Odorant verification using UV spectrometry for gas network safety

PETER KIENKE

Gas Quality, Odorization, Process Gas Analyzer & UV Spectrometry.

When extracted from the earth, natural & liquefied petroleum gases and hydrogen are almost completely odorless to human sense of smell. In order for potential leaks to be noticed and eliminated in a timely manner these gases are supplemented with an odorant (Odorized) in the gas distribution network. However how is this qualified? Well for the first time ever a New Process Gas Analyzer which uses UV spectrometry for the legally required odorization check has been produced.

1. Odorants and current verification processes.

The odorization of gas with strong-smelling substances and their monitoring is a varied subject, for this purpose there are a variety of different substances usually compounds containing sulfur which have to be added to the gas in different concentrations.

Table 1: Common odorizing substances with minimum concentration values in accordance with German Scientific and Technical Association for Gas and Water (DVGW) worksheet G 280 (see above)

THT	10 mg/m³
Acrylate-based sulfur-free odorants	8 mg/m³
Ethyl acrylate/THT mixture	6 mg/m³
THT/mercaptan mixture	3 mg/m³
Mercaptans	3 mg/m³ (natural gas)
	8 mg/m³ (liquefied petroleum gas)

Table 1 Shows the substances commonly used in Germany and their lower limit values. The dosing of odorants in natural gas is legally required and must be checked at regular intervals to determine the concentration of common sulfurous odorants like tetrahydrothiophene (THT) and tert-butyl-mercaptan (TBM) or the sulfur-free odorant Gasodor® S-Free in natural gas.

The challenge is to ensure the minimum concentration for achieving a sufficient warning odor for user safety while also ensuring economically frugal use of the odorant, these limit values must be regularly monitored in accordance with the legal specifications. The previous recommended standard technology for this is in German Scientific and Technical Association for Gas and Water (DVGW) worksheet G 280. Whereby gas chromatographs using the sequential separation of components in a separation column and subsequent verification by an electrochemical sensor is used, which due to its composition is not free of its own problems.

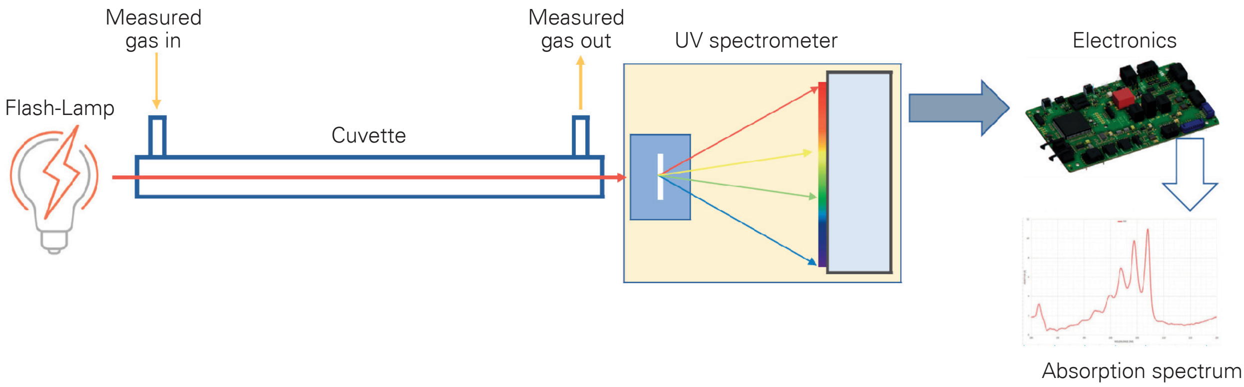


Figure 1: Schematic representation of UV spectroscopy

It is also cost intensive due to the consumable material used (carrier/calibration gas and chemicals). To achieve the required reproducibility adjustments must be made several times a day, with knowledgeable technicians is also required for operation of the devices.

DVGW worksheet G 280 does not exclude the use of alternative measuring processes thanks to the "commonly used gas chromatography" wording, which includes easy-to-perform concentration determination using electrochemical sensors.

The measured gas flows directly through these sensors. The gas entering the sensor generates an electrical measured value due to a chemical reaction. This technology is preferred in handheld devices for the compulsory verification of odorizing substances in use, but it is only accepted under certain conditions according to current rules. These sensors are less expensive, but exhibit problems with selectivity with some odorants. This represents a growing problem in light of the increasing addition of H2 to natural gas.

For this reason, network operators and gas suppliers see a need for another verification process which separates out the questionable components based on a stable physical process and can be integrated into modern process measuring devices with the usual features like automatic sequences, networking and Internet access.

2. UV spectrometry

In the industrial arena (Chemicals, Foodstuffs, Pharmaceuticals etc.), UV spectrometry is a tried tested and versatile routine process for the quantitative verification of countless substances.

This involves an optical measuring process which in principle does not measure poisoning or aging effects. Broadband UV radiation generated by a flash lamp is absorbed in the cuvette through which the gas flows, depending on the substance. A high-resolution UV spectrometer records the intensity spectrum created as a result.

In combination with cyclic measurement sequences between a reference gas and measured gas the absorption spectra can be determined based on this, from which the concentrations of the odorants can be calculated (Figure 1).

Sulfurous compounds THT and TBM used for odorization, as well as the sulfur-free Gasodor® S-Free, exhibited good absorption behavior at the required concentrations and therefore have high verifiability in laboratory tests carried out at the Engler-Bunte Institute (EBI) in Karlsruhe, Germany, among others.

Figure 2a-c shows the absorption spectra of the three common odorizing substances:

3. Measurement sequence and mathematical determination of concentrations

Two spectra are required for a measurement sequence, the first is the intensity spectrum recorded with a zero gas in the cuvette, and then a second spectrum is the intensity spectrum measured with the process gas in the cuvette.

In the first step, these spectra are checked for systematic errors and are standardized, allowing for measurement errors such as the saturation of individual lines to be detected. Standardization allows for compensation changes in the intensity of the emitter.

Figure 2:
Absorption spectra of various different odorizing substances in the UV range

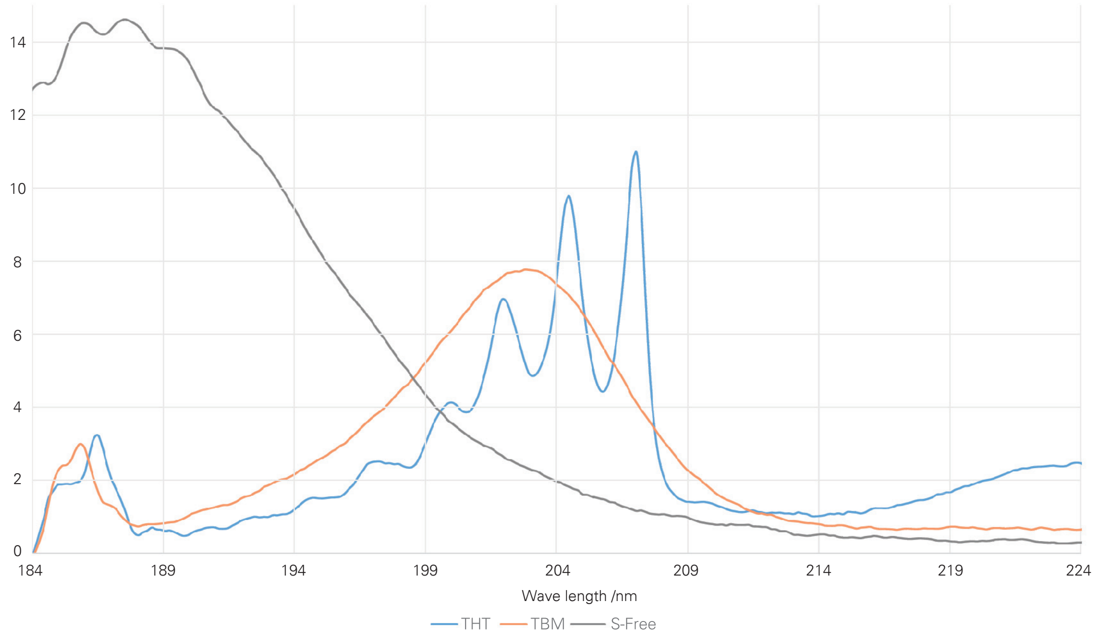
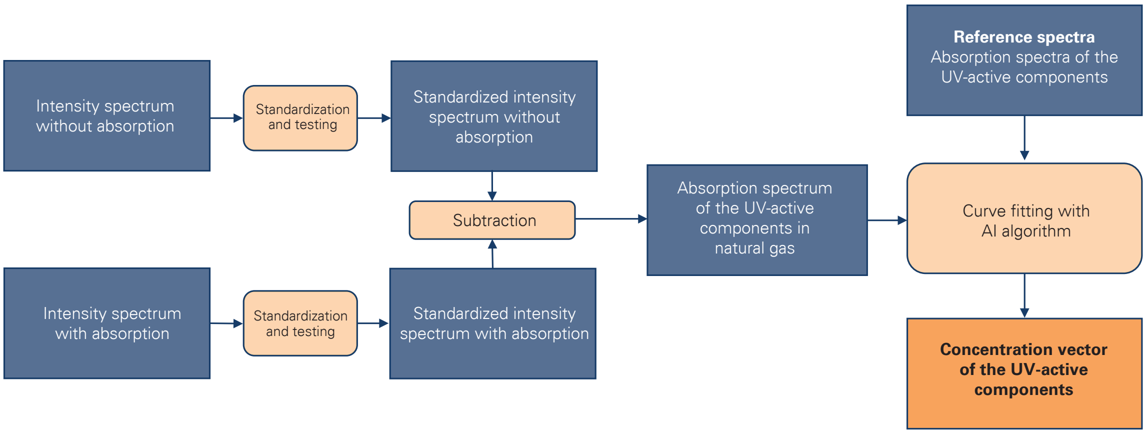


Figure 3:
Graphical representation of the mathematical sequences



By subtracting the standardized spectra, what you are left with is the absorption spectrum showing the absorption of all UV-active gases in the cuvette.
So, using a curve-fitting algorithm on this absorption spectrum, a concentration vector leads to the best possible representation of the measured absorption spectrum via superposition the reference spectra weighted with the concentration vector is determined.
The use of AI-based evaluation reliably prevents incorrect results and identifies unwanted cross-sensitivities, which is superior to the traditionally used matrix algorithms, as it prevents the calculation of negative concentrations, among other things **(Figure 3)**.

The functional structure of this UV sensor is shown in **Figure 4**: A flash lamp mounted directly to the cuvette generates a flash lasting a few nanoseconds which radiates through the measured gas within the cuvette.
A lens focuses the light onto a fiber-optic cable which directs it to the high-resolution UV spectrometer. In the spectrometer the different wave lengths of the light are separated via diffraction and mapped on a photodiode array which then a digital recording of the spectrum of radiated light is made. The data obtained is transferred to the electronics. The electronics determine the concentrations of odorants according to the sequence described above and corrected with the measured temperature and pressure of the gas in the measuring cuvette.

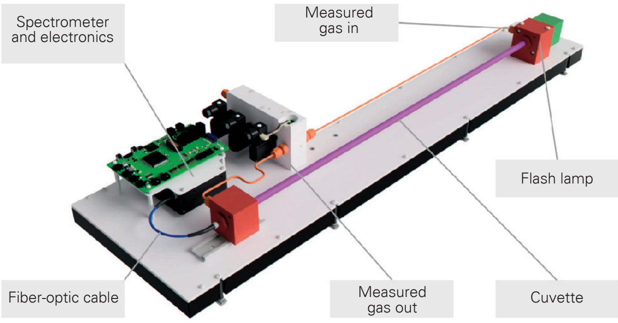


Figure 4: Structure of the UV sensor

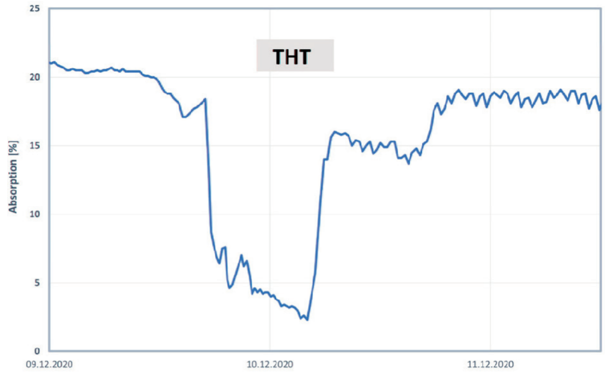


Figure 5: Concentration curve showing a problem with odorization

Combining this with an additional measuring process based on another physical measurement principles it is possible to expand the device into an evidential measuring device. This has been implemented very successfully for the TBM substance, which is very hard to detect due to its low concentration, but thanks to the integration of an innovative hydrogen-resistant and highly selective electrochemical sensor this can be achieved.
The result of such is an easy-to-install and easy-to-operate measuring device. The device boasts high operational reliability which can also be improved even further through the use of redundant measurement technology.

4. Experience from the field

UV spectrometry is verification-sensitive and a time resolving process, the test measurements carried out in the field showed consistent concentration curves for different odorants.
One test carried out in Mecklenburg-Vorpommern, Germany recorded a sudden drop in concentration of 20 mg/m3 (**Figure 5)**. Contact with the network operator revealed the cause was an odorization outage. This result showed that continuous monitoring of odorization increases the safety of natural gas, as detection of problems can be identified and remedied early on.

5. Summary

In many areas of industries, UV spectrometry is being used as a standard process for the reliable ascertainment of countless substances. It's also completely suitable for the verification of odorizing substances in natural gas, Biomethan and hydrogen in the field.

Long-term stability, a simultaneous measurement principle with immediate availability of results and poison resistance (both generally and in particular to hydrogen) are among the advantages typical of the process.
As part of its SIRA measuring device series, Union Instruments will be introducing a UV process gas analyzer for odorization monitoring to the market.

Author

Peter Kienke

UNION Instruments GmbH,
Director |
Phone: +49 721 680 381-0 |
info@union-instruments.com