# REPORT

## A 2.3.2 M13:

## *A brief survey about the available techniques for fast online measurement of hydrogen in natural gas*

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# Contents

# 1. Introduction

Since the 2015 United Nations Climate Change Conference (COP 21)[1] held in Paris and the "Paris Agreement" 2016 [2] at the latest, which determines a goal of global warming "well below 2 °C" compared to pre-industrial levels, it has become increasingly clear that greenhouse gas emissions must be reduced drastically in the coming years. The main targets for decarbonization are proposed in the field of electrical power generation, heating of buildings, transportation, and chemical process energy. In this context, the utilization of hydrogen as energy carrier and its generation preferably from renewable resources ("Green Hydrogen") has become the most important tool for climate-friendly transformation of society and industry.

Hydrogen, as the lightest chemical element and also the lightest of all chemical molecules has the highest content of chemical energy per mass unit of all chemical compounds. However, due to the very low volume-related density of about 0.09 kg/m$^3$ [3] (reference conditions[1]) it carries a quite low amount of chemical energy per volume unit of only about 12.79 MJ/m$^3$, compared to methane of about 39.84 MJ/m$^3$ [4]. This also applies to the comparison of compressed hydrogen with other energy gases or condensed fuels, such as coal or petrol. Thus, transportation and distribution in gaseous form via pipeline network is considered to be the most efficient and economical way for the wide-spread utilization of hydrogen.

Fortunately, it has turned out that the existing grid for natural gas transport, which exists in most of the industrialized countries for a long time, qualifies also for the transport of hydrogen [5]. Moreover, injections of gaseous hydrogen into the natural gas grid, as available, can gradually replace fossil methane in the fuel gas. In this way, hydrogen injections into existing natural gas grids can contribute to a successive transition from the use of fossil energies to a fully sustainable, green economy based on hydrogen as energy carrier.

A sustainable way to produce "green" hydrogen is the generation by electrolysis, favorably by surplus wind or solar energy. It is clear that generating hydrogen by volatile resources, like wind or solar power, implies daily or seasonally variations of hydrogen production. Managing these variations will become a permanent challenge for grid and storage operators and gas suppliers, who on the one hand must sell a clearly defined product with respect to composition and calorific value and on the other hand, a product that complies with technical and regulatory requirements.

As far as the operation of gas grids with combined hydrogen/methane content is affected, in the near future mainly two types of hydrogen sensors will become necessary:

- Hydrogen sensors for process monitoring and control
- Hydrogen sensors for gas quality control and legal metering

While the requirements for the former are only defined by the process, which is monitored or controlled by means of the sensor, the demands for sensors for quality control or legal metering within the EU are resulting from international standards [6] and national regulation of the gas markets (i.e., [7]).

Ever since, hydrogen has found widespread use in industry and as lifting gas for airships, there has been a long-lasting necessity for the measurement of the hydrogen content in industrial process gases. Up to now, most metering systems in this area mainly rely on the indirect and hence unspecific determination of hydrogen by measuring thermal conductivity or velocity of sound, sometimes with additional information from other physical properties of the gas mixture. These

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[1] $p$ = 1013.25 hPa, $T$ = 273.15 K

properties are indirectly correlated to the calorific value, Wobbe index, or hydrogen content of the gas mixture (correlative sensing systems [8]). Most of these physical properties are mainly influenced by the hydrogen content of the gas mixture, but they are also dependent on the total gas composition. Theoretically, a reliable determination of the hydrogen content by determining solely these physical properties is only possible if hydrogen is present in a well-defined and thus precisely known gas matrix. However, in future scenarios of the fuel gas grids, feed gas for the injection into the grid will be blended from different sources, dependent on prevailing availability. These sources will be diverse in composition depending on the origin, for example, natural gas with different calorific values, LNG qualities from various world regions, biogas, etc.

Regarding the timeframe for the continuous replacement of fossil gas by hydrogen, in a first step, the hydrogen injections in the natural gas grids can approach 20 Mol % [9]. However, in the following steps and dependent on availability of green hydrogen, hydrogen content in gas grids can exceed 98 % and become rather close to pure hydrogen, as proposed in DVGW G260 [10] as quality for fuel gas applications.

Since the last 30 years, a huge amount of hydrogen sensors had been proposed, but only a few have been commercialized up to now. Most of the hydrogen sensors available on the market are capable to quantify the hydrogen content only up to 4 Mol %, which also is the lower explosion limit (LEL) of hydrogen/air mixtures. Consequently, this type of sensors is mainly used on the field of safety applications.

Only a small subset of all presently commercially available hydrogen sensors qualifies for a fast and reliable quantification of hydrogen injections in natural gas at levels above 4 Mol % hydrogen.

The “H2Sense Hydrogen Sensor Database” of the *Bundesanstalt für Materialforschung und -prüfung* (BAM) as of 2015 [11] comprises 420 entries from 99 companies or distributors. Many of them are restricted to a limited operational range or do not fulfill the demand for a specific and composition-independent response for hydrogen, as they are correlative meters based on thermal conductivity or the speed of sound. Of the remaining 25 sensors with a measuring range of more than 20 % hydrogen, 12 proved unsuitable after closer examination (catalytic sensors, see below), or are no longer available on the market, or they do not attain the desired accuracy of at least 3 Mol%. The last 13 sensors belong to the family of Pd-resistive sensors and are manufactured by only one US company[2].

Since the establishment of the BAM hydrogen sensor database some new hydrogen sensor principles were published [12], but only one new sensor had been commercialized by end of 2022. Beyond that, in the field of process chromatography, one instrument with extended capabilities for fast hydrogen quantification for process control has appeared.

In the following section, we will give a brief survey over the sensing principles for hydrogen sensors. Most of the solid-state sensors find their application mainly in the surveillance of explosion hazardous areas. In the course of this short review, we will give a short assessment of the advantages and disadvantages of each type of sensor with respect of the demands for process control or legal metering. In this context, the authors also want to refer to the comprehensive publication on hydrogen sensors by Hübert et al. from 2018 [13]).

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[2] H2Scan Ltd., Valencia CA (USA), see also Section 5 (addresses of manufacturers)

## 2. Methods for hydrogen determination in gas matrices

There are four basic principles to detect the presence and measure the concentration (= partial pressure) of hydrogen in gas mixtures. Each of these principles can be applied to the quantitative determination of hydrogen:

a) by measuring bulk gas properties, which are mainly influenced by molecular transport properties: speed of sound, thermal conductivity, viscosity (Section 1).
b) by detecting the consequences of a specific interaction of hydrogen with matter: catalytic or electrochemical detection, metal-oxide and semiconductor sensors, metal-hydride based sensors (Sections 2 – 5).
c) by determining the interaction of hydrogen or hydrogen ions with electromagnetic radiation (optical spectroscopy) or by electromagnetic fields (mass spectroscopy) (Sections 6 – 7).
d) by separation of hydrogen from matrix constituents combined with unspecific detection (gas chromatography) (Section 8).

Each of these principles has been realized in the form of different technical approaches, which differ substantially in their metrological characteristics as discussed below.

### *1) Sensors utilizing the difference of transport phenomena between hydrogen and other gases*

The term “transport properties” in gases is mainly related to the basic state properties, such as thermal conductivity, viscosity, and speed of sound. Compared to all other gases apart from helium, hydrogen has very different properties in this respect. These physical properties of a gas mixture can be measured directly and very precisely with moderate technical effort. However, in complex mixtures with several components together with hydrogen, the composition of the gas mixture must be known as exactly as possible to quantify the hydrogen content with acceptable accuracy. This technology is thus very suitable to control well-characterized process gas streams (also called “correlative determination”). Usually, for the determination of certain basic properties of complex fuel-gas mixtures, like calorific value or Wobbe index, some unspecific and/or cheap sensors for $CO_2$-content and density are being combined and the resulting data are processed using multivariate approaches. For determination of hydrogen content, sensors based on thermal conductivity are very widespread and can cover ranges from below 1 Mol % to almost 100 Mol % of hydrogen in a methane matrix, while being reliable and not very expensive. However, correlative meters typically do not qualify for the legal requirements for billing in gas grids with specially pre-treated natural gases [14]. So, their suitability for legal metering of hydrogen in complex and varying gas mixtures is questionable. In contrast, their eligibility for process control strongly depends on the individual process under observation and the tolerance of the particular process against variations of hydrogen content.

### 2) Sensors based on catalytic detection

Catalytic sensors are based on the very sensitive measurement of the heat generated during the catalytic combustion of hydrogen in the sample. This heat is measured either by means of a Wheatstone bridge circuit or by taking advantage of the thermoelectric Seebeck effect. Frequently, these catalysts are based on palladium compounds which have a very high affinity for hydrogen. However, the catalytic combustion is not selective for hydrogen, since other oxidizable compounds with positive combustion enthalpy are also covered. Furthermore, the effect is sensitive to catalyst poisons and inhibitors, limiting the operating range to 4 Mol %, and, moreover, a certain amount of oxygen must be present in the sample to enable the combustion process. Due to their long lifetime without need for maintenance, these sensors find widespread application for monitoring potentially explosive atmospheres in hazardous areas. Because of the absence of oxygen, this class of sensors usually is not suitable for applications in natural gas grids.

### 3) Electrochemical sensors

Electrochemical sensors detect changes in charge transport or electrical properties due to electrochemical reactions at a sensing electrode within an environment which allows ion transport between the electrodes. These sensors can either be classified as “amperometric”, that measure electric current, or “potentiometric”, that measure the electromotoric force (EMC) between the electrodes. The physical processes are governed by the Nernst equation and Faraday’s law. The main disadvantages are a low long-term stability (especially under reducing atmospheres without the presence of oxygen), and only a moderate selectivity. The operating range usually is below 4 Mol% hydrogen. Thus, they are not applicable for legal metering in natural gas grids. Mostly, these sensors are employed in safety applications.

### 4) Metal-oxide and semiconductor sensors

A wide variety of solid-state sensors based on metal oxides and metal-oxide semiconductors (MOS) has been used in industry for several years. These sensors operate on the change of charge density in the structure or changes of the work function (i.e., the minimum energy required to remove an electron from a solid surface to infinity) in semiconductor structures after the ad- or absorption of hydrogen. Their main shortcoming is a relatively low selectivity. In some instances, selectivity is improved by combination of the work-function effect with the selective interaction of hydrogen with palladium (see below). However, most of the prototypes show a limited operational range of up to only 4 Mol % and a poor linearity. These sensors share a low energy consumption, which makes them very appropriate for mobile applications (fuel cell vehicles).

### 5) Metal hydride-based sensors

Some metals, such as palladium (Pd), yttrium (Y) and magnesium (Mg), show the capability to absorb hydrogen and form metal hydrides. The permittivity of the metal and the specific phase volume is modified by the insertion of hydrogen atoms into the metal lattice. Both permittivity change and volume expansion can be used to translate the hydrogen concentration to optical signals, electrical signals, or a change of mechanical properties.

Especially the unique interaction of hydrogen with palladium has been exploited successfully in almost countless variants of hydrogen sensors. In all these cases, sensing of hydrogen using palladium is a two-step process. In the first step, molecular hydrogen is adsorbed on the surface of palladium and dissociates to elementary hydrogen which then diffuses into the palladium lattice, causing a phase transition, accompanied by a lattice expansion. The main principle of hydrogen sensing by palladium is the conversion of the α-phase (conductive metallic phase) to the β-phase (semiconductive and transparent phase) [15], showing a volume expansion of about 10 % [16]. The process is fully reversible. Some commercially available sensors cover hydrogen concentrations between 0.5 and nearly 100 Mol %. The sensors of this type are suitable for process control and are promising candidates for the exact determination of hydrogen in the context of legal measurement. Disadvantages are a sometimes-limited mechanical stability of the metal layer due to permanent volume changes with associated effects of hysteresis and baseline-shifts. These problems can be, at least partially, overcome using palladium alloys instead pure palladium layers. A recent review of optical hydrogen sensors based on metal hydrides (particularly Pd, but also Y and Mg) is given by Chen et al [12].

## *6) Opto-spectrometric detectors*

Hydrogen, for being the lightest element and the lightest molecule, shows only very weak absorption of electromagnetic energy in the UV and infrared region. Thus, almost none of the established opto-spectrometric technologies, like UV-spectrometry or infrared-spectrometry, can be applied to quantify or even to detect molecular hydrogen in the presence of other gases. Only recently, by using advanced, tunable diode lasers and the application of elaborated methods of signal processing, the determination of hydrogen in presence of atmospheric gases by infrared absorption spectroscopy had been made possible [17,18]. However, up to now none of these instruments had found its way to commercial applications.

In contrast to the very weak infrared absorption of molecular hydrogen due to only a quadrupole moment, the hydrogen molecule is Raman-active. However, due to the weak nature of the Raman-effect in gases under ambient pressure, Raman spectroscopic methods need either powerful excitation lasers or sophisticated enhancement technologies to ensure sufficient sensitivity. In 2010, a first quantitative Raman analyzer for synthesis gas (CO and $H_2$) was demonstrated by Eichmann et al. [19]. Since then, the method was developed further and applied to hydrogen-containing natural gas as well [20]. Meanwhile, at least two commercial instruments for the analysis of natural gas including hydrogen have reached prototype status [21, 22]. In principle, this technology is suitable over the entire hydrogen concentration range from ppm to nearly 100 Mol %.

## *7) Mass spectrometry*

Mass spectrometers analyze molecules or atoms after ionization and/or fragmentation on base of the mass/charge (*m*/*z*) ratio in a mass filter. The various instruments differ by the mechanism of ionization, molecule fragmentation, and mass filter and show different complexity. Although nowadays, very compact instruments are available on the market (i.e., Pfeiffer-Vacuum PrismaPro®), all mass spectrometers are quite bulky instruments with a relatively high energy consumption, and even the simplest instruments with ion-trap or quadrupole mass filter and simple electron-impact ionization require trained personal to be operated. There are special instruments for process gas analysis which focus on small molecules and permanent gases (i.e., IPI Products GAM300®, ThermoScientific PrimaPro®). Dependent on the ionization and detection method, the sensitivity and the analytical range of the instruments can be very high from sub-ppb to the 100 Mol % level. However, due to the complex process of molecule ionization and fragmentation in an ultra-high vacuum system, analytical accuracy of these instruments is limited compared to other methods [23]. Moreover, hydrogen as element is present in nearly all possible contaminants, essentially water, which can be introduced accidentally into the high-vacuum system of a mass spectrometer. This is the reason for a low signal-to-noise ratio and elevated blanks just for hydrogen, especially in instruments where maintenance is often neglected. Although the instruments are suitable for fast online analysis, the high complexity of the instruments, the risk of flawed results due to contaminations, together with a sophisticated and costly maintenance procedure prevent mass spectrometers for widespread process analytics in natural gas analyses.

### *8) Gas chromatography*

For more than 30 years, gas chromatography is the workhorse of gas composition analysis for legal metering of the calorific value of fuel gases [24]. While gas chromatography is a discontinuous analytical method, fast separation of up to 13 components in a natural gas sample can be possible within 5 minutes, fast enough for process control applications. The determination of hydrogen in natural gas matrix is possible even within one minute [25]. Industrial process gas chromatographs (PGCs) usually combine up to three different separation columns each with individual temperature control, together with a common sample inlet system and a thermal conductivity detector (TCD). The separation of the permanent gases hydrogen, oxygen, nitrogen, methane, and carbon monoxide from natural gas usually is achieved by molecular sieve columns. To improve analytical precision, most applications in the field of natural gas analysis are operated isothermally. To accelerate sample throughput in a measurement campaign, gas analysis is performed by a complex system of column switching and backflush procedures. For natural gas analysis, the carrier gas is normally helium to allow for sufficiently sensitive determination of higher hydrocarbons. However, due to the well-known anomalous behavior of helium/hydrogen mixtures in respect to their thermal conductivity [26], the determination of hydrogen is accompanied by relatively high measurement errors in most commercially available PGCs. This particular problem can be overcome by the application of argon or nitrogen as carrier gas. In that case, with TCDs, the working range for the determination of hydrogen is at least between minimum 1 and 100 Mol % [27]. Today, process gas analysis with thermal conductivity detector is a standard application which does not need special equipment. Notably, for hydrogen determination which argon or nitrogen as carrier gas, usually a non-linear calibration curve has to be applied. Thus, many process gas chromatographs on the European market can determine the hydrogen content in natural gas with a relative accuracy of about 3% and better, and recommendations for standard laboratory instruments are also existing [28]. Nevertheless, in Germany up to now no commercially available instrument has met the special requirements for legal metering of hydrogen in natural gas with concentrations higher than 20 Mol %.

## 3. Overview of commercially available techniques for fast online measurements of hydrogen in natural gas

In the following section, we will focus on sensors which fulfill some basic requirements, originating from the demands of legal metering, process control, and the already suggested first-stage level of hydrogen injections into natural gas grids.

1) The working range covers at least the region between 1 Mol % at the lower and more than 20 Mol % at the higher limit.
2) High specific response for hydrogen, low cross-sensitivity for other components in natural gas

3) Attaining at least 3% relative accuracy for process control and less than 1% relative accuracy for legal metering with respect to the concentration of hydrogen, following in parts the demand of OIML R140 [6]
4) Response time < 5 minutes
5) Commercially available in December 2022 on the European or world market

For applications in gas grid installations in the EU, all instruments must comply with current directives to protect from explosion risks (ATEX). These specifications are not addressed in the current survey. **Table 1** gives an overview of commercially available techniques for fast online measurements of hydrogen in natural gas which met the abovementioned specifications with respect to working range, specification for hydrogen, accuracy, response time, and commercial availability.

As shown in the table, the number of these sensors is quite limited. The large number of hydrogen sensors based upon measurement of velocity of sound or thermal conductance do not qualify because they are not hydrogen specific. The selected sensors can be categorized into only two groups: sensors on basis of/ based on palladium (either resistive or optical) and gas chromatographs. As already mentioned, the separation of permanent gases in gas chromatographs is mainly achieved by molecular sieve columns. The ability to determine the hydrogen content in natural gas with an accuracy of 3% and better is a common application for (process-) gas chromatographs with molecular sieve column and thermal conductivity detector. However, only three process gas chromatographs available on the German market meet the special requirements for the legal measurement of hydrogen contents in natural gas up to 20 mol% and are therefore included in the table. The instrument from MeterQ operates with helium as carrier gas, the other two instruments operate on argon for the determination of hydrogen.

All the technologies are hydrogen-specific with low cross sensitivity for other gases or contaminants. The analytical accuracy, as indicated by the manufacturer, is comparable for all instruments in the region of 1 % or better.

## 4. Conclusion and outlook

A great variety of hydrogen sensors and detectors is currently available on the market. However, most of them find their application field either in leak detection or are unspecific gas sensors which measure common properties of the gas mixture, such as thermal conductivity or speed of sound, that need further information on gas composition to correctly interpret the results. At present, only very few sensors and not more than 3 process gas chromatographs can analyze a hydrogen content in natural gas larger than 20 Mol % with an accuracy equal or better than 1%. Three further sensors, which had been available on the market according to information given in the 2014 “H2Sense Hydrogen Sensor Database” published by BAM [11], have been withdrawn since then (COSA Xentaur, Applied Nanotech) or presumably never entered market (Makel Engineering).

The energy policy with a switch to renewable energy sources together with the extended use of hydrogen for energy transport demands for highly specific and cost-efficient sensors combined with increased analytical accuracy. Many laboratories are working on the improvement of existing or on the development of new hydrogen-specific sensors. The most promising pathway seems to be the utilization of the unique hydrogen-specific interaction of hydrogen with palladium, generating an electrical or optical signal [29].

The future will also see higher performance of gas chromatography for hydrogen analysis. The full analysis of a common gas matrix together with a hydrogen content up to theoretical 100 Mol % with a single carrier gas only within a reasonable analytical error and in a very short time is claimed by only one manufacturer (**Table 1**). However, this instrument is not yet approved for legal metering in Germany by today. It is expected that other manufacturers will launch their products rather sooner than later.

A new approach is the hydrogen analysis by Raman spectroscopy. The optical detection method shares some inherently favorable properties with other optical methods, such as stable calibration, stable operation, and highly dynamic range with possible factory calibration. Gas Raman spectroscopy can be applied to all gas matrices and can analyze, apart from hydrogen, nearly all components in natural gas simultaneously within one minute, except for some higher hydrocarbon isomers of $C_5$ and $C_6$ alkanes [20]. An additional benefit in the future would be collecting information about the isotopic composition, namely H:D and $^{12}C$:$^{13}C$ ratios, respectively, to identify the reservoir or the origin of natural gas or to give information about the "color" of hydrogen sources (generated by electrolysis or after separation and deposition of $CO_2$ (CCS))[30][31][32].

The market-availability of a sensor with properties claimed by the manufacturer itself is no proof of the qualification of a sensor for a special purpose. There are many technical properties to consider, and these properties should be certified by an independent and approbated organization. National metrology institutes should be principal to establish competences for the qualification of hydrogen sensor technology. To the authors' knowledge, this did not happen up to now. It can be expected that the entire market for hydrogen applications and, simultaneously, the market for hydrogen metering sensors will expand rapidly in the next nears. Consequently, there will be an increasing need for performance testing of metering sensors soon.

## 5. Addresses of manufacturers

1) H2Scan, https://www.h2scan.com, 27245 Turnberry Ln, Valencia, CA 91355, USA
2) H2Sense, https://www.h2sense.com, NW2-601, Suzhou Nanopolis, No. 99 Jinjihu Road, SIP, Suzhou 215123, PR China
3) MeterQ Solutions GmbH, https://meterq.de, Robert-Bosch-Str. 10, 35510 Butzbach, Germany
4) RMG Messtechnik GmbH, https://www.rmg.com, Otto-Hahn-Str. 5, 35510 Butzbach, Germany
5) Elster Messtechnik GmbH, https://www.hongastec.de/produkte/messtechnik-honeywell-elster/, Osterholzstr. 45, 34123 Kassel, Germany
6) InProcess Instruments, https://www.in-process.com/start.html, Sophie-Germain-Str. 1, 28201 Bremen, Germany
7) ThermoFisher Scientific Inc., https://corporate.thermofisher.com/content/tfcorpsite/us/en/index.html, Ion Path, Road Three, Winsford, Cheshire CW73GA UK

**Table 1:** Overview of commercially available techniques for fast online measurements of hydrogen in natural gas:

| No | Manufacturer | Origin | Model | Technology | Application | Range* | Accuracy* | Response time* | Costs* |
|---|---|---|---|---|---|---|---|---|---|
| 1 | H2Scan | U.S.A. | HyOptima 5000 | Pd-resistive | process control, process monitoring | 0.5 % - 100 Vol % | < 1.5 % | < 90 sec | 15 k€ |
| 2 | H2Sense | China | Model 5100 | Pd-resistive | process control, process monitoring | 0.5 % - 100 Vol % | 1 % | ≤ 30 sec | 3 k€ |
| 3 | MeterQ GmbH | Germany | MCG-hydrogen | Gas chromatography | process monitoring metering | 0 % - 100 Vol % | < 1 % | 45 sec | 80 k€ |
| 4 | RMG Messtechnik GmbH | Germany | RMG 9304 | Gas chromatography | process control, legal metering | < 20 Vol % | < 1 % | 3-4 min | 99 k€ |
| 5 | Elster Messtechnik GmbH | Germany | Elster Quad | Gas chromatography | process control, legal metering | < 20 Vol % | < 1 % | 3 min | 98 k€ |

* Data from manufacturer

# 6. References

[1] The Twenty-first Session of Conference of the Parties (COP) and the Eleventh Session of the Conference of the Parties serving as the meeting of the Parties to the Kyoto Protocol (CMP) held 2015 in Paris, retrieved from https://unfccc.int/event/cop-21

[2] *Paris Agreement*, UN Framework Convention on Climate Change, archived from EUR-Lex, retrieved June 14th, 2023 from https://eur-lex.europa.eu/content/paris-agreement/paris-agreement.html?locale=en

[3] DIN 1871:1999-05, *Gasförmige Brennstoffe und sonstige Gase*

[4] ISO/TR 29922:2017-03, *Natural gas – Supporting information on the calculation of physical properties according to ISO 6976*

[5] *HyWay 27: hydrogen transmission using the existing natural gas grid?*: Final report for the Ministry of Economic Affairs and Climate Policy, PricewaterhouseCoopers Advisory N.V., Amsterdam 2021

[6] *Measuring systems for gaseous fuel,* International Recommendation OIML R 140, Organisation Internationale de Métrologie Légale 2007

[7] *Gesetz über das Inverkehrbringen und die Bereitstellung von Messgeräten auf dem Markt, ihre Verwendung und Eichung sowie über Fertigpackungen (Mess- und Eichgesetz MessEG)*, Bundesministerium der Justiz, Berlin 2015, retrieved from https://www.gesetze-im-internet.de/messeg/index.html on 06/26/2023

[8] Wiegleb, G., *Gasmesstechnik in Theorie und Praxis*, Springer Vieweg, Wiesbaden 2016

[9] ENTSOG *Roadmap 2050 for gas grids*, ENTSOG AISBL, Brussels 2019 (https://entsog.eu) p. 32

[10] DVGW G 260: *Technische Regel – Arbeitsblatt Gasbeschaffenheit (Gas Quality)*, Deutscher Verein des Gas- und Wasserfaches e. V., Bonn 2021, p. 25

[11] *H2Sense Hydrogen Sensor Database*, BAM Bundesanstalt für Materialforschung und -prüfung, Berlin 2015 (https://netzwerke.bam.de/_SharedDocs/DE/Downloads/Projekte/h2sense-database.html)

[12] Chen, K., Yuan, D., Zhao, Y., *Review of optical hydrogen sensors based on metal hydrides: Recent developments and challenges,* Opt. Laser Technol. **137** (2021), 106608. https://doi.org/10.1016/j.optlastec.2020.106808

[13] Hübert, T., Boon-Brett, L., Buttner, W.J., *Sensors for Safety and Process Control in Hydrogen Technologies,* CRC Press Boca Raton, London, New York 2018

[14] Jaeschke, M., *Realgasverhalten von speziell aufbereiteten Erdgasen,* Gas-Erdgas **146**(1) (2005), 58–63

[15] Wienecke, M., Godenrath, L., Zacharias, B., *Sensitivität und Selektivität optischer und neuartiger MEMS-Wasserstoffsensoren*: 20. GMA/ITG Fachtagung Sensoren und Messsysteme (2019) 256–263. https://doi.org/10.5162/sensoren2019/3.3.2.

[16] Flanagan, T.B., Oates, W.A., *The palladium-hydrogen system,* Ann. Rev. Mater. Sci. **21** (1991), 269–304. https://doi.org/10.1146/annurev.ms.21.080191.001413

[17] Avetisov, V., Bjoroey, O., Wang, J., Geiser, P., Paulsen, K.G., *Hydrogen sensor based on tunable diode laser absorption spectroscopy*, Sensors **19** (2019), 5313. https://doi.org/10.3390/s19235313

[18] Liang, T., Qiao, S., Liu, X., Ma, Y., *Highly sensitive hydrogen sensing based on tunable diode laser absorption spectroscopy with a 2.1 µm diode laser*, Chemosensors **10** (2022), 321. https://doi.org/10.3390/chemosensors10080321. Correction, ibid. **11** (2023), 41, https://doi.org/10.3390/chemosensors11010041

[19] Eichmann, S.C., Weschta, M., Kiefer, J., Seeger, T., Leipertz, A., *Characterization of a fast gas analyzer based on Raman scattering for the analysis of synthesis gas*, Rev. Sci. Instrum. **81** (2010), 125104. https://doi.org/10.1063/1.3521397

[20] Petrov, D.V., Matrosov, I.I., Zaripov, A.R., Tanichev, A.S., *Raman natural gas analyzer: Effects of composition on measurement precision,* Sensors **22** (2022), 3492. https://doi.org/10.3390/s22093492

[21] Stratmann, A., *Gleichzeitiger Nachweis unterschiedlichster Gase für Wasserstoff- und Erdgasversorger*, gwf Gas+Energie 163(3) (2022) 82–83

[22] Harr, K., Heffels, C., *Analyzer for measuring the composition of natural gas containing high amounts of hydrogen,* GAS Analysis Paris 2022, oral presentation

[23] Velasco-Rozo, E.A., Ballesteros-Rueda, L.M., Baldovino-Medrano, V.G., *A Method for the Accurate Quantification of Gas Streams by Online Mass Spectrometry*, J. Am. Soc. Mass Spectrom. **32**(8) (2021), 2135–2143. https://doi.org/10.1021/jasms.1c00090

[24] Anders, B., *15 Jahre Brennwert- und Normdichtebestimmung mittels Gaschromatographie im gesetzlichen Messwesen*, gwf Gas-Erdgas **147**(11) (2006), 663–672

[25] Zajc, A., *Gasbeschaffenheitsmessung in 45 Sekunden mit Hilfe der Prozessgaschromatographie*, gwf Gas+Energie **12** (2018), 52–60

[26] Snavely, K., Subramaniam, B., *Thermal conductivity detector analysis of hydrogen using helium carrier gas and HayeSep® D columns*, J. Chromat. Sci. **36** (1998), 191–196. https://doi.org/10.1093/chromsci/36.4.191

[27] Yao, W., *Analytical accuracy of hydrogen measurement using gas chromatography with thermal conductivity detection*, J. Sep. Sci. **38** (2015), 2640–2646. https://doi.org/10.1002/jssc.201500230

[28] Zhang, J., *Refinery gas analysis using the Agilent 990 Micro GC*, Agilent Application Note, Agilent Technologies Inc., Santa Clara CA 2019, retrieved from https://www.agilent.com/cs/library/applications/ on 06/26/2023

[29] Darmadi, I., Nugroho, F.A.A., Langhammer, C., *High-performance nanostructured palladium-based hydrogen sensors — Current limitations and strategies for their mitigation*, ACS Sens. **5** (2020), 3306–3327. https://doi.org/10.1021/acssensors.0c02019

[30] Korepanov, V.; Yu, C.-C., Hamaguchi, H., *Hyper-Raman investigation of intermolecular vibrations of water and ice*, J. Raman Spectr. **49**(11) (2018), 1742–1746. https://doi.org/10.1002/jrs.5459

[31] Griffith, D.W.T., Jamie, I., Esler, M., Wilson, S.R., Parkes, S.D., Waring, C., Bryant, G.W., *Real-time field measurements of stable isotopes in water and* $CO_2$ *by Fourier transform infrared spectrometry*, Isotopes in Environmental and Health Studies **42**(1) (2006), 9–20. https://doi.org/10.1080/10256010500503098

[32] Kääriäinen, T., Richmond, C.A., Manninen, A., *Determining biogenic content of biogas by measuring stable isotopologues* $^{12}CH_4$, $^{13}CH_4$, *and* $CH_3D$ *with a mid-infrared direct absorption laser spectrometer*, Sensors **18**(2) (2018), 496. https://doi.org/10.3390/s18020496