Development of an IR-based Sensor for Natural Gas

Christoph Wagner, Wolfgang Ritter and Bernhard Lendl
Institute of Chemical Technologies and Analytics, Vienna University of Technology
A-1060 Vienna, Austria http://www.iac.tuwien.ac.at

Abstract

Scope: Investigation of the feasibility of an online sensor system for the detection of THT in natural gas.

Tetrahydrothiophene (THT) is added to natural gas on purpose to odorize it. The components of natural gas consist of 98 Vol% methane, larger hydrocarbons, carbon dioxide and nitrogen. Especially in the field of online measurement techniques IR spectroscopy has great potential because of its possibility for continuous measurements. This fact makes it the ideal choice for the online measurement of THT.

A hollow waveguide, with a polymer coating as its dielectrical layer, was used as a gas sample cell. This polymer layer shielded the silver layer from the sulfur gas stream. The usage of the hollow waveguide reduced the needed sample volume and increased the absorption pathlength.

An online adsorption system was developed and evaluated to increase the sensitivity of the sensor. The adsorption of natural gas was proven although no selective enrichment of THT could be achieved. To show the potential of the developed sensor system a linear calibration curve of THT in nitrogen was generated. The level of detection reached was of the magnitude of 13,5 ppmV. The linear range spans over the entire area measured from 13,5 to 670 ppmV.

Using the sharp emission line of the laser the detection of a narrow absorption line of THT in the gas phase will be achievable.

Response Time

A response time of 5 minutes was achieved. Since the measured response time includes the sample preparation time and the measurement time, an accurate statement of the measurement time can not be given yet.

Stability of the Waveguide

A sample gas stream with a concentration of approximately 1000 ppmV of THT was pumped through the waveguide over a period of 6 hours and the absorbance values for three different bands of THT were investigated. The experiment was repeated several times within 2 weeks and the light throughput of the waveguide did not decrease during this period. The stability of the waveguide against the sulfur gas stream was proven.

Calibration

The achieved LOD for the highest absorbance of THT was 13 ppmV. At the absorption band of interest (1448 cm⁻¹) the LOD was 29,3 ppmV.

In the figure below concentration values from different days are plotted to demonstrate the stability of the sample preparation method.

Selection of the Laser Wavelength

Due to overlapping spectral features of the sample matrix and THT in all spectral regions the measurement of THT with FTIR spectroscopy could not be achieved. To overcome this problem a Quantum Cascade Laser with an emission line of 1446,5 cm⁻¹ was selected. At this wave-number no interferences of THT and water vapour should occure.

Enrichment

To increase the sensitivity of the sensor system an online adsorption system was investigated. Electrical contacts were applied to a carbon monolith and the sample gas was purged over this monolith. The sample gas was adsorbed on the surface and after heating the carbon with electrical energy a desorption was achieved.

Unfortunately no selective enrichment of THT was obtained. But it appears that a separation of methane and ethane took place.

Conclusion

The measurement of 13 ppmV THT in a nitrogen gas stream were demonstrated by FTIR spectroscopy.

Using a QCL will allow the measurement of THT in natural gas without interferences as a result of its sharp emission line.

Because the effective light power of a QCL is up to three orders of magnitude higher than the power of a FTIR spectrometer the absorption length can be increased. This will allow the detection of 10 ppmV of THT.

Interpreting the gained signals from the QCL setup as "micro spectra" will permit the application of multivariate calibration models.