

# **Development of instruments suitable for measurement and optimization of harmful emission in gas industry**

*Summary of PhD thesis*

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## *Introduction*

The optimization of industrial processes in aspect of environmental protection comes to the front more and more as part of the integrated environmental policy. While in the past economy was the most important factor in optimization, nowadays environmental protection is equally important.

The Photoacoustic Research Group at the University of Szeged has been successfully developing instruments in cooperation with MOL Plc. for several years. The presented instruments were also developed upon the request of MOL Plc. They have been constructed for very different industrial applications; however, the purpose was the optimization of a given process in aspect of environmental protection in both cases.

In one case the task was to develop an instrument for analyzing the end products of a hydrogenation process. The purpose of these reactions is the conversion of long-chain waste hydrocarbons into utilizable liquid phase compounds. Side products are also formed during these reactions in gas phase; these are methane, water vapor, carbon-dioxide, carbon-monoxide and heavier hydrocarbons mixed into the hydrogen carrier gas. Most of these gases are greenhouse gases. Furthermore, methane is flammable, but its formation requires large amount of hydrogen, which is not economical. The parameters of hydrogenation, such as pressure or temperature can be changed and by the analysis of the end product, the process can be optimized. Consequently, it is sufficient to monitor the concentrations of the side products.

In second case an instrument was required for the determination of benzene and toluene emission of glycol regenerators. The natural gas contains BTEXs (benzene, toluene, ethylbenzene, xylenes; from that the most important are benzene and toluene) in  $\mu\text{g/l}$ - $\text{mg/l}$  range. The natural (wet) gas is contacted with monoethylene-glycol (called lean glycol) at some gas plants of MOL Plc. as part of natural gas pretreatment. Glycol functions as hydrate inhibitor in the gas cooled to  $-5^{\circ}\text{C}$ . The dry gas and rich (wet) glycol are separated. Rich glycol is led to a glycol regenerator, where it is heated to  $110^{\circ}\text{C}$  and its water content decreases from 30% to 20%. A part of water vapor condensates and is led to a slop tank, the other part releases to the atmosphere. BTEXs are very well soluble in glycol, so they accumulate in it. But they are very volatile; therefore majority of them leaves the regenerator with boiled water and most of them releases to the atmosphere.

This emission must be measured. A standard method to determine benzene and toluene emission has not been introduced yet. One solution can be the application of ARL („atmospheric rich/lean glycol”) method that calculates the emission from the measurement of volume flow rate and benzene and toluene concentration of lean and rich glycol. The efficiency of the whole gas pretreatment process can be examined, if the benzene and toluene concentrations of gases (besides glycols) are monitored.

## *Objectives*

My aim was to develop an instrument which is capable of continuous determination of the concentration of methane, carbon-monoxide and carbon-dioxide with 0.05 V/V% detection limit and water vapor with 0.01 V/V% detection limit in hydrogen carrier gas.

Moreover, my aim was to construct an instrument which is capable of quasi continuous measurement of the concentration of benzene and toluene in gas and liquid samples in explosive areas.

Sub-aims:

- selection and test of the selective measurement method, optimization of the measurement parameters,
- construction and calibration of the prototype and demonstration its field applicability,
- solving the incidental problems of the prototype,
- calculation of emission based on the measurements of the constructed instrument.

## *Applied methods*

### **1. Photoacoustic spectroscopy**

The principle of photoacoustic spectroscopy is the following: if a sample is illuminated with light modulated at an appropriate frequency and the sample absorbs part of the light, then the sample emits sound with frequency equal to the modulation frequency. First, the sample absorbs the light, then the illumination is interrupted and the extra energy is emitted as heat, which causes pressure increase. The excitation is periodic; consequently there is a periodic pressure change, which is sound.

A photoacoustic system suitable for measurements in gases contains a photoacoustic cell, in which the photoacoustic phenomenon takes place. Besides, a light source with possibly narrow bandwidth and stable light power is necessary which can be modulated. The sound is detected by a microphone. An important part of the system is the electronic unit which controls the laser and evaluates the signal with lock-in technique.

### **2. Gas chromatography**

Gas chromatography is a separation method which is based on dynamic partitioning of the components between a mobile (carrier gas) and a stationary phase. The components which bond better to the stationary phase pass through the system slower than which bond less. Therefore the components separate in time until the end of the column, which contains the stationary phase. The detector is located at the end of the column. The chromatogram is the signal of the detector represented as the function of time. The area under the curve is proportional to the concentration of the component.

## *New scientific results*

### **I. Development of an instrument suitable to measure methane, water vapor, carbon-dioxide and carbon-monoxide concentration in gas containing high amount of hydrogen**

It was necessary to develop a new photoacoustic cell instead of those generally used by the Photoacoustic Research Group at the University of Szeged, since the sound velocity increases because of the high hydrogen content of the measured gas compared to sound velocity in air/nitrogen/natural gas. I have used two diode lasers for multicomponent analysis.

Slight alteration of gas composition can change the sound velocity greatly because of its high hydrogen content. It has an effect on instrument response and operation of the diode laser.

*1. I have developed a photoacoustic instrument which is capable of multicomponent analysis in a gas containing high amount of hydrogen and having widely varying composition. I have worked out a method to control photoacoustic signal alteration originating from the measurement frequency change. The basis of the suggested method is the normalization of the signal by the transfer function of the corresponding resonator [1].*

Methane, water vapor and heavier hydrocarbons absorb at the wavelength tuning range of one laser and carbon-monoxide and carbon-dioxide absorb at the emission range of the other laser. I have selected the measuring wavelength for all of the measured components.

I have prepared gas mixtures containing 0-5 V/V% methane, carbon-monoxide, carbon-dioxide, ethane/propane and hydrogen as carrier gas to calibrate the system. I have controlled the water content by setting the dew point of hydrogen.

I have separated the microphone from the measured gas with a stainless steel membrane and I have calibrated the system with and without it. I have found that the system with membrane is appropriate in the aspect of long term stability.

*2. I have calibrated a photoacoustic instrument, which is suitable for multicomponent analysis, for four components. I have found spectral cross-sensitivity for methane,*

*water vapor and heavier hydrocarbons, which I have solved with measurements on three wavelengths. The minimum detectable concentrations are 0.13 V/V% for carbon-monoxide, 0.16 V/V% for carbon-dioxide, 0.06 V/V% for methane,  $3 \cdot 10^{-3}$  V/V% for water vapor and 0.09 V/V% for heavier hydrocarbons. I have proved suitability of the instrument under industrial conditions by measurements with gas chromatography [1].*

## **II. Determination of benzene and toluene emission of glycol regeneration units at gas plants**

Previous works of the Photoacoustic Research Group and my former measurement results shown that benzene, toluene and other natural gas components cannot be distinguished at the tuning range (2-3 nm) of a near infrared diode laser; therefore I have used chromatographic separation. The previously developed photoacoustic systems of the Photoacoustic Research Group are suitable for gas analysis, so I have converted the measured component from liquid to gas phase. I have used adsorbent to bring the sample instantaneously to the column.

I have optimized the parameters of the measurement (thermodesorption temperature of the adsorbent, temperature of the column, flow rate of the carrier gas). I have planned a system capable of achieving the required minimum detectable concentrations.

*3. I have developed a method, by which the benzene and toluene concentrations of natural gas and monoethylene-glycol samples can be determined in the range of 5-1000  $\mu\text{g/l}$  and 5-500  $\text{mg/l}$ , respectively. It is a gas chromatograph, in which I have applied nitrogen as carrier gas, Carbotrap adsorbent for sampling, bis-methoxy-ethyl-adipate on Chromosorb as stationary phase. The detection was made by photoacoustic spectroscopy. I have used bubbling extraction to carry the measured components into gas phase from glycol samples [2].*

I have calibrated the prototype for benzene and toluene both in gas and in glycol. In the case of gas the volume of natural gas or nitrogen sample was 1 l, with which I have forwarded a given amount of benzene or toluene to the adsorbent. In the case of glycol the volume of the sample was 1.5 ml, which the instrument has sampled from a 0.5 l stock

solution in which the concentrations of benzene and toluene have been increased gradually.

***4. I have calibrated the automatic prototype, which was made on the basis of the measurement method introduced in point 3. The calibration was performed for both benzene and toluene in natural gas and also in monoethylene-glycol. I have found that the sensitivity is independent of the carrier gas, which carries the measured components to the adsorbent. It can be nitrogen, air or natural gas. Minimum detectable concentrations in natural gas were found to be 2.5 µg/l for benzene and 4 µg/l for toluene, while 1.5 mg/l for benzene and 3 mg/l for toluene in glycol. I have proved suitability of the instrument under industrial conditions by measurements at a gas plant of MOL Plc. [2].***

The gas sampling was made by a mass flow controller in the prototype; however, its operation depended on the gas composition. Since the gas composition can change widely, therefore the volume of the gas sample was not constant; nevertheless it is a requirement for correct measurements. The volume of the gas sample can be made constant with a piston pump if the pressure is constant (atmospheric). Besides, it can be used in explosive areas if it has pneumatic operation and control.

During field measurements I have experienced that the binding capacity of the used absorbent depends on the temperature, especially for benzene; therefore I have exchanged it. During laboratory measurements it has come to light that the bubbling extraction is temperature-dependent, too.

***5. I have improved the instrument introduced in point 4 to be suitable in explosive areas. I have applied a pneumatic controlled piston pump to gas and glycol sampling. It has assured that the volume of the gas sample is constant and independent of its composition, and that the sampling is explosion proof. I have minimized the temperature dependence of sampling by exchanging the adsorbent from Carbotrap to Carbotrap X and by temperature stabilization of glycol-air contactor. I have proved suitability of the further developed instrument under industrial conditions by measurements at a gas plant of MOL Plc. [3, 4].***

The instrument which can be used in explosive areas has been built with cooperation of Videoton Holding Plc. I have calibrated it in the same manner as the prototype; the only difference was that the volume of the gas (natural gas or ambient air) sample was 0.7 l, and the volume of the glycol sample was 2 ml.

The instrument was installed at a gas plant of MOL Plc., where it was operating for several months. I have calculated emission based on the measured data.

***6. I have calibrated the instrument, which has Ex Certificate of Conformity and is capable of measuring benzene and toluene concentrations of gas and liquid samples, in both natural gas and monoethylene-glycol for both components. Minimum detectable concentrations in natural gas were found to be 2 µg/l for benzene and 3 µg/l for toluene, while 5 mg/l for benzene and 6 mg/l for toluene in glycol. I have proved suitability of the instrument under industrial conditions by measurements at a gas plant of MOL Plc. [4].***

### ***Papers related to the present thesis***

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2. V. Hanyecz, Á. Mohácsi, S. Puskás, Á. Vágó, G. Szabó: Photoacoustic spectroscopy-based detector for measuring benzene and toluene concentration in gas and liquid samples; *Measurement Science and Technology* 22 (2011) 125602  
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***Presentations, posters, exhibitions and awards related to the present thesis***

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6. Photoacoustic spectroscopy based instrument for measuring benzene and toluene emission of glycol regenerators; “InnoMatch”- Regional Innovation Fair (Arad, 3-4 April 2013)
7. V. Hanyecz, Á, Mohácsi, S. Puskás, Á. Vágó, G. Szabó: Field-usable detector for determining benzene and toluene in gas and liquid samples, Első közép- és kelet-európai nemzetközi olaj- és gázipari konferencia (2011)
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