ReCal – an Innovative Mathematical Procedure to Determine the Date of Timely Recalibration for Sensor Systems with Metal Oxide Gas Sensors

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Abstract— Sensor systems with Metal Oxide Gas (MOG) sensors with tin oxide as base material are well established as gas sensing devices for threshold applications like the monitoring of hazardous materials and dangerous situations. However, MOGs have one inherent disadvantage; they are subject to unavoidable aging processes. Therefore, the sensor systems have to be recalibrated regularly. This paper presents an innovative mathematical procedure called ReCal, which is able to determine the proper time for recalibration of the sensor system. The method of ReCal is demonstrated by simulation calculations and it is shown how to determine the parameters in real applications.

Keywords-sensor system; metal oxide gas sensors; threshold apllications; timely recalibration; date of recalibration; simulation calculations.

I. INTRODUCTION

There is a broad field of economic online and in-situ field analysis applications like the online monitoring of volatile components in chemical and biochemical processes, quality monitoring in food processing, discriminated monitoring of toxic gas leakages, etc. In the field of monitoring hazardous materials and situations, metal oxide gas (MOG) sensors with tin oxide as base material are especially well established as gas sensing devices due to their high sensitivity and low costs. These MOGs can be operated either isothermally or, for example, in a thermo-cyclical mode [1][2]. In the first mode, only one single measurement result is available and thus no substance identification can be performed. In the second mode, a series of measurement results is sampled, which leads to so-called "Conduction over Time Profiles" (CTPs) [3]-[6]. These CTPs can be considered as a "fingerprint" of the substance under consideration and enable substance identification as well as concentration determination, by applying a sophisticated calibration and evaluation procedure like ProSens, which is explicitly described in [7]. As could be shown, ProSens is a powerful tool for substance identification and concentration determination for multi-component gas mixtures even in the case of varying environmental conditions like varying humidity or varying environmental temperature. Figure 1 shows examples of some CTPs of different gases. Figure 1 also clearly shows the specific fingerprints of the various gases.

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In previous investigations it was shown that this approach is a very powerful tool for monitoring hazardous materials, for example in the detection of ammonia leakages [8] or cable fires [9].

Other approaches in the field of monitoring hazardous materials in the environment are described in detail in [10].



Figure 1. CTPs of different samples at the same concentration level.

Although the MOGs are very powerful gas sensing devices, they have one disadvantage: their long-time stability is often very poor. One possibility to improve this disadvantage is to pre-age the sensors before field application. However, this approach does not solve the problem; it only reduces the rate of decay. The aging process of the sensors may additionally lead to misleading results, causing e.g. no alarm being given in case of hazardous situations. Therefore, the sensor has to be recalibrated from time to time. This raises the issue of choosing the proper time for recalibration.

The necessary recalibration can be easily performed by a recalibration procedure like ProCal, which is explicitly described in [11].

In this paper, we introduce ReCal, a procedure which finds the appropriate time for recalibration of the sensor system. Measurement results are regarded as random variables and simulation calculations will demonstrate the efficacy of this approach. The rest of this paper is organized as follows. Section II describes the mathematical calibration model and the feature values, which correspond to the gas concentrations. Section III describes the general application scenario. Section IV addresses the mathematical model used in this paper. Section V describes an application of the method using simulation calculations. The conclusions and a section "Future Work" close the article.

II. CALIBRATION MODEL AND FEATURE VALUES

To apply calibration and evaluation procedures for monitoring and alarming, if necessary, in real field applications, the substance under consideration has to be calibrated using calibration measurements. Based on these measurements, the mathematical calibration model can be calculated using calibration procedures like ProSens. In this calibration model, feature values are extracted from the calibration measurements, which allow the evaluation procedure to determine the concentration of a measured sample. The feature values correspond to concentration values and vice versa. For example, there is a feature value, the alarm feature value, for the alarm level that corresponds to a concentration value where an alarm must be given. On the other hand, there is also a feature value, the zero feature value, for the "zero-situation", when no hazardous gas under consideration is present and only the ambient air is measured.

III. APPLICATION SCENARIO

In so-called threshold applications requiring monitoring hazardous materials and situations, the gas under consideration is continuously or frequently measured by the sensor system and an alarm is raised, when the concentration of the gas exceeds a determined value, the threshold value. As mentioned above, there is a one-to-one relation between concentrations and feature values. However, due to the aging process of the sensor, the sensitivity of the sensor will drop over time. That means that the feature values will become lower and will no longer represent the actual gas concentration. When the features have been significantly reduced in amplitude, the sensor has to be recalibrated to guarantee that an alert is still raised when the actual gas concentration exceeds the alarm threshold.

Even though the ambient air does not change, the sensor's measurement of the ambient air changes due to aging. This gradual reduction of the zero feature values goes in hand with the features value reduction for the alarm case, potentially failing to detect dangerous situations.

This reduction of the zero feature values enables the determination of the proper time for recalibration of the sensor system as will be shown in the following chapter.

Of course, varying environmental conditions may also influence the sensor drift. If they are incorporated in the calibration model, sophisticated calibration and evaluation procedures like ProSens can recognize this source of drift. Otherwise, the sensor system has to be recalibrated and the relevant varying conditions have to be incorporated in the calibration model.

IV. MATHEMATICAL MODEL

As mentioned above, features are an appropriate mean to determine the concentration of a gas under consideration. Features are the results of measurements, which are subject to measurement errors. Therefore, features can be considered as random variables F. It is common and, in most cases realistic, to consider these random variables F as normally distributed around the actual concentration with mean μ , variance σ^2 and standard deviation σ , respectively.

That means:

$$F \sim N(\mu, \sigma^2).$$
 (1)

In case of the "zero-situation", the mean of the random variable is denoted as μ_0 and the corresponding standard deviation as σ_0 . In case of an "alarm-situation", the mean of the random variable is denoted as μ_a and the corresponding standard deviation as σ_a .

From the mathematical theory, it is well known that in case of normally distributed random variables, 95% of all realizations (here measurements and the resulting features) of the random variables are within the interval (μ -2 σ , μ +2 σ). In other words, 5% of the realizations are outside this interval, especially 2.5% of the realizations are lower than μ -2 σ . That means that if the zero future value is in 2.5% of the measurements smaller than μ 0-2 σ 0, the sensor system should be recalibrated, because a significant drift of the sensor has likely occurred.

V. APPLICATION AND SIMULATION CALCULATIONS

To demonstrate the application and performance of the procedure ReCal, simulation calculations were performed.

The following assumptions were chosen: the zero feature value F, which corresponds to the zero-measurement, is normally distributed with mean $\mu_0 = 0$ and standard deviation $\sigma_0 = 1$.

In a first step, random variables F were simulated according to the zero measurement case. Next, a drift of -0.01 per measurement was added to these random variables F to simulate a drift of the sensor system. Figure 2 shows the simulated values of random variables in time (Features Zero, pink curve). These values fluctuate around the mean zero line μ_0 (Mean Zero, blue line) and are in mostly within the interval (μ_0 - $2\sigma_0$, μ_0 + $2\sigma_0$), which is between the lower threshold and the upper threshold.

In addition, the values of the "manipulated" features (Features Drift, green curve) are also plotted in Figure 2. They fluctuate around the drift line (Mean Drift, black line) and often fall below the lower threshold. This is clear evidence of the sensor drift.

Of course, if the values of the zero feature are lowered, the values of the alarm features are also lowered. This results in the fact that the determination of the gas concentration is too small and an alarm will not be given, even if the alarm level is reached.

Therefore, a timely recalibration must be performed to ensure that the secure applicability of the sensor system can be guaranteed. In this example, 100 measurements are assumed to be performed over the time. 2.5% of 100 realization are 2,5. That means that if 3 realizations are lower than the lower threshold, the sensor system has to recalibrated to give a timely alarm.

The mathematical procedure ReCal recognizes that in the 55th measurement the according feature value falls for the third time below the lower threshold and indicates that the sensor system should be recalibrated (see Figure 3).



Figure 2. Features and manipulated features of measurements over the time.



Figure 3. Features and manipulated features of measurements till the time of recalibration.

In real applications, first, it is necessary to determine the mean μ_0 and the standard deviation σ_0 , which is the square root of the variance σ_0^2 of the zero future value F.

As known from the mathematical theory, the mean value of a random variable can be estimated from a population of n identically and independent random variables using the following equation:

$$\boldsymbol{\mu} = 1/\mathbf{n} * \boldsymbol{\Sigma} \, \mathbf{x}_{\mathbf{i}} \,. \tag{1}$$

where x_i are the realizations of the random variables and the sum runs from 1 to n.

The variance σ^2 can be estimated using the following equation (2):

$$\sigma^2 = 1/n * \Sigma (\mathbf{x}_i - \boldsymbol{\mu})^2.$$
⁽²⁾

where again the sum runs from 1 to n.

To be able to calculate the mean and the standard deviation, samples only containing the ambient air have to be measured by the sensor systems n times.

This is not very costly and time-consuming in respect to the gain of timely detection of a hazardous situation.

VI. CONCLUSIONS

Sensor systems with metal oxide gas sensors with tin oxide as base material are well established as gas sensing devices especially for threshold applications. However, there is an unavoidable drift in the MOG sensors due to their aging process. Therefore, the sensor systems have to be recalibrated from time to time. The mathematical procedure ReCal, introduced in this paper, allows to determine the proper time for recalibration, as was shown by simulation calculations. This is a very important result, because it assures that the sensor systems are suitable for reliable alerting in dangerous situations.

VII. FUTURE WORK

The very promising results obtained by simulation calculations will be tested in a long-term investigation with real measurement data from a real sensor system.

Additionally, a mathematical model will be elaborated, which allows to estimate the drift of other feature values based on the drift of the zero feature values. This approach would enable to recalibrate the sensor system without further calibration measurements. This would be an important progress in the application of sensor systems, because calibration measurements are very time-consuming and costly.

Of course, this approach has also to be verified in a longterm investigation with real measurement data.

REFERENCES

- H. Kohler, J. Rober, N. Llink, and I. Bouzid, "New applications of tin oxide gas sensors – I. Molecular recognition by cyclic variation of the working temperature and reasonable numerical analysis", Sensors & Actuators B: pp. 163-169, 1999.
- [2] H. Kohler, M. Bauer, and I. Bouzid, "Gas Recognition Using SnO2 Gas Sensors: Analysis of volatile organic substances dissolved in water"; Proceedings Sensor Congress Nürnberg, Vol. I AMA Service, Wunstorf. Germany: pp. 125-128, 1999.
- [3] A. Jerger, H. Kohler, F. Becker, H. B. Keller, and R. Seifert, "New applications of tin oxide gas sensors II. Intelligent sensor system for reliable monitoring of ammonia leakages",

Sensors and Actuators B: Chemical, 81, 2-3, pp. 301-307, 2002.

- [4] K. Frank et al., "Metal oxide gas sensors for field analysis: Novel SnO2/La2O3 sensor element for analysis of dissolved toluene/ethanol binary mixtures", Sensor 2005: 12th Internat. Conf., Nürnberg, May, 2005, Proc. Vol. 2, AMA Service GmbH, Wunstorf, pp. 207–209, 2005.
- [5] K. Frank et al., "Improving the analysis capability of tin oxide gas sensors by dynamic operation, appropriate additives and an advanced evaluation procedure", Sensor 2007: 13th Internat.Conf., Nürnberg, May, 2007, Proc. Vol. 1, AMA Service GmbH, Wunstorf, pp. 139–144, 2007.
- [6] K. Frank et al., "Chemical Analysis with Tin Oxide Gas Sensors: Choice of Additives, Method of Operation and Analysis of Numerical Signal", Sensors Letters 6, pp. 908-911, 2008.
- [7] R. Seifert, H. B. Keller, K. Frank, and H. Kohler, "ProSens an Efficient Mathematical Procedure for Calibration and Evaluation of Tin Oxide Gas Sensor Data", Sensor Letters, Vol. 9/1, pp. 7-10, 2011.
- [8] A. Jerger, H. Kohler, F. Becker, H. Keller, and R. Seifert, "New applications of tin oxide gas sensors II. Intelligent Sensor System for Reliable Monitoring of Ammonia Leakages", Sensors and Actuators B, 81, pp. 301-307, 2002.
- [9] R. Seifert, H. Keller, N. Illyaskutty, J. Knoblauch, and H. Kohler, "Numerical Signal Analysis of Thermo-Cyclically Operated MOG Gas Sensor Arrays for Early Identification of Emissions from Overloaded Electric Cables", Sensors & Transducers journal, Vol. 193, Issue 10, pp.74-79, 2015.
- [10] A. D. Wilson, "Review of electronic-nose technologies and algorithms to detect hazardous chemicals in the environment", Procedia Technol. 2012, 1, pp. 453-463, 2012
- [11] R. Seifert, H. B. Keller, K. Frank, and H. Kohler, "Batch-wise Mathematical Calibration of Thermo-CyclicallyOperated Tin Oxide Gas Sensors", Sensor Letters, Vol. 9/2, pp. 621-624, 2011.