

LOW YET RELEVANT

An increasing number of applications rely on measurements of low gas concentrations. VSL produces primary reference materials to calibrate the equipment used for such challenging applications. To analyse both the primary reference materials and the pure gases used for their preparation, highly sensitive instruments are needed. For these purposes, VSL operates a growing number of laser spectrometers, both commercial and in-house developed instruments. These in-house developed instruments are presented here, as well as a number of their applications.

STEFAN PERSIJN

Introduction

In spectroscopy, electromagnetic radiation is directed onto a sample and the response to the stimulus is observed. One well-known spectroscopic method is laser absorption spectroscopy, where the laser wavelength is varied and the absorption of light by the sample is measured (Figure 1). This way, an absorption spectrum is obtained that provides direct information about the kind of molecules present in the sample and about their concentrations. Applications focusing on sensitive gas measurements typically use lasers in the infrared (IR) region, where many gases absorb strongly. To boost the sensitivity further, special measurement cells are used that can provide absorption path lengths up to many kilometers.

Reliable measurement of low concentrations of gases is key for monitoring the trends in greenhouse gases in atmospheric research, analysing purity of hydrogen for fuel-cell vehicles, or controlling the quality of high-purity gases applied in the semi-conductor industry. VSL produces primary reference materials to calibrate the measurement equipment used in these and many other applications (Figure 2). Frequently, highly sensitive instruments are needed to analyse both the primary reference materials and the pure gases used for their preparation. For these purposes, VSL operates a growing number of laser spectrometers, of which the in-house developed instruments are described below.

Spectrometers operated at VSL

Measurement of gases at low amount fractions ($\mu\text{mol/mol}$ and nmol/mol) requires the use of sensitive instrumentation.



Primary reference materials at VSL.

About 25 years ago, traditional measurement methods started to be replaced gradually by laser-based spectrometers for specific applications. The enabling factors for this were the rapid progress in laser technology and the invention of new, highly sensitive spectroscopic methods. Ten years later, VSL started to develop its own spectrometers for sensitive gas analysis. These systems combine a long optical path length with the use of mid-IR light sources, a wavelength region where many gases absorb strongly.

Optimum wavelengths

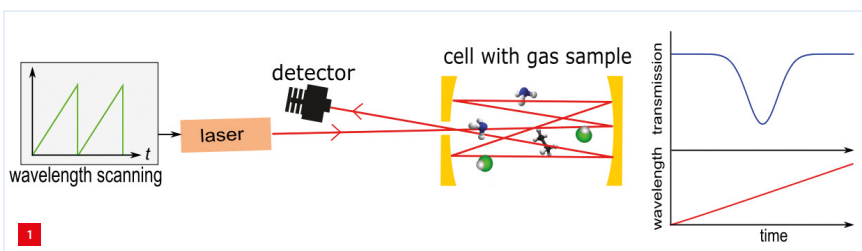
The IR wavelength region, and in particular the mid-IR spectral range ($2.5\text{-}25\ \mu\text{m}$), is highly suitable for sensitive gas analysis, as many gases show strong and characteristic absorption spectra in this region (Figure 3).

At VSL, two different kinds of tuneable mid-IR sources are used in the spectrometers: an in-house built optical parametric oscillator (developed in collaboration with the Radboud University in Nijmegen (NL)), which can tune over an extensive wavelength range ($2.3\text{-}5.1\ \mu\text{m}$); and several commercial quantum cascade lasers or interband cascade lasers, which can tune over a relatively narrow wavelength range. The tunability of a laser enables the recording of spectra that provide information on the IR-absorbing gases present in the gas sample.

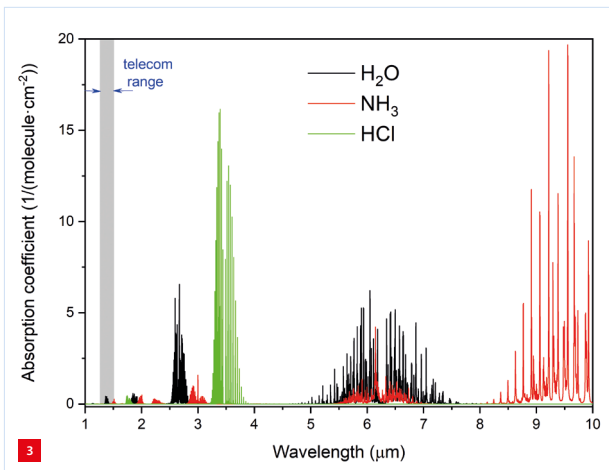
AUTHOR'S NOTE

Stefan Persijn is a scientist in the chemistry group at the national metrology institute VSL, located in Delft (NL). He develops sensitive laser-based spectrometers and applies these instruments in the field of gas metrology (mainly for environmental and energy-transition applications).

spersijn@vsl.nl
www.vsl.nl

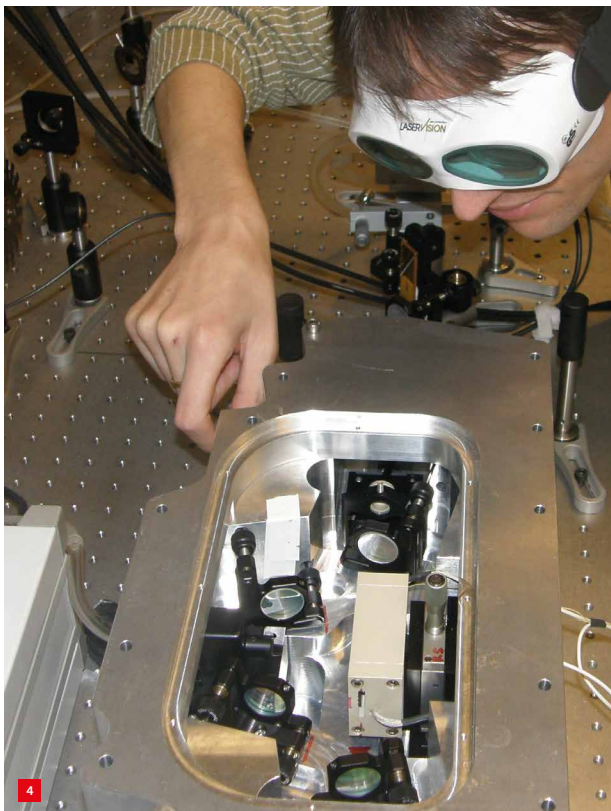


Principle of laser absorption spectroscopy.

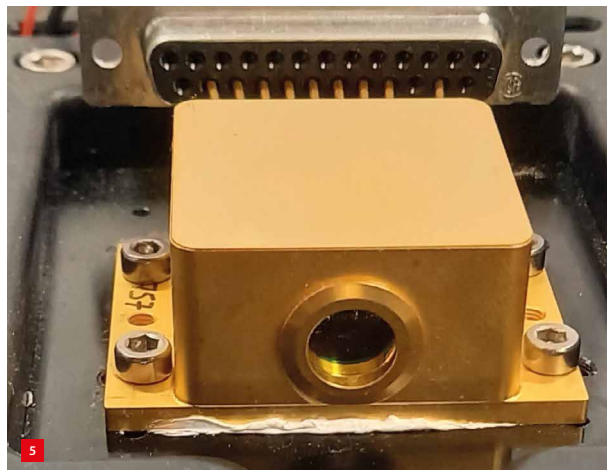


Examples of absorption spectra of gases in the near- and mid-IR wavelength region (simulation based on HITRAN database [1]). Commercial instruments typically use cheap diode lasers operating in the telecom region (part of the near-IR). The VSL spectrometers are based on mid-IR sources operating in the 2.3-10 µm region, where absorption by gases is typically 10 to 100 times stronger than in the near-IR.

An optical parametric oscillator (OPO) converts an input laser wave (called the 'pump') into two output waves with lower energy, known as 'signal' and 'idler'. The conversion occurs inside a nonlinear crystal in the OPO cavity (Figure 4). The OPO is pumped by a 10-W narrow-linewidth fibre laser operating at 1.064 µm. The signal wave (wavelength 1.34-1.98 µm) resonates in the OPO cavity. The idler beam (wavelength 2.3-5.1 µm) is used as a light source for the



OPO with the nonlinear crystal contained in a small oven inside the cavity.



A QCL operating in the 9,537-9,585 nm (1,049-1,043 cm⁻¹) range dedicated to the measurement of ammonia and methanol.

spectroscopic measurements. The OPO is housed in a solid aluminium housing and shielded from air currents, which results in a high passive stability of both the output power and the idler wavelength.

Many different gases can be measured due to the wide tuning range of the OPO. The high OPO idler output power (up to 3 W) also makes it a suitable source for techniques benefitting from high laser intensities, such as photoacoustic spectroscopy.

A quantum cascade laser (QCL) and an interband cascade laser (ICL) are both semiconductor lasers that emit radiation in the mid-IR (QCL and ICL) and even far-IR (QCL) wavelength region. Due to their compact size, such lasers are well suited for space exploration (an ICL has been used to measure isotopes on board of the Curiosity rover on Mars), while NASA plans to use QCLs to find water on the moon. The lasers operated at VSL have an output power of typically tens of mW and a narrow tuning range of a few wavenumbers (1 cm⁻¹ = 10⁻⁷ / nm), allowing measurement of typically one or two different gases.

Creating long optical path lengths

To obtain high sensitivity, the spectrometers constructed at VSL use measurement cells with a large effective optical path length. The cells can be classified into two main categories: classical multi-pass cells and cells for cavity-enhanced methods.

In direct absorption spectroscopy, the laser light transmitted by a cell containing the gas sample is measured using a photodetector. Typically, the laser is scanned at a high frequency (tens of Hz up to tens of kHz) over the gas absorption lines. An absorption spectrum is obtained by comparing the photodetector signals with and without absorbing gas inside the cell. To enhance the sensitivity of direct absorption spectroscopy, a multi-pass cell is used, which provides a relatively long absorption path. In classical

multi-pass cells, the light follows a geometrical path between mirrors (typically gold or silver coated).

Many different multi-pass cell configurations exist, including:

- Circular multi-pass cells in which the light propagates in a star-shaped pattern.
- Herriott cells, which are based on two mirrors of which one mirror contains a single hole for the input and output beam. These cells are typically equipped with spherically curved mirrors. The cell operated at VSL uses astigmatic mirrors (Figure 6). This configuration provides a better optical path length to cell volume ratio (here, 76 m for a cell volume of 0.5 L).

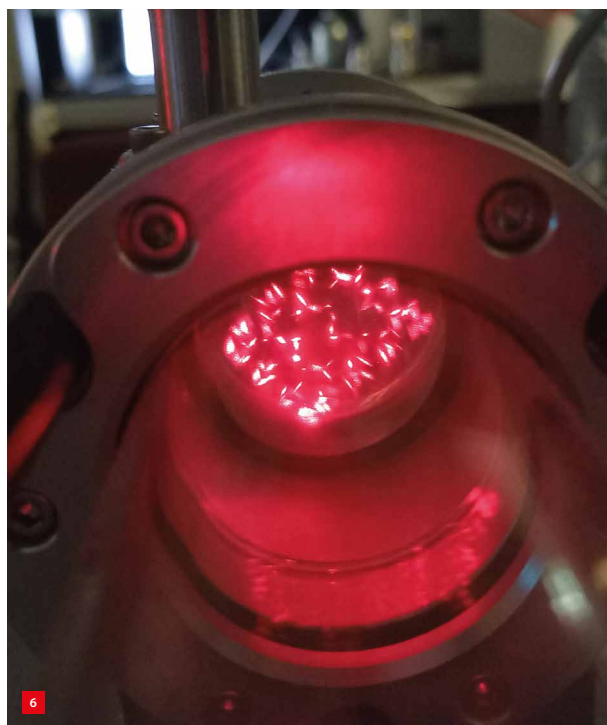
Cavity-enhanced methods for gas analysis were invented in the 1980s and 1990s. These methods can reach exceptionally large absorption path lengths (kilometers) in a compact measurement cell. The two main variants built and operated at VSL are:

- Cavity ring-down spectroscopy (CRDS):
The technique makes use of an optical cavity consisting of two highly reflective concave dielectric mirrors ($R \sim 99.99\%$ for the mid-IR wavelength region). IR laser light is coupled into the cavity. The intensity of light inside the cavity follows an exponential decay over time as some light leaks out of the cavity via the mirrors. This decay is monitored by measuring the light leaking out of the cavity using a fast photodetector. The time needed for the intensity of light to fall to $1/e$ of its initial intensity is called the ring-down time.

Without absorbing gas present inside the cavity, decay times up to about $20 \mu\text{s}$ can be achieved for a cell with a length of 50 cm. This corresponds to an optical path length of 6 km as light travels 300 m in $1 \mu\text{s}$. With an absorbing gas present inside the cavity, the decay will be faster (Figure 7). By measuring the decay time at different wavelengths, a spectrum is obtained. From this spectrum, the absorbing species can be identified and the amount fractions can be derived.

A big advantage of CRDS is the small cell volume of typically 0.1 L or less. Note that in the near-IR wavelength region, mirrors with higher reflectivity are available (R up to 99.999%), yielding optical path lengths up to even tens of kilometers.

- Cavity-enhanced absorption spectroscopy (CEAS):
The technique makes use of a similar cavity to that of CRDS. Here, the laser wavelength is rapidly swept at a rate of tens of Hz up to even kHz, and the light transmitted through the cavity is measured. This way, an absorption spectrum can be recorded rapidly (nearly real time), in contrast to the slower CRDS.



Spot pattern (made visible by a HeNe laser) inside a multi-pass cell using astigmatic mirrors.

Material compatibility

Reliable measurement of, for instance, impurities in new-energy gases is challenging due to the low amount fractions, as well as the reactivity of many gases. One example is ammonia, an impurity that needs to be monitored in hydrogen used to fuel cars, as well as in biomethane injected into the gas grid. Such reactive gases can react or adsorb while taking the gas sample, either in the tubing used to transfer the sample or in the measuring instrument itself. This can lead to long stabilisation times or, even worse, unreliable measurements.

Therefore, a careful choice of materials is essential for all these parts. Typically, polymer materials or stainless steel with a silicon-based coating are good choices [2]. In addition, all parts that are in contact with the gas are required to have a small internal volume and a small surface area.

These factors were taken into account in the design of the spectrometers developed at VSL. For instance, in the OPO-based CRDS spectrometer, all stainless-steel parts of the sampling system (mass-flow controller and tubings) and the CRDS cell have a silicon-based coating applied by chemical vapour deposition (Figure 8). This results in a good time response, even for some of the most difficult-to-handle gases, such as nitric acid.

Applications

The applications of the laser spectrometers at VSL are concerned mainly with the measurement of low amount

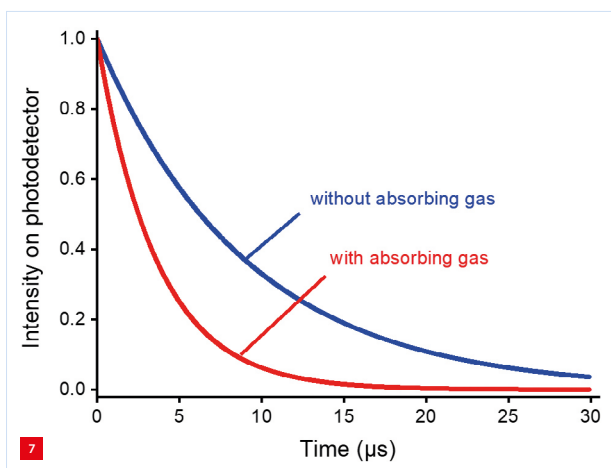
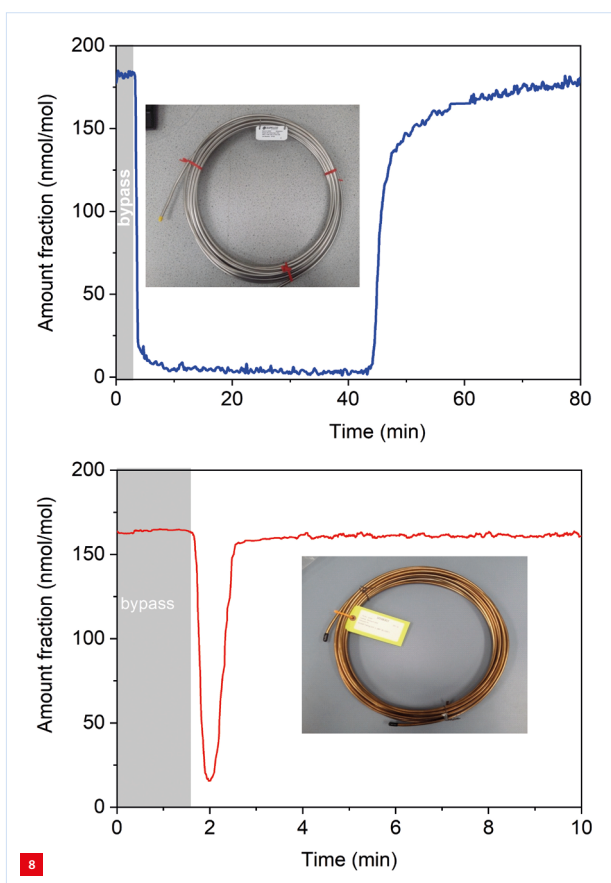


Illustration of the observed decay time with and without absorbing gas present in the measurement cell.

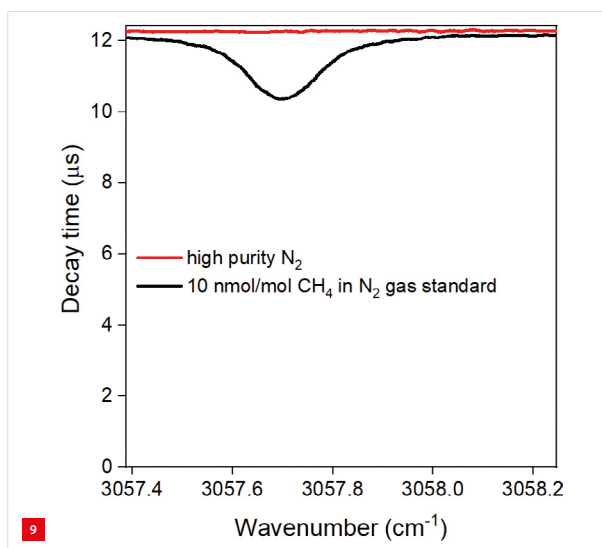
fractions and gases that are reactive. Here, two of these applications are discussed in more detail.

Purity analysis of gases for production of primary reference materials

Primary reference materials are used by the specialty gas industry and in fields such as custody transfer,



CRDS measurement of methanol going through a stainless-steel tubing without (upper panel) and with (lower panel) a silicon-based coating. When the tubing has not been coated, the methanol adsorbs strongly to the wall of the tubing, giving rise to long stabilisation times.



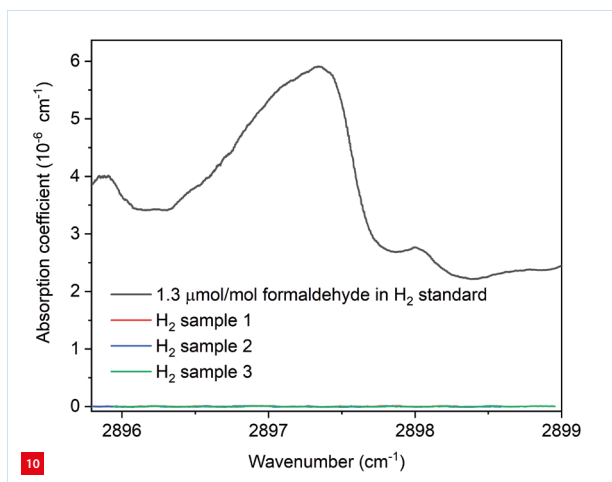
CRDS measurement of CH_4 in high-purity N_2 used for the preparation of primary reference materials, and of a 10 nmol/mol CH_4 in N_2 gas standard.

environmental monitoring and medicine, for calibration and quality control purposes. VSL produces primary reference materials by weighing the individual components into a clean cylinder. The gravimetric method, specified in ISO 6142-1 [3], is the most accurate method for preparing primary reference materials. The purity of the gases used to prepare the reference materials is critical, in particular when preparing reference gas standards at $\mu\text{mol/mol}$ or even lower amount fractions.

Specifications of the pure gases by the specialty gas industry are in some cases incomplete (i.e. one or more major impurities are not specified), but more often they are conservative, i.e. the actual amount fractions of the impurities are much lower than the specified amount fraction. VSL performs a rigorous analysis of the 'pure' gases used to prepare the primary reference materials (Figure 9). Consequently, primary reference materials with amount fractions down to 2 nmol/mol and with an expanded uncertainty down to 0.1% can be realised.

Measurement of impurities in new-energy gases

The electricity grid alone cannot support all current demands for energy. Already now, at the beginning of the energy transition, Dutch regions such as Noord-Brabant and Limburg are facing serious issues due to grid congestion [4]. Energy gases will therefore have to play a key role during the energy-transition phases and afterwards. Natural gas is the dominant energy gas, but in order to fulfil Europe's climate targets it will eventually be replaced by 'low-carbon' gases such as biomethane, biogas, synthetic methane and hydrogen [5]. Utilisation of these new-energy gases comes with a number of new measurement needs; here, some of these are discussed for hydrogen and biomethane.

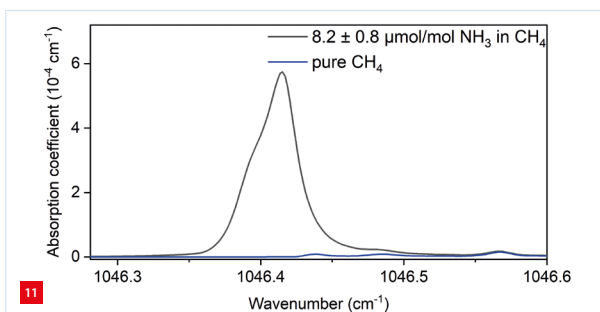


CRDS measurement of formaldehyde in H_2 samples produced by steam methane reforming. Also shown is a measurement of a formaldehyde reference gas standard. The amount fraction of formaldehyde in all H_2 samples is well below the ISO 14687 specification for fuel-cell vehicles of 200 nmol/mol (and even below the instrument quantification limit of 7 nmol/mol).

Hydrogen used for fuel-cell electrical vehicles (FCEVs) needs to be of very high purity, as impurities may impact the performance and lifetime of the proton-exchange membranes (PEMs) in an FCEV. For instance, trace amounts of carbon monoxide or hydrogen sulphide can poison PEMs severely. Hence, standardisation organisations have issued quality standards such as ISO 14687, for hydrogen at the dispenser nozzle [6] [7]. This ISO standard sets a minimum H_2 purity of 99.97%, a limit value for particulates and limit values for 14 gaseous compounds (or classes of gases) down to the 4 nmol/mol level!

In order to guarantee that the purity of the H_2 fulfils the purity regulations, both fit-for-purpose reference gas standards for calibration and fit-for-purpose measurement methods are needed. H_2 is the 'ideal' matrix for IR spectroscopy, as it does not absorb IR radiation and hence does not cause spectral interference (Figure 10). VSL has analysed 25 samples from two main H_2 production processes as part of a large European measurement campaign [8].

Biogas is a renewable fuel produced from the anaerobic digestion of organic matter, which after cleaning of impurities and upgrading is called biomethane. The EN 16723 standard regulates the use of biomethane for both injection into natural gas pipelines [9] and use in transport [10]. The specifications in these standards cover impurities such as carbon monoxide (CO) and ammonia (NH_3) [11] (Figure 11). Biomethane contains high amount fractions of methane and carbon dioxide, both strong absorbers in the IR. Therefore, a careful selection of the wavelength is needed for reliable measurement of the impurities.



Measurement of NH_3 in methane and of pure methane using direct absorption spectroscopy and a QCL-laser. The EN16723-1 specification for NH_3 is 10 mg/ m^3 (about 14 $\mu\text{mol/mol}$). Careful selection of the wavelength in combination with a low cell pressure (leading to a narrowing of the absorption lines) enables virtually interference-free measurement of NH_3 in biomethane.

Conclusions and future outlook

Laser spectrometers are now routinely operated at VSL to analyse the purity of gases used in the preparation of primary reference materials, to measure (reactive) impurities in new-energy gases such as hydrogen and biomethane, and in several other applications. An existing limitation is that only small molecules can be detected with good selectivity. Large molecules have relatively broad absorption features and thus cannot be selectively measured by lasers that have a relatively narrow tuning range. Recent advances in mid-IR laser sources covering a much broader spectral range, such as frequency-comb lasers and supercontinuum sources, will likely overcome this hurdle in the coming decade.

REFERENCES

- [1] Gordon, I.E., et al., "The HITRAN2020 molecular spectroscopic database", *Journal of Quantitative Spectroscopy and Radiative Transfer*, vol. 277, 107949, 2022.
- [2] Väitinen, O., et al., "Adsorption of ammonia on treated stainless steel and polymer surfaces", *Applied Physics B*, vol. 115, pp. 185-196, 2014.
- [3] International Organization for Standardization, "ISO 6142: Gas Analysis - Preparation of Calibration Gas Mixtures - Gravimetric Method", 2002.
- [4] capaciteitskaart.netbeheernederland.nl
- [5] Murugan, A., et al., "Vision for a European metrology network for energy gases", *Environmental Research: Infrastructure and Sustainability*, 2(1), 012003, 2022.
- [6] Beurey, C., et al., "Review and survey of methods for analysis of impurities in hydrogen for fuel cell vehicles according to ISO 14687: 2019", *Frontiers in Energy Research*, vol. 8, p. 615149, 2021, doi.org/10.3389/fenrg.2020.615149
- [7] ISO/TC 197 - Hydrogen Technologies, "ISO 14687 Hydrogen Fuel – Product Specification – Part 2: Proton Exchange Membrane (PEM) Fuel Cell Applications for Road Vehicles", 2019.
- [8] Bacquart, T., et al., "Hydrogen fuel quality from two main production processes: Steam methane reforming and proton exchange membrane water electrolysis", *Journal of Power Sources*, vol. 444, p. 227170, 2019, doi.org/10.1016/j.jpowsour.2019.227170
- [9] CEN (European Committee for Standardization), "EN 16723-1 Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network – Part 1: Specifications for biomethane for injection in the natural gas network", first edition, 2016.
- [10] CEN, "EN 16723-2 Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network – Part 2: Automotive fuels specification", first edition, 2017.
- [11] Culleton, L.P., et al., "Characterization of Fourier Transform Infrared, Cavity Ring-Down Spectroscopy, and Optical Feedback Cavity-Enhanced Absorption Spectroscopy Instruments for the Analysis of Ammonia in Biogas and Biomethane", *Analytical Chemistry*, vol. 94 (44), 15207-15214, 2022, doi.org/10.1021/acs.analchem.2c01951