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Evaluation of a Colorimetric Sensor System for Early Fire Detection †

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Abstract: The use of colorimetric reactions as a sensitive, selective and low-cost method for the detection of fire related gases is evaluated in this work. As the most relevant fire gas carbon monoxide CO is addressed in the first place. A rhodium-based metal-organic complex has been selected, which a colorimetric material sensitive for CO. For the optical readout a compact setup has been developed which provides the option for spectroscopy in transmission and attenuated total reflection in parallel. The detection of CO in concentrations relevant for fire detection has been demonstrated in synthetic gas mixtures as well as in real fire gas.

Keywords: gas sensor; colorimetry; carbon monoxide; fire detection

1. Introduction

A complex mixture of various compounds can be detected in fire gases, where composition and concentrations are depending on the materials involved and the various additional parameters like temperature and oxygen concentration. Especially, toxic gases like CO and NO_2 are of emerging interest, since they arise in an early stage of fire often earlier than aerosols and smoke. Therefore, they provide a mean for improved early fire detection [1].

Nevertheless, the chemical species in fire gases which is generated in concentrations accessible with available sensor technologies are limited [2]. CO as a main target gas for fire detection is evaluated in this work. For the detection of CO in fire detectors, electrochemical cells are already used in commercial products and European standards exist for their qualification, but their range of application is restricted by lifetime and price. An additional challenge is the low concentration range of CO particularly in early fire detection. For recognition of evolving fires, CO concentrations have to be detected typically in the range <10 ppm.

Colorimetric reactions have already been identified as a promising technology for the detection of fire related gases [3]. Various rhodium-based metal-organic complex compounds exhibit a fast, selective and reversible reaction towards CO [4]. A system for detection of CO comprising highly sensitive and selective colorimetric materials combined with a compact optical readout could provide a low-cost approach for early fire detection and is presented here.

2. Materials and Methods

For the evaluation of the detection characteristics in fire gases, a compact optical system has been developed (Figure 1). It consists of a compact spectrometer in the UV/Vis range (BWTEK Compass™ X), a UV/VIS light source (Ocean Optics HL-2000) and a measurement cell, which is designed to allow the readout of colorimetric samples in transmission or attenuated total reflection (ATR) mode. The light source and the spectrometer are coupled to the test chamber by appropriate optical fibers. Spectra have been recorded in the wavelength range from 200 nm to 800 nm at a time interval of ten seconds. Spectral data is presented as absorbance according to the Beer-Lambert law.

Test gas with defined CO concentrations in humidified air has been provided by an automated test bench with a total flow of 1 L/min at a relative humidity of 40%.

In order to monitor the actual CO concentration, a FTIR gas analyzer (Ansyco DX4015) has been used, while commercial electrochemical CO sensors (Nemoto NAP-505) have been included for comparative studies. Fire tests have been performed in a fire test room under conditions closed to the related standard EN54. Fire gas has been extracted on the ceiling at a height of 4 m.

The colorimetric material used for CO detection is based on a binuclear rhodium complex as described in [5]. Colorimetric dyes have been applied on glass slides with a size of 28 × 8 × 1 mm with a film thickness of typically 3 µm.

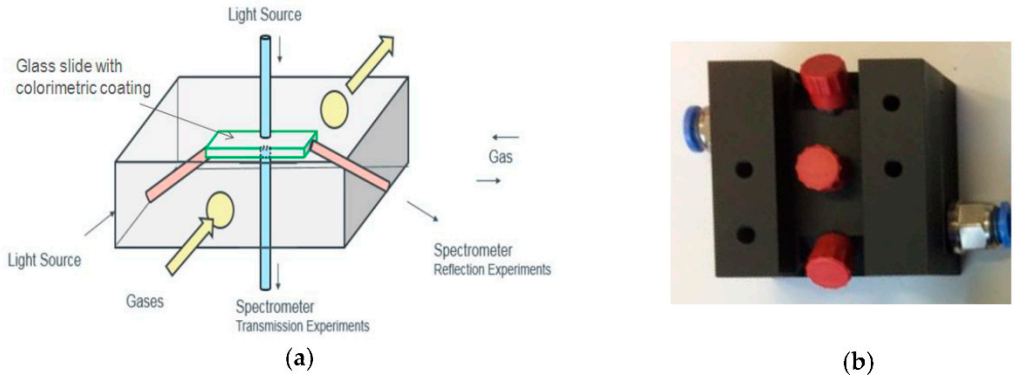


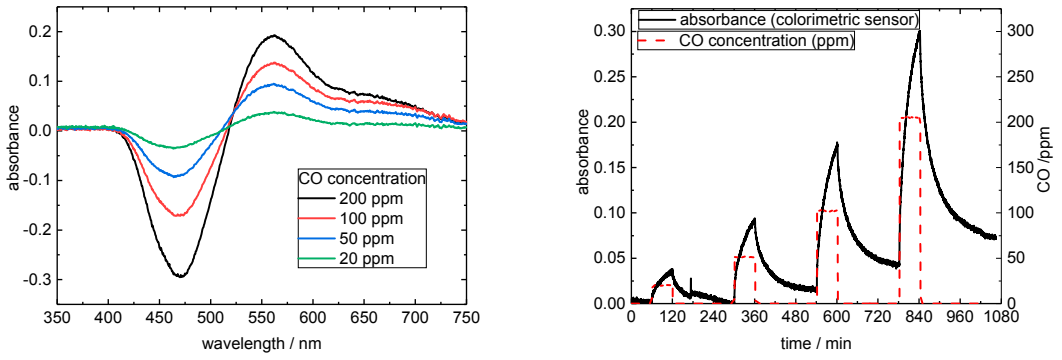
Figure 1. Experimental setup for the optical readout of colorimetric materials. (**a**) schematic depiction of the optical measurement cell; (**b**) Photograph of the combined transmission/ATR measurement cell in top view, optical connectors with red covers, gas inlet with blue connectors.

3. Results

The spectral response of a binuclear rhodium complex to CO in varying concentrations is presented in Figure 2a. The strongest response to CO is observed at wavelengths in the range of 470 nm and 550 nm. The transient response of a colorimetric sample in ATR mode at a wavelength of 470 nm to varying CO concentrations in synthetic air at 40% relative humidity is presented in Figure 2b. A clear immediate response to CO can be seen even at low CO concentrations, although the time to reach an equilibrium state is in the hour range for response and recovery.

The difference in sensitivity to CO of a colorimetric sample between the optical readout in transmission and ATR mode is given in Table 1. By using the ATR mode, the sensitivity to CO has been increased by a factor >20, while the noise level is not changed significantly. Therefore, all further investigations have been performed in ATR mode in order to obtain the optimum signal quality.

The response of a colorimetric sample in ATR mode to the gases evolving from a smoldering wood fire according to test fire TF2A, as described in EN54, is compared to the corresponding CO concentration detected by and electrochemical (EC) sensor, see Figure 3a. A clear response in the colorimetric signal can be seen already in the onset of the smoldering fire 10 to 15 min after the experiment has been started, where also the first onset of the response of the electrochemical sensor at CO concentrations <1 ppm is observed. The slightly earlier response of the colorimetric system can be related to a response of the dye to other fire-related gases which occur in an earlier phase of the emerging fire than CO.



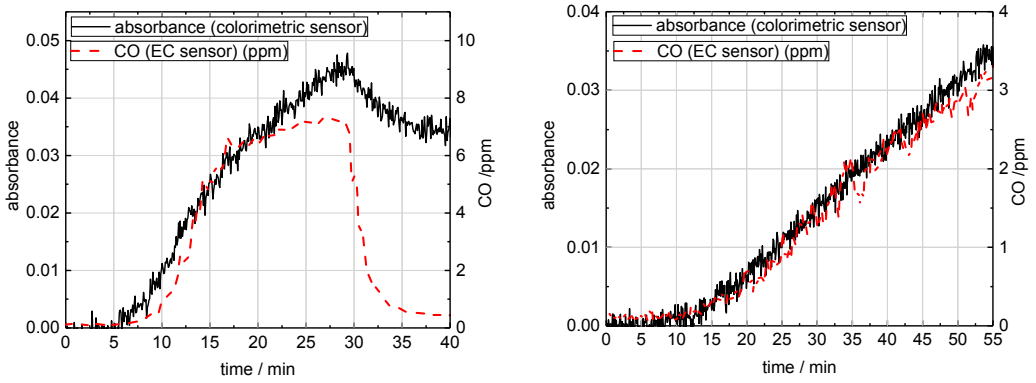
(**a**) (**b**)

Figure 2. (**a**) Spectral response of a binuclear rhodium complex to CO concentrations from 20 ppm to 100 ppm in ATR mode; (**b**) Transient response of a colorimetric sample to CO concentrations in the range from 20 ppm to 200 ppm in ATR mode at 470 nm.

Table 1. Comparison of the sensitivity to CO in transmission and ATR mode.

Optical Setup	Sensitivity [1/ppm]
Transmission	2×10^{-5}
ATR	5×10^{-4}

For a very slowly evolving fire, the transient response of the colorimetric sample over time is very similar to the increase of the CO concentration (Figure 3b).



(**a**) (**b**)

Figure 3. Comparison of the response of a colorimetric sample in ATR mode at a wavelength of 470 nm and the measured CO concentration (**a**) to gases from a smoldering wood fire type TF2a as described in EN54; (**b**) to gases from a slowly evolving smoldering wood/plastics fire.

4. Discussion and Conclusions

The detection of CO as target gas for early fire detection has been demonstrated with a compact spectroscopic system using a binuclear rhodium complex as CO sensitive dye. The direct comparison of transmission and ATR spectroscopy reveals a clear advantage of the ATR setup regarding the obtained signal quality. In fire tests, a colorimetric response has been obtained, which allows the detection of low CO concentrations of <10 ppm in real life environments as required for early fire detection.

As next steps, the spectral response of colorimetric materials to CO, NH_3 and NO_2 as fire related gases will be evaluated and the use of partial least square analysis for interpretation of the spectra will be investigated. Further investigations are directed to optimize the sensor setup and to select wavelengths for light sources and sensors suitable for a lowcost sensor system.

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Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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