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Detection of Hydrogen Peroxide (H_2O_2) at Exposed Temperatures for Industrial Processes

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Abstract: An H_2O_2 sensor for the application in industrial sterilisation processes has been developed. Therefore, automated sterilisation equipment at laboratory scale has been constructed using parts from industrial sterilisation facilities. In addition, a software tool has been developed for the control of the sterilisation equipment at laboratory scale. First measurements with the developed sensor set-up as part of the sterilisation equipment have been performed and the sensor has been physically characterised by optical microscopy and SEM.

Keywords: Gas sensor, hydrogen peroxide, sterilisation, catalytic decomposition.

Introduction

For the sterilisation of enclosures in which products, like food, medical equipment and drugs are handled or packaged, there exists a manifold of methods including superheated steam, dry heat, radiation, and aqueous and gaseous sterilants such as formaldehyde, glutaraldehyde and ethylene oxide. Due to some benefits, in the last years, the use of hydrogen peroxide vapour (HPV) as sterilant became more relevant [1,2]. Hydrogen peroxide (H_2O_2) spontaneously decomposes to the harmless products of water and oxygen unlike formaldehyde, glutaraldehyde and ethylene oxide, which pose hazards to the environment and operating personnel. Due to the effectivity in terms of antimicrobial activity and the environmental sound behaviour, the sterilisation with HPV is widely used in common aseptic packaging plants [3]. The advantage of HPV over H_2O_2 liquids is the cost-saving principle due to lower concentrations of H_2O_2 used by the HPV method. Therefore, the consumption of H_2O_2 by using the liquid method is about three times higher than applying the vapour method [4]. For the HPV sterilisation, the package or sterilisation good is placed under a continuously flowing vapour stream. The microbial kill rate depends on the time at which the package is placed under the stream, the H_2O_2 concentration, the temperature, the humidity and the massflow of the stream. In industrial processes, the retention time is fixed (< 1 s) and the parameters, like temperature (> 200 °C) and H_2O_2 concentration (1-15 Vol.%) are adjusted by using statistical methods with a set of control samples of the sterilisation good. It is perspicious that a regulation of the sterilisation equipment with such an extensive method is not possible and the realisation of a low-cost H_2O_2 sensor for such rude conditions is essential.

Beside a series of electrochemical sensors for the liquid phase, like amperometric or potentiometric sensors, there are only a few concepts for measuring H_2O_2 in the gas phase. For the amperometric detection, a working electrode (Pt, Au, Pd, carbon fibre) has to be polarised on a potential of 0.7 to 0.8 V against a standard reference electrode [5-7]. The measured current flowing through the measurement chain is proportional to the H_2O_2 concentration. One drawback of this arrangement is the interference with those analytes, which are also electroactive in this potential range. For reducing such interference problems, the electrodes can be covered with additional membranes [7-9] and the electrodes themselves can be modified with different catalysts [10-12], or alternatively new materials for the working electrodes can be used [13]. The selectivity can also be improved by using biological catalysts, like catalase and horseradish-peroxidase. To solve the problem of measuring H_2O_2 in the gas phase, an additional layer has to be applied between the reference and working electrode. These membranes, like ion-carrier membranes, Nafion, poly-HEMA and solid-state electrolytes collect the analyte and work as supporting electrolyte [3,14-17]. Different combinations of these concepts are suitable for low concentrations of H_2O_2 and especially, for low temperatures (room temperature) but not adequate for the given conditions in HPV sterilisation plants. Temperature-resistant methods are the testpaper method, UV-photolysis, photometry [18], colorimetry and the application of metal-oxide semiconductor-sensors. For the testpaper method, a paper is treated with a reagent, so that a colour change appears when the testpaper is in contact with H_2O_2. This colour change can be detected with usual spectroscopic methods. The main disadvantage of such chemoindicators is the response time of the colour-changing process, which can be up to 12 min. [19], so that an on-line measurement is not yet possible. The UV-photolysis, the photometry and colorimetry are representing cost-intensive

methods, whereby the UV-photolysis is very unspecific. For this method, OH-radicals are generated by UV-light and detected by fluorescence measurements. As one can see, all molecules whose dissociation energy is lower than that of H_2O_2 will be dissociated and may be detected.

Due to the high costs of the measurement equipment, all these methods are not appropriate for an on-line detection of H_2O_2 in industrial processes. In contrast, metal-oxide gas sensors might be very useful for their usage as H_2O_2 sensor, since they have to be heated with an internal heater. On the other hand, they are very sensitive to humidity variations and have to be calibrated by performing measurements with all combinations of temperature, humidity and H_2O_2 concentrations that are possible within the sterilisation recipe. Additionally, temperature compensation should be inserted [20-22]. All these methods exhibit possible methods for the measurement of H_2O_2, but most of them have high restrictions with regard to the temperature used during HPV sterilisation, the required H_2O_2 concentration, selectivity and costs.

The aim of this work is to develop a new type of H_2O_2 sensor for the gas phase to perform on-line measurements under real-time conditions. Therefore, an automated sterilisation equipment at laboratory scale has been constructed in order to perform experiments with the developed new sensor type. The detection principle of the sensor takes benefit on the exothermic decomposition of H_2O_2. While H_2O_2 decomposes to water and oxygen, it leads to an enthalpy change of -98 kJ/mol, which should be measured quantitatively by the sensor device.

Experimental

Sterilisation equipment

In order to perform sensor tests under conditions, like in industrial processes, the sterilisation equipment at laboratory scale has to be similar to those in industrial packaging facilities. In addition, equivalent parts for the simulation of failures in the sterilisation process have to be included. The block diagram of the sterilisation apparatus is shown in Fig. 1.

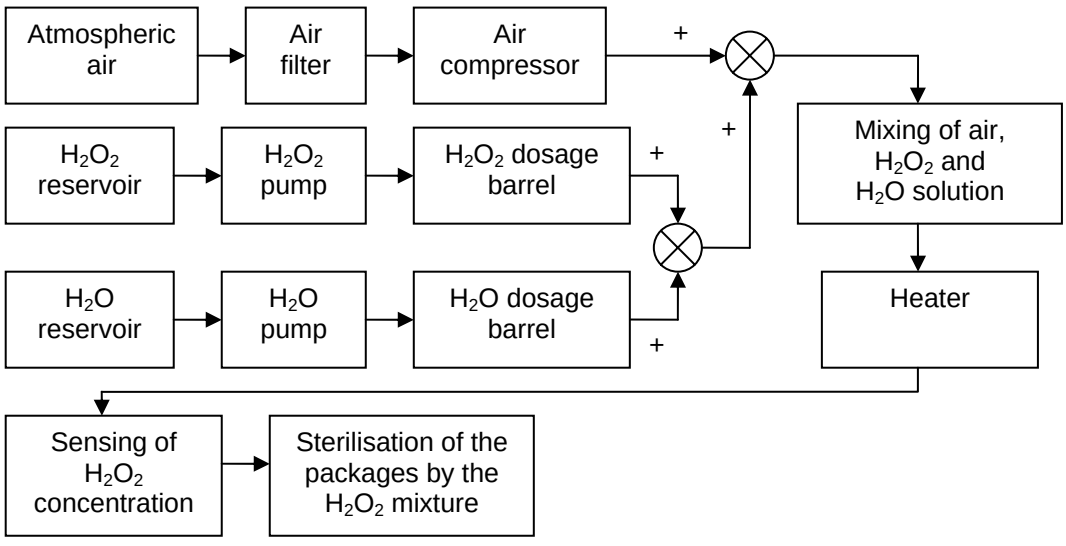

Figure 1. Block diagram and principle of the sterilisation apparatus.

As sterilant, 35% H_2O_2 solution (stabilised) was used, which was feed through a dosage barrel into the carrier stream (air) and then, the aerosol was heated up to > 200 °C, so that the whole mixture was in the gaseous phase. This sterilisation gas was then feed in a distributor, where the gas was flowing through several sterilisation pipes under which the sterilisation good can be placed. In the case of testing the sensor, an additional exhaust was positioned under the sterilisation pipes. As already mentioned before, for the simulation of failures, different water concentrations can be additionally added, and the massflow and the temperature of the gas can be varied. To control the sterilisation equipment, a software tool has been developed that allows to operate up to eight analogue channels, where the data can be read out and the equipment can be adjusted to defined input values.

Fig. 2 shows a photograph of the user interface of the realised software tool. At the left side, the parameters of the DAQ (Data Acquisition) card can be changed and the data can be stored; moreover, the parameters of the spreadsheet file can be prompted. At the right side, the analogue input channels can be chosen and named, and the counter output for the dosage barrels can be chosen. In the upper part of the user interface, the dosage barrels can be switched on and off and the concentration of added H_2O_2 solution or water in µl/s can be adjusted by a list or by the user's input. To control the dosage barrels for the H_2O_2/H_2O mixture, a frequency is feed through an optocoupler to the sterilisation apparatus. The frequency is proportional to the current H_2O_2/H_2O content and therefore, to the concentration in the sterilisation pipe; the frequency is fixed by the 20 MHz onboard clock of the DAQ card.

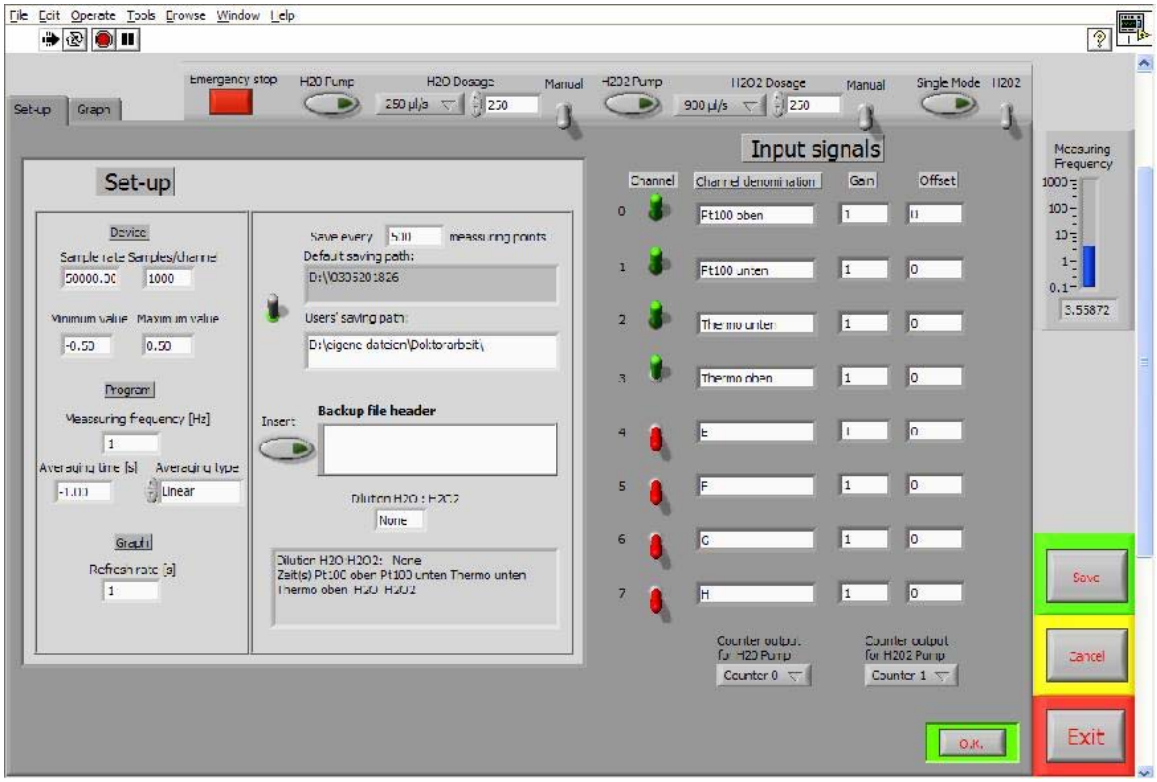

Figure 2. User interface of the developed software.

The dosage barrels, the heater and the distributor were identical to those used in industrial packaging plants; they were made of stainless steel. To apply the sensors to the sterilisation pipes (where the H_2O_2 concentration is of interest), self-made adaptors have been constructed to fix different

types of sensors into the pipes. Additionally, measuring cells, which can optionally work as diffusion cells, can be applied. With this set-up it is possible to vary the H_2O_2 concentrations from 0 Vol.% up to 20 Vol.% with different concentrations of water, and with varying temperatures and flow rates.

Sensor set-up

As sensor set-up, an array of temperature-sensitive PT100 thermistors or thermocouples has been chosen as transducer materials. Ideally, these stainless steel-covered temperature sensors possess no catalytic activity by themselves. Due to the contamination with dust particels or undesired corrosion, it is necessary to clean and passivate the steel; this has been done by rinsing them in liquid H_2SO_4 and then placing them in H_2O_2 solution. To realise a H_2O_2-sensitive temperature sensor, the thermistor and thermocouple are covered both with a catalytically active layer (with a defined activity) that has been fabricated by heating the transducer structure up to 400 °C and then, putting a droplet of $HMnO_4$ on its surface. By placing the transducer structure for 2 hours at 450 °C in an oven, a layer of Mn_xO_{x+1} is grown. After the baking process, the resulting sensor has been washed in 35% H_2O_2 solution and then, been wiped with a tissue. With this cleaning process, redundant grains will be removed from the sensor surface. In Fig. 3, an array of temperature sensors is depicted. Here, the upper and the lower sensor are representing reference sensors that were placed in measuring cells. In the middle part, the H_2O_2-sensitive temperature-sensor device is fixed with a pipe clamp.

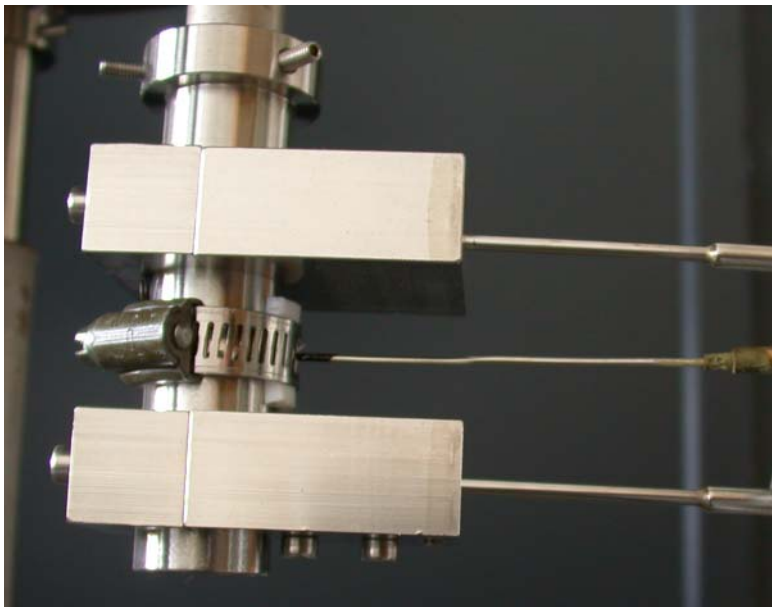

Figure 3. Array of three temperature sensors in measuring cells which can optionally used as diffusion cell.

Fabricated H_2O_2 sensor

The H_2O_2-sensitive temperature sensor has been physically characterised by optical microscopy and by SEM (scanning electron microscopy). Fig. 4 exemplarily shows a photograph of an H_2O_2-sensitive thermocouple. The length of the steel-covered thermocouple is 120 mm and the catalytic layer covers about 1/3 of the sensor surface on the left side.

Figure 4. Photograph of the H_2O_2-sensitive temperature sensor.

Fig. 5 presents a corresponding SEM image of the developed H_2O_2 sensor. It can be seen that the surface is grainy without any porosity. The SEM investigations could validate that the catalytically active layer has a thickness of about 0.4 µm and the composition is about 50% MnO_2 and 50% Mn_2O_3 (analysed by EDX (energy dispersive X-ray) investigations). Such a composition yields a high catalytic activity, which is advantegeous in terms of the decomposition of the H_2O_2 on the surface during the redox-active process.

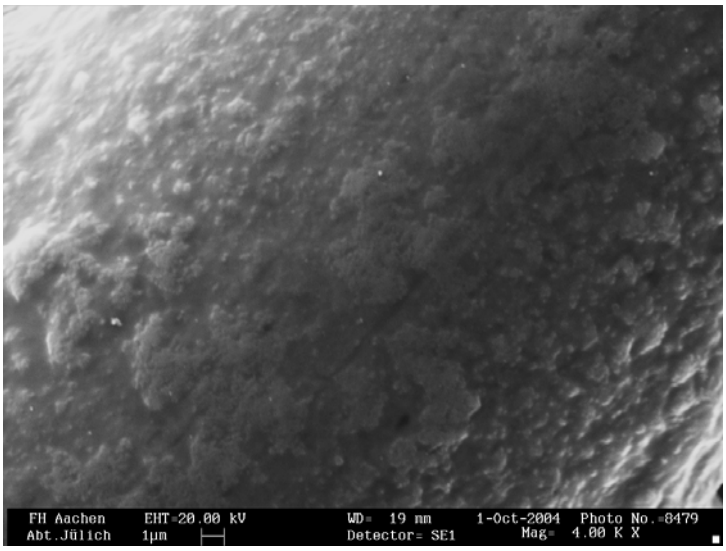

Figure 5. SEM image of the sensor surface with a magnification of 4000.

H_2O_2 measurement with the sensor array

Preliminary measurements have been realised with a differential set-up of two reference temperature sensors together with one H_2O_2-sensitive temperature sensor. The investigations have been performed in the developed automated sterilisation apparatus at laboratory scale. A constant air flow of 10 Nm^3/h (standard cubic metre per hour) has been choosen with a gas temperature of about 270 °C and different dosages of H_2O_2 concentrations. In Fig. 6, a typical measurement cycle with the differential set-up is given: In the beginning of the measurement cycle (0-5000 s), there was just an air flow and the heater of the automated sterilisation equipment has been switched on. After 5000 s, the system seemed to be in equilibrium and the gas stream was heated to a temperature of 173.5 °C at the outlet of the sterilisation pipe. After 9250 s, a dosage of 250 µl/s H_2O_2 solution (~2.5 Vol.%) has been feed to the constant air stream. The temperature signal of all three sensors has been immediately arised at this moment. This behaviour can be explained due to the thermal conductivity of H_2O_2 and water in the gas stream (in the case of the reference temperature sensors) as well as due to the additional decomposition of H_2O_2 in the case of the catalytically active H_2O_2 sensor. Further dosages of H_2O_2

have been added after 11417 s (500 µl/s H_2O_2), 14252 s (450 µl/s H_2O_2) and 16066 s (500 µl/s H_2O_2). After 19014 s, the dosage profile has been switched off. As can be seen from the diagram, an increase in the H_2O_2 concentration is accompanied by a raise in the sensor signal within the differential measurement set-up for both the reference sensors and the H_2O_2 sensor. The higher the H_2O_2 content, the higher the temperature change due to the (catalytically induced) heating effect.

In Fig. 7, the normalised temperature curves of Fig. 6 are presented. The normalisation has been carried out when the system is in equilibrium at the beginning of the measurement cycle, where no H_2O_2 is dosed. Equilibrium conditions have been achieved after a time period of 9000 s, where all temperature signals (reference sensors, H_2O_2 sensor) are shifted to a temperature of 173.5 °C. When the varying H_2O_2 content is dosed, the temperature step of the two reference sensors is nearly equal.

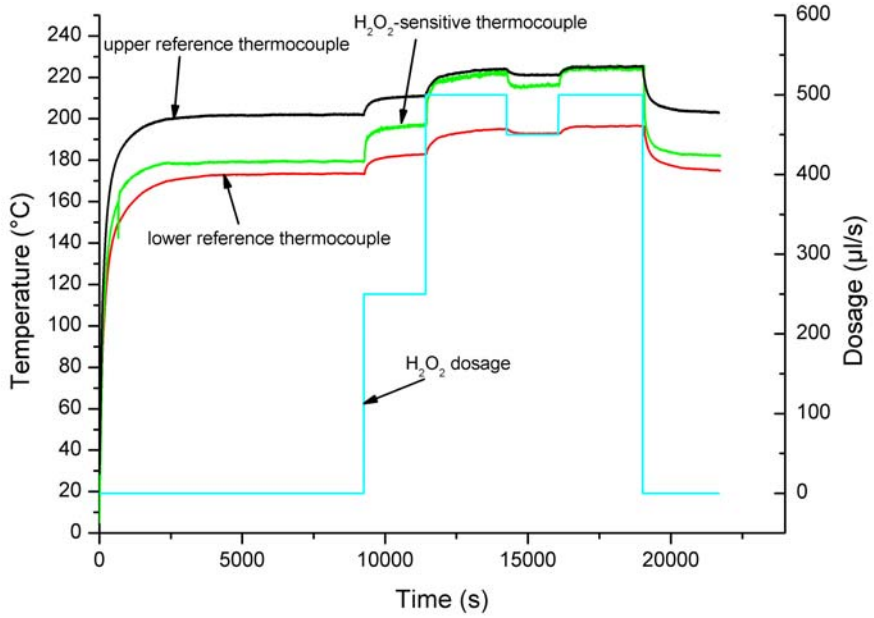

Figure 6. H_2O_2 detection with the differential measurement set-up.

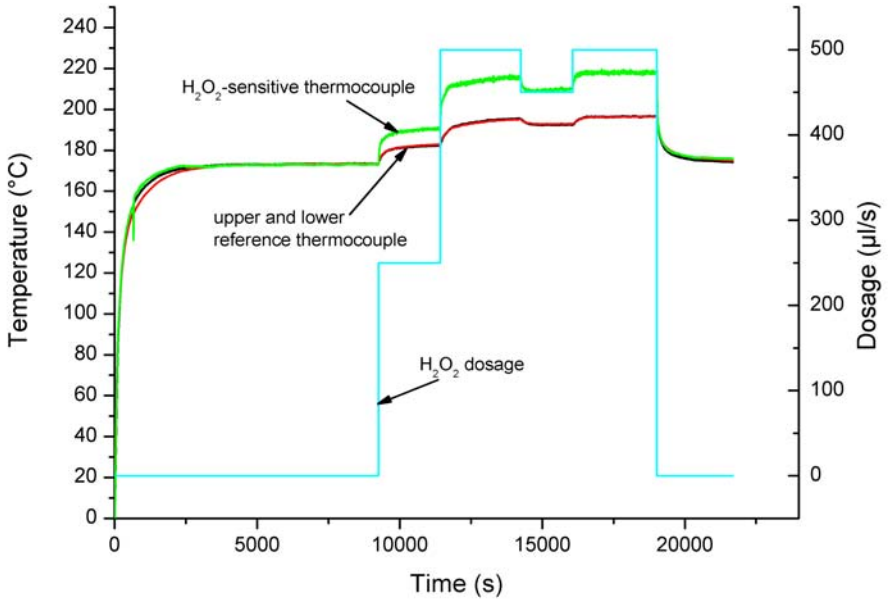

Figure 7. Normalised temperature signal of all sensors.

The temperature increase of both reference sensors from air to a dosage of 500 µl/s H_2O_2 solution is about 21.7 °C. In contrast, the increase of the H_2O_2-sensitive temperature sensor is about 42.4 °C, which can be explained due to the additional catalytic decomposition of H_2O_2 on the sensor surface.

In Fig. 8, the difference of the normalised H_2O_2-sensitive temperature-sensor signal (obtained from Fig. 7) and the reference signal has been evaluated. The diagram clearly demonstrates the response of the H_2O_2 sensor in the presence of H_2O_2 in the sterilisation process with regard to the reference sensor. Between a dosage of 0 and 500 µl/s H_2O_2, which is equal to a concentration of about 5 Vol.%, the resulting sensor signal increases for about 21.5 °C. There is a nearly linear dependence of the sensor signal with an average sensitivity of about 4 °C/ Vol.% H_2O_2.

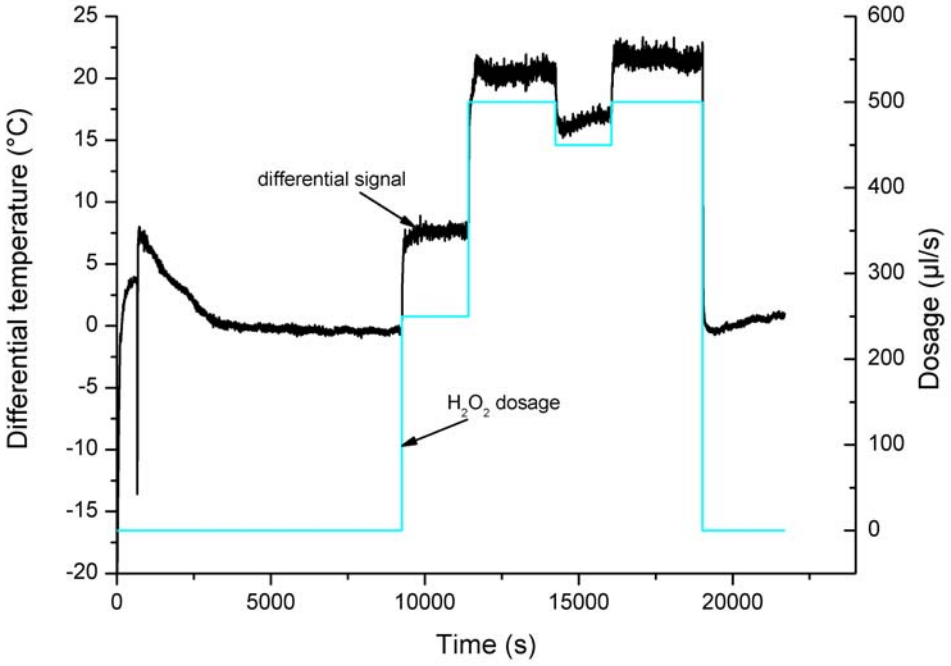

Figure 8. Difference signal of the normalised temperature of one reference sensor and the H_2O_2-sensitive temperature sensor.

Summary and conclusions

An H_2O_2 sensor set-up at laboratory scale for industrial sterilisation processes has been developed, which fullfils the following requirements:

- low-cost fabrication process of sensors,
- temperature-resistant behaviour (< 300 °C),
- stable sensor signals at H_2O_2 concentrations of up to 10 Vol.%,
- no cross-sensitivity towards humidity, massflow, etc., and
- low response time.

The H_2O_2 sensor, which basically consists of a steel-covered temperature sensor with an additional catalytic Mn_xO_{x+1} layer, has a sensitivity of about 4 °C/Vol.% H_2O_2. Due to the differential sensor set-

up including additional reference sensors, the resulting sensor signal is not affected by changes in the heat conductivity of the gas stream. With respect to practical applications in industrial processes, the differential sensor set-up has been integrated to an automated sterilisation apparatus. The main parts of the laboratory scale equipment, like dosage barrels, heater, distributor and sterilisation pipe, are identical to those used in industrial sterilisation and packaging plants. The equipment is software-controlled, so that different concentrations of H_2O_2 can be adjusted. Further investigations will cover the long-term behaviour of the developed sensor set-up in harsh industrial environments as well as the characterisation of alternative temperature-sensitive transducer structures and material compositions.

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