Methyl Ethyl Sulfide (MES)
- Tetrahydrothiophene (THT)

The odorants used in different European countries is presented as a table in [8] (e.g., in Hungary, THT+TBM, in Ireland, TBM+DMS...). A typical odorant blend called NB (New Blend) is comprised of 75-80% TBM and 20-25% DMS. This odorant is used for example in the UK.

Arkema [9] produces a series of odorants under the name Spotleak®: Spotleak®1001: 80% TBM, 20% DMS, Spotleak®1005: 30%TBM, 70%THT, Spotleak®1007: 80%TBM, 20%MES,



Spotleak®1009: 79%TBM, 18% IPM, 3%NPM, Spotleak®1039: 50% TBM, 50%THT, Spotleak®1420: 75% TBM, 25%DMS and Spotleak®1450: 10% TBM, 70%IPM, 10%NPM, 10%DMS.

100% THT is commonly used across Europe and in Sweden to odor biomethane.

Dilutions of NB with hexane (e.g. NB (34%) + hexane (66%) mixture called Standby Odorant 2) are also proposed as odorants [10] [11].

The major issue with use of S-based odorants is that they form sulfur dioxide (SO₂) when the gas is used for combustion applications. If the gas with S-odorants is used for fuel cells application a desulfurizer must be installed to remove the odorant that will cause poison of the catalyst.

Sulfur-free odorants are also used in natural gas. These compounds include alkyl acrylates, vinyl or alkyl ethers, n-valeric acid, ethyl acrylates, cyclohexane etc.

An example of those is Gasodor® S-free. It consists of a mixture of acrylates (37.5% of methyl acrylate and 60% of ethyl acrylate) together with methyl ethyl pyrazine (2.5%). This odorant is used by several German gas distribution companies [12]. Another example is a S-reduced odorant Spotleak Z (a mixture of ethyl acrylate and THT).

Finally, two other S-free odorants, 5-ethylidene-2-norbornene and ethyl isobutyrate, are mentioned in a UK study [10] [11].

Some of odorants may be chemically unstable (e.g. acrylic ester) and may require larger concentrations compare to mercaptans. Moreover, some nitrogen-containing odorants (e.g. pyrazine) can cause an enhanced formation of nitrogen oxides.

Thus, for example, thermal decomposition of pyrazine above 1200 K produces HCN [13] which is well-known precursor of NO_x formation in combustion applications [14]. Therefore, all H-C-N containing odorants can contribute to NO_x emissions when natural gas or NGH₂ blends are used in combustion applications.

Sulfur-free odorants can readily be smelled, however, the smell resembles rather to garlic. Therefore, the human common sense does not associate this type of smell with the typical smell of combustible gas, because the citizen is accustomed to the mercaptan smell [4].

The level of the odorant added [7], that determines the odor intensity, is based on different factors. The objective is that the population humans with a functional sense of smell will be able to smell odorized gas before its concentration reaches the specified dangerous level (typically 20 % lower flammability limit) and thus take the appropriate safety protection actions.

3 Suitability of odorants used in natural gas for hydrogen

Several studies have been done to investigate applicability of known odorants for use with hydrogen or natural gas/hydrogen blends. In a recent study from Marcogaz [15], it has mainly been discussed for blend of natural gas and hydrogen (H₂NG). A short review of preliminary works is presented which concluded that at least two types of studies need to be performed in a near future: performance tests to determine the suitability of odorants for different H₂NG mixtures and investigation of the propagation of smell for new odorants in presence of hydrogen. In the report, the effect of hydrogen addition to natural gas odorization is discussed. Three effects are mentioned: possible chemical reactions between hydrogen and odorants, physical effects in the grid and possible masking of odor

by hydrogen. The report concluded that no evidence of problems in odorization after addition of hydrogen to NG was found but experiences were limited. Moreover, more information is needed regarding possible effects on odorization due to differences in physical properties of the mixture of gas and odorants, possible chemical reactions between hydrogen and odorant at high pressure conditions, possible effects of high concentrations of hydrogen on odorant and the influences from possible impurities in H₂ (from hydrogen production).

The authors of the project “H₂-Ready-Assets” claimed that the previous experience of the German gas industry pointed towards a possibility of odorization using sulfur odorants for mixtures of NG with up to 60% of hydrogen [8] [16].

Sulfur-based odorants are not suitable for applications where PEM (Proton Exchange Membrane) fuel cells are used. According to ISO14687:2019 [17], the concentration of total sulfur compounds in hydrogen used for fuel cell vehicles must be below 4 nmol/mol whereas odorants commonly used in natural gas can present at much higher levels (typically in the μmol/mol range). Conventional S-based odorants will also not be suitable for use for stationary fuel cell appliances for the same reason and therefore a (costly) desulfurizer has to be installed before the fuel cell appliance [18].

Further aspects of odorization in hydrogen have recently been studied such as perception and escape detection properties.

In a study from Mouli-Castillo *et al.* [19], the authors have examined the use of sulfur-based odorants (NB, Standby odorant 2 and THT) to be used in a 100% hydrogen gas demonstration network in the UK and undertook a comparative testing programme to evaluate the escape detection properties of odorized hydrogen against odorized methane and natural gas. The results showed that the odorants currently used within natural gas tend to have a similar effectiveness in allowing escape detections when used with hydrogen and that small escapes of hydrogen are detectable in a comparable way to a natural gas escape in an equivalent room volume.

Hydrogen gas samples odorized with five different odorants (NB, Standby odor 2, THT, Gasodor S-free and 5-ethylidene-2-norbornene) were analyzed to determine odor detection threshold, the odor intensity, its hedonic tone (assessment of the pleasantness of odorants at different dilution levels) and character (oil, sulfur, onion, musty...) [10]. The odor hedonic testing revealed that 5-ethylidene-2-norbornene was perceived as pleasant by the panel, which should rule it out as a standalone alternative to odorants currently in use. The other four odorants met requirements for use in UK gas distribution network. The study highlighted that further work is needed to determine the physical and chemical stability of the odorant during transport, storage, and end use within a hydrogen network. Some tests were then performed for pipeline, flame boiler and PEM fuel cell.

For pipeline testing [18], X42 carbon steel (7 barg) and PE80 polymer (ambient pressure) made pipes were exposed to air, hydrogen and five odorants in hydrogen. The presence of any of those odorants made no difference to the results.

While testing the five odorants in a boiler [18], the results indicated that the S-free odorants would not induce corrosion whereas the S-containing odorants were found to be more corrosive compared to the S-free ones but not more than similar S-containing odorants in natural gas.

In combustion, the SO₂ is the final product. Assuming that the combustion is “clean” (that is the case for a lean and stoichiometric combustions), then there is no S-accumulation on the (soot/nano-) particles (as in the case of rich combustion). Therefore, all S -(odorants, H₂S, OCS, CS₂ SO₂, etc.) in the

NG or NGH₂ blends will end up as SO₂. The maximum amount of SO₂ in the stack gas depends on the country and some numbers are given in the table below [20]:

Country	France	Belgium	Italy	Germany	Spain	UK	Czech republic
Boilers (3% O ₂) (mgS/m ³ (n))	79	184	184	53	184	53	
Turbine (15% O ₂) (mgS/m ³ (n))	159	191		191		159	
Engines (5% O ₂) (mgS/m ³ (n))	177			53		296	207

As one can see the most stringent requirement for SO₂ emissions are in Germany (53 mg/Nm³) for the most energy contributing sector (power plant/domestic boilers). That number gives the outmost amount of the S in the fuel including possible odorants. Typically use of THT or mercaptans can give up to 15 mg/Nm³ in S addition [20]. This is in general quite low amount compared to the numbers given in the above Table. Therefore, the S in odorants can contribute up to 28 % in total SO₂ emissions (out of the lowest 53 mg/Nm³).

When testing PEM fuel cells [18], the odorants containing sulfur caused noticeable (and expected) degradation of the fuel cell. The loss of cell voltage when subjecting the fuel cells to hydrogen containing the non-sulfur odorants (norbornene and acrylates), was significantly lower compared to the tests performed with S-odorants. Further testing (longer test duration tests and comparisons against pure hydrogen) would be required to conclude suitability of norbornene and acrylates.

A study performed by DNV shows that mixtures of NGH₂ and pure H₂ can be sufficiently odorized with commonly used odorants across Europe [21]. In total 12 different mixtures were prepared and analyzed with THT, Gasodor® S-free and Spotleak® 1001 odorants. The THT results in the best recognition and association with (natural) gas.

4 State of the art on certified reference materials for odorant concentration measurements

ISO 13734:2013 [6] specifies requirements and test methods for organic compounds suitable for odorization of NG and NG substitutes (e.g., biomethane). According to ISO 13734:2013, the mass fraction of the declared chemical product in the undiluted odorant shall be at least 95 %. The composition of the odorant shall be determined by gas-chromatographic analysis. Any gas chromatographic method giving sufficient component separation and detection may be used.

During the EMRP project ENG01 “Characterization of energy gases”, the first SI-traceable reference gas mixtures of sulfur-free natural gas odorants were produced, and their compositions validated [22]. The mixtures, prepared gravimetrically in accordance with ISO 6142-1:2015 [23], contained methyl acrylate (MA), ethyl acrylate (EA), 2-ethyl-3-methyl-pyrazine (EPM) with a total odorant mass concentration of 11 mg/m³, (as this is the middle of the range of mass concentrations typically found in natural gas networks), in methane (CH₄) in 10 liter aluminium cylinders with the internal surfaces



treated using the “Spectraseal” passivation technique or in 5 liter aluminium cylinders using the internal “Aculife IV” passivation technique. *The reference gas mixtures produced were shown to be stable in passivated aluminium cylinders for at least eight months* and have been validated for MA and EA (to within 6 % or less) by interlaboratory measurements at three National Measurement Institutes (NPL, VSL and RISE).

Analysis at NPL, VSL and RISE was performed using a gas chromatography equipped with a flame ionization detector and mass spectrometer with different gas chromatography columns: a DB-624 column (75 m length, 0.53 mm internal diameter, 3 µm film thickness) at NPL, a WCot fused silica CP Sil 5CB column (60 m length, 0.32 mm internal diameter, 0.25 µm film thickness) at VSL and a BPX5 column (50 m length, 0.32 mm internal diameter, 1 µm film thickness) at RISE.

Performing accurate measurement of EPM was found to be highly challenging (probably due to the highly adsorptive nature of the compound, and the very low amount fraction - approximately 55 nmol/mol) in the multi-component mixtures produced in this study. More reliable measurements of EMP can be achieved with better passivation of the internal surfaces of gas cylinders and transfer lines.

The impact of hydrogen on the stability of gaseous mixtures of THT has been recently studied for a period of 900 days [8]. The gaseous mixtures of THT were prepared in 10-liter aluminum cylinders (manufactured by Luxfer) with Teflon-passivated inner surfaces. The mixtures were prepared using the modified manometric method based on ISO 6146 (manometric method for preparing calibration gas mixtures) [24]. Liquid THT and a complementary gas (mixtures of *methane/hydrogen 92/8 v/v, methane/hydrogen 90/10 v/v, methane/hydrogen 85/15 v/v or natural gas of group E (methane content >96%)/hydrogen 98/2 v/v and natural gas of group E/hydrogen 85/15 v/v*) were introduced in sequence into the cylinder. The stability of gaseous mixtures of THT containing hydrogen was controlled based on the measurement of THT concentration, performed using the method of gas chromatography with selective detection for sulfur compounds (PFPD). *The results showed that there was no clear impact of the addition of hydrogen (up to 15 %) on the stability of THT.* The authors concluded that *it is likely that THT mixtures will remain stable even for several years*, since most of the reactive components begin to exhibit losses immediately after the preparation of the mixture.

For the study reported in [18], NPL prepared five Primary Reference Mixtures (PRMs) in hydrogen: odorant NB (1.51 µmol/mol of TBM and 0.43 µmol/mol of DMS), standby odorant 2 (hexane 1.28 µmol/mol, TBM 0.51 µmol/mol, DMS 0.13 µmol/mol), THT 4.99 µmol/mol, gasodor S-Free (EA 1.12 µmol/mol, MA 0.7 µmol/mol, EPM 0.05 µmol/mol) and 5-ethylidene-2-norbornene 17 µmol/mol but the stability of these mixtures were not indicated.

In the HyDelta project stability of various odorants in H₂ was investigated [25]. Three candidate odorants (THT, Gasodor® S-Free and 2-hexyne) were tested for chemical stability in an atmosphere of 100 bar hydrogen over a three-month test period by gas chromatographic analysis. All odorants THT, Gasodor® S-Free and 2-hexyne, were found to exhibit stable behaviour, allowing them to exert their effect for a longer period of time.

A gas leak from a mixture of an odorant in hydrogen behaves like a singular gas cloud and no separation of the odorant and hydrogen occurs. It is possible that the concentration of the mixture in space is not the same everywhere due to stratification, but this effect also applies to natural gas. With regard to the distribution of gas in a room and the smell of a gas leak, odorization of hydrogen is just as effective as odorization of natural gas [25].



These studies show that it is feasible to prepare long-time stable S-/S-free odorant mixtures in CH₄, CH₄/H₂ and pure H₂. This is an important result because high CRM's production costs and a permanent need for CRM's for instrument calibrations and validations.

5 Analysis methods that have been developed for odorants – offline and online

Gas chromatography (GC)-based methods are widely used for major/minor on-line/off-line gas composition measurements in energy gases like natural gas (NG), biomethane and H₂. Bench-top GC's are used for measurements in the lab while micro-GS's are commonly used for on-site measurements. A GC system can be equipped with various detectors such as flame photometric (FPD), thermal conductivity (TC), flame ionization (FID), electrochemical or even with a mass-spectrometer (MS). FPD is highly sensitive and specific for sulfur in any volatile form and FID responds to any organic sulfide. TC detectors are used in some micro-GC systems. A GC-MS system is the most advanced and expensive and normally used for measurements at (very) low gas concentrations.

GC system developments for natural gas (and later biomethane) have been driven by gas market demands. No problems so far were reported with GC-based measurements of odorants in H₂ [11]. One can expect that odorants analysis with use a GC system in NGH₂ mixtures will also not have any issues unless some further chemical reactions between e.g. C₁-C₅ hydrocarbons and H₂ in a heated capillary column of the GC can happen.

Other methods used for odorants measurements are based on a broadband absorption spectroscopy technique in infra-red (IR) or ultraviolet (UV) spectral ranges. Although odorants can be measured in IR with use of e.g., a combination of a Fourier-Transform IR spectrometer (FTIR) and a long multi-pass gas cell, the most sensitive measurement technique is the UV absorption spectroscopy. Odorants have unique absorbance spectra in 184 -250 nm spectral range accessible by commercial UV spectrometers. Moreover, an UV-based spectroscopy system can easily be integrated for on-line measurements on pipelines [26] [27] [28].

Odorant UV absorption spectra have absorption structures with widths much larger than a typical spectral resolution of small commercial UV spectrometers. This means that once measured reference spectra for each odorant can be used for a variety of UV systems if the measurement conditions such as pressure and temperature are kept in the same range. Therefore, the CRM's described in the Sec. 4 can be used for "one-time" reference measurements at given temperature, pressure and spectral resolution ranges of the UV spectrometers intended for use with the UV systems. This is in contrast to GC systems where a periodic calibration with a CRM is a must.

Overall, both GC and UV/IR absorption spectroscopy methods can be used for odorants (both S- and S-free) measurements on- and off-line. Both methods require a CRM 's for instrument calibration and validation. However, especially UV spectroscopy methods have two significant advantages over the GC ones: only one-time reference data set with use CRM is needed and 2) lower operation and maintenance costs. However, the UV-based methods have not yet received a wide dissemination and acceptance in relevant organizations, while the GC-based ones are more commonly used by the gas operators and standardization authorities. The normative acts do not normally exclude the use of alternative measurement methods and with an appropriate further developments and validations the



UV absorption spectroscopy can be considered together with GC methods for odorant measurements in the future.

5.1 Sulfur containing odorants

Many analysis methods have been developed for S-compounds (not specifically for odorants) under various EMPIR funded projects related to the composition of biogas (project ENG54), biomethane (project 16ENG05) and hydrogen (project 16ENG01), Many of these methods are based on GC techniques.

However, the detection limits of trace S-compounds in hydrogen are much more stringent than for the odorants if the H₂ is intended to use for high-demanding applications such as H₂ fuel cells. Some of the developed methods can be used for S-containing odorants as well.

S-odorants contribute to the total S-balance in the gas. Test methods proposed in EN16723 standard are intended for use with natural gas. For the total sulfur, the Wickbold combustion method (ISO 4260 [29]) and the Lingener combustion method (ISO 6326-5 [30]) for total sulfur can be used.

GC (ISO 19739 [31]) or potentiometry (ISO 6326-3 [32]) methods can be used for individual sulfur compounds (such as hydrogen sulfide, H₂S or carbonyl sulfide, COS) or specific groups of sulfur compounds (e.g. thiol sulfur).

The standard ISO 6326-1 [33] gives a comparison of standardized methods and provides information for the choice of the method.

For measurements of sulfur compounds in hydrogen at a very low level, the following methods are reported: GC-SCD (Sulfur Chemiluminescence detector) with (ASTM D7652 [34]) or without pre-concentrator (Murugan and Brown [35]). Both methods are intended to be used for H₂ purity analysis for fuel cells vehicles where high purity H₂ is required to prevent degradation of the fuel cell system.

The JIS K 0512 [36] standard describes a method based on GC-FPD (Flame Photometric Detector) with pre-concentrator for H₂ purity assessment in H₂ electrolysis process.

A gas chromatography method with selective detection for sulfur compounds (PFPD: Pulsed Flame Photometric Detector) is used in [8] to study the stability of THT in CH₄ and natural gas mixtures containing up to 15% hydrogen.

S-odorants have unique absorbance spectra in 200 -250 nm spectral range accessible by conventional (low costs) UV spectrometers [26] [24] [28]. It should be noted that neither H₂ nor natural gas (free from odorants) have an UV absorbance in 200 -250 nm. Therefore, any UV absorbance in that range can only be caused by impurities such as odorants, oxygen, water or other trace organics (e.g. benzene).

UV absorption by oxygen and water (if any) has a continuum shape and can easily be separated from the odorants absorption with an appropriate data analysis (e.g. with use of differential spectroscopy tools). Then various chemometrics methods can be used for a quantification of particular organic components in the odorant.

An UV-based spectroscopy system can easily be integrated for on-line measurements on pipelines also at elevated pressures. Examples of use UV absorption method for on-line measurements are given in [26] [28]. In [37], an example of applicability of an IR absorption method for on-line odorant monitoring is given.



5.2 Sulfur-free odorants

S-free odorants can be measured with use both known GC- and UV/IR-based methods. Thus, for example, combinations of GC-FID and GC-MS systems with different GC columns have been used in [16] for characterization of S-free CRM's (see Sec. 4). Commercial Gasodor® S-free odorant can be measured with the UV absorption spectroscopy extended towards 184 nm [38].

While the GC-based methods [16] are suitable for only laboratory use, the UV one can also be applied for real-time on-line measurements as it has been reported in the [38].

6 New types of odorants

The THT odorant is widely used for NG. Many research show that the THT is also suitable for H₂ and NGH₂ mixtures. However, THT has two major drawbacks: because it contains sulfur 1) it cannot be used in fuel cells by reasons mentioned above and 2) in combustion applications a release of SO_x is inevitable. Therefore, in the recent years, alternative odorants, and in particular S-free odorants, have been considered. Thus, for example, in the “Alternative Odorants for Hydrogen” project several possibilities of use alternative S-free odorants for H₂ have been investigated [39].

Based on a literature search a long list of possible odorants has been made [39]. Using the so-called elimination method, all candidate odorants were assessed, and three substances were selected for the research. The selected candidates were:

- 5-ethylidene-2-norbornene;
- methyl tert-butyl ether;
- 2-hexyne.

All three candidate odorants are patent-free and none of them have been used as odorant commercially.

It was found that the 2-hexyne is the only one out of three investigated that appears to be suitable for use as a S-free odorant in H₂. However further research about influence of a pipeline material and other traces in the H₂ on the stability of 2-hexyne is needed before 2-hexyne can replace the THT odorant in the existing pipeline infrastructure [39].

There are many patents where inventors proposed new S-free odorants, e.g. [40]. In [41], the inventors claim about a method of evaluating of H₂ properties and for selecting proper odorants and in [42] many examples of new odorants are given.

It should however be noted that a patent is not a peer-reviewed publication and evaluated only by special patent examiners not necessarily having a deep and broad knowledge and experience in the field. A choice of new S-free odorants suitable to substitute known S-based ones is a complicated task where several odorant aspects related to gas transportation, storage and use need to be addressed. It requires a substantial research where various odorant gas-, surface-, long-, short-time interaction processes need to be taken into account. This is frequently cannot be achievable within many patent applications. Therefore, all patents claims have to be considered with precaution.



7 Conclusions

Safety is paramount in the gas industry. As for other gases, the objective of odorization of hydrogen and NGH₂ is to enable that appropriated measures to protect 1) itself, 2) the gas supply infrastructure and 3) the environment, can be taken before an unwanted event (explosion, leak) can happen. For this purpose, an average human with an average functional sense of smell must be able to smell odorized gas before its concentration reaches a dangerous level.

The choice of the odorants is based on several factors: the gas odorant shall have a strong, unpleasant, distinctive (universally associated with gas) odour, being at very low concentration, be stable during transportation and storage and when it is mixed with hydrogen and NGH₂/CH₄H₂ it shall not change physical/chemical properties of the carrier gas. The physical characteristics to consider when selecting an odorant or odorant blend include vapor pressure, gassy odour, soil penetrability and resistance to oxidation. Other requirements include freezing point, boiling point and stability.

Odorants must be used in gas infrastructures where it can be difficult to position any detector/sensor and where there is a risk for gas accumulation.

While significant research has been undertaken on the odorization of natural gas in pipelines, there is a lack of information regarding odorization of hydrogen and H₂NG/H₂CH₄ mixtures in regard to odorant stability (fading) and a need in new and validated on-line measurements methods. The few available studies tend to show that the odorants used for natural gas can also be used for hydrogen and hydrogen blends with NG/CH₄, however more studies must be conducted to confirm these preliminary results especially for new S-free odorants.

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