Advanced Mathematical Calibration Procedure for Sensor Systems Measuring Multi Component Gas Mixtures

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Abstract—**Although sensor chips for multi gas sensors are usually batch wise fabricated, each sensor chip has to be individually calibrated to yield a high analytic performance. For multi gas applications, a sensor chip normally has to be measured for calibration at least at 3 calibration points for every component. An advanced mathematical procedure for batch wise calibration called ProCal2.0 is introduced to reduce the calibration effort nearly by a factor of three even for multi gas-analysis. By application of the procedure to sensitivity data sampled at binary Ethanol/H_2 gas mixtures, it is demonstrated that, with this efficient calibration procedure, the analysis results are very close to those which are obtained when each sensor chip is individually calibrated.**

***Keywords* - multi gas sensors; batch wise calibration; multi gas applications; multi gas analysis; analysis error.**

I. INTRODUCTION

Economic online and in-situ field analyses applications like discriminated alarming of smouldering fire or toxic gas leakages, monitoring of volatile components in chemical and biochemical processes, quality monitoring in food processing, etc., rely on reliable and economic analytical solutions by sensor systems.

In this context, the isothermally operated Metal Oxide Gas sensors (MOGs) with tin oxide as base material have been introduced due to their high sensitivity, long term stability and low price. Their sensitivity to specific gas components, however, cannot be cultivated with high discrimination to others. Therefore, other approaches are necessary like a gas sensor array of MOGs [1][2] or a thermo-cyclic operation of the MOG and simultaneous sampling of the conductance which finally leads to the mathematical analysis of the so called Conductance-over-Time-Profiles (CTPs) [3]. These CTPs show characteristic profile shapes reflecting gas composition and gas component concentrations depending on the choice of additives. It can be shown that, using this approach, valuable signal information can be extracted to be numerically analyzed for substance identification and concentration determination even in the case of varying environmental conditions (e.g. humidity) [4].

The effort for calibration of the sensor elements is very time consuming and costly. Sensor elements are usually batch wise fabricated. But, unavoidable production inaccuracies of the sensor elements lead to unreproducibilities of the gas analytic attributes. Therefore, although the signal patterns of the various sensor elements of a production batch are quite similar, each sensor element has to be calibrated, in order to yield high analytic performance, and this can be very costly. The number of components to be simultaneously analyzed determines the dimension of the calibration field and, for good analysis results, as was experimentally shown, about three to five or even more calibration points for every dimension are necessary depending on the accuracy demands of the analysis.

In this report, an advanced mathematical calibration procedure called ProCal2.0 is introduced which is able to drastically reduce the calibration effort of batch wise fabricated sensor chips measuring multi component gas mixtures.

In Section 2, the considered application field is briefly described. A short outline of the advanced calibration procedure ProCal2.0 is given in Section 3. Different calibration models to compare the performance of the procedure are introduced in Section 4. In Section 5, the analysis results are presented. Section 6 summarizes the results of this report.

II. APPLICATION: BINARY ETHANOL/H_2 GAS MIXTURES

The application, on which the outline of ProCal2.0 is described and the analysis results are presented, is measuring binary Ethanol/H_2 gas mixtures. The measurements are performed using the sensor system, which is described in detail in [5]. The sensor system is armed with batch wise fabricated sensor chips and runs in the above mentioned thermo-cyclic mode.

III. OUTLINE OF PROCAL2.0

As mentioned above, even if the sensor chips are fabricated in a batch wise manner, each sensor chip has to be individually calibrated to gain reasonable analysis results. To calibrate a sensor chip, calibration measurements have to be performed, which are very time consuming and, therefore, costly. In the case of binary Ethanol/H_2 gas mixtures, the gas mixture has to be measured at least at three concentration levels of each component and all concentration combinations. That leads to at least 9 calibration measurements to determine a reasonable mathematical calibration model.

Table I shows the considered calibration field.

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TABLE I. CALIBRATION FIELD OF 9 CONCENTRATION POINTS (CP) AND RELATED APPROXIMATION FUNCTIONS

Ethanol H_2 in ppm		Ethanol H_2 in ppm		Ethanol H_2 in ppm	
50-10	CP1	50-20	CP4	50-30	CP7
100-10	CP2	100-20	CP5	100-30	CP8
175-10	CP3	175-20	CP6	175-30	CP9
Function f(i,10)		Function f(i,20)		Function f(i,30)	

ProCal2.0 is an extension of the procedure ProCal [6], which was only designed for calibrating single gases.

ProCal2.0 is developed to drastically reduce the calibration effort for multi component gas mixtures.

Therefore, one sensor chip of the batch wise fabricated sensor chips is chosen as the so-called reference chip. Using this reference chip, the binary Ethanol/H_2 gas mixture is measured at all 9 calibration points.

With all the other sensor chips of the batch, the binary Ethanol/H_2 gas mixture is measured only at the calibration points CP2, CP5 and CP8, the so-called reference calibration points, which are written in red in the calibration field in Table I.

Next, approximation functions are determined which map the signal patterns, in our case the CTPs, of the reference chip in a best manner to the signal patterns of the other, non-reference, sensor chips at the reference calibration points. That means, we get 3 approximation functions for each non-reference chip.

For example, function f(i,10) in Table I is the best approximation function for mapping the signal pattern of CP2 of the reference chip to the corresponding signal pattern of sensor chip i. The signal pattern of sensor chip i at CP1 is calculated by mapping the signal pattern of the reference chip at this calibration point, using this approximation function f(i.10).

This procedure is performed in a similar way for all non-reference sensor chips and for all calibration points.

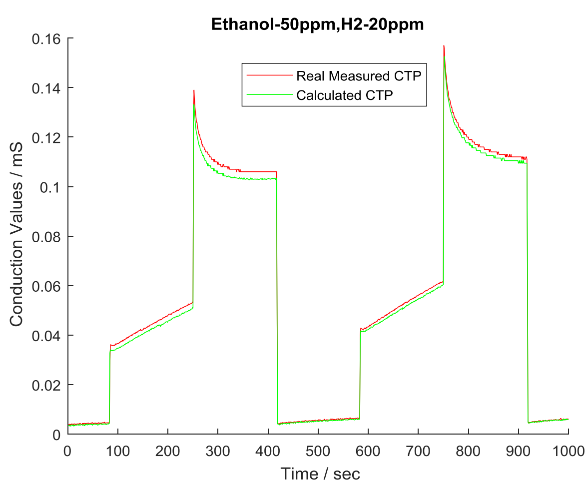

Figure 1. Comparison of real measured CTP and calculated CTP.

Therefore, we get all the needed signal patterns to determine the related mathematical calibration models. However, only 3 instead of 9 calibration measurements are needed for all non-reference chips. This reduces the calibration effort by factor of 3.

It can be shown that ProCal2.0 is also able to determine the best choice of the reference chip and also to detect outliers. That means, ProCal2.0 can identify chips of the production batch which cannot be reasonably calibrated using this procedure.

IV. MATHEMATICAL CALIBRATION MODELS

To demonstrate the performance of the above described procedure ProCal2.0, three mathematical calibration models are established. The ”individual model of each chip” means that each sensor chip of the batch is individually calibrated. This is a very costly and time consuming calibration process and leads to the best possible analyses results. Using the ”class reference model”, only one sensor element of a batch (here, the reference chip) is completely calibrated and the calibration model of this sensor chip is assigned to each one of the other chip of the batch. This leads to very poor analysis results will be shown later in the paper. The third calibration model is the above mentioned “batch wise calibration model” using procedure ProCal2.0 with reduction of the complete calibration effort by a factor of 3.

The data analysis is performed with the calibration and evaluation program ProSens [7].

V. ANALYSIS RESULTS

In this section, we consider 4 sensor chips of a batch, called S1, S2, S3 and S4. Sensor chip S4 was chosen as reference chip.

Binary Ethanol/H_2 gas mixtures at the concentration points given in Table II are measured using the 4 chips and the concentration determination is performed using the 3 calibration models mentioned above.

TABLE II. CONTRATION POINTS FOR DATA ANALYSIS

Ethanol-H_2 in ppm	Ethanol-H_2 in ppm	Ethanol-H_2 in ppm
50-10	50-20	50-30
100-10	100-20	100-30
135-10	135-20	135-30
175-10	175-20	175-30

The red marked line is additionally measured for data analysis.

A. *Analysis Results of Sensor Chip S1*

The following tables show the analysis results of sensor chip S1 using the 3 calibration models. Table III shows the analysis results using the individual calibration model, Table IV the results using the class reference model and Table V using the batch wise calibration model. The bold values are the dosed values and the values in the table are the calculated values (all values in ppm).

TABLE III. ANALYSIS RESULTS USING THE INDIVIDUAL MODEL

Ethanol/H_2	10	20	30
50	50.3-10.1	47.9-20.1	54.6-27.6
100	95.1-11.1	111.3-18.9	92.7-32.8
135	127.0-11.1	139.9-20.2	134.5-31.2
175	175.1-9.7	168.5-21.0	179.4-28.7

TABLE IV. ANALYSIS RESULTS USING THE CLASS REFERENCE MODEL

Ethanol/H_2	10	20	30
50	60.2-4.5	59.3-18.3	69.7-26.1
100	106.4-9.9	121.7-18.5	114.0-30.7
135	141.3-10.4	149.6-20.1	156.4-28.7
175	156.4-28.7	177.6-20.7	202.2-25.6

TABLE V. ANALYSIS RESULTS USING THE BATCH WISE CALIBRATION MODEL

Ethanol/H_2	10	20	30
50	46.2-11.7	48.0-19.6	54.8-26.5
100	89.2-11.3	110.5-18.6	84.3-32.3
135	119.6-11.2	138.9-20.4	120.0-31.7
175	163.8-10.0	165.7-21.7	157.3-30.4

Tables VI to VIII show the relative analysis errors.

TABLE VI. RELATIVE ANALYSIS ERRORS IN % USING THE INDIVIDUAL MODEL

Ethanol/H_2	10	20	30
50	0.6-0.8	4.1-0.7	9.3-7.9
100	4.9-**11.1**	**11.3**-5.7	7.3-9.3
135	5.9-10.9	3.6-1.1	0.4-3.8
175	0.1-2.5	3.7-5.0	2.5-4.5

TABLE VII. RELATIVE ANALYSIS ERRORS IN % USING THE CLASS REFERENCE MODEL

Ethanol/H_2	10	20	30
50	20.3-**55.1**	18.7-8.5	**39.4**-12.9
100	6.4-0.9	21.7-7.6	14.0-2.2
135	4.6-4.4	10.8-0.3	15.9-4.4
175	11.5-6.3	1.5-3.7	15.5-14.8

TABLE VIII. RELATIVE ANALYSIS ERRORS IN % USING THE BATCH WISE CALIBRATION MODEL

Ethanol/H_2	10	20	30
50	7.6-**17.5**	4.0-2.1	9.6-11.5
100	10.8-12.6	10.5-6.9	**15.7**-7.6
135	11.4-11.9	2.9-1.8	11.1-5.5
175	6.4-0.1	5.3-8.5	10.1-1.3

The red marked numbers indicate the largest relative analysis errors in the related tables.

It can be clearly seen that, as expected, the best the analysis results are obtained using the individual calibration model. The analysis results using the batch wise calibration are very close to these best results but the calibration effort is reduced by the factor of 3. Using the class reference model, the analysis results are very poor.

B. *Analysis Results of the Other Sensor Chips*

The analysis results of the other sensor chips based on the 3 calibration models are very similar to those of sensor chip S1.

The following Tables IX to XI show the maximum analysis errors of the components Ethanol and H_2 using the sensors S1, S2 and S3 and the related calibration models.

TABLE IX. MAXIMAL ANALYSIS ERRORS IN % FOR SENSOR S1

Maximal Analysis Errors in %	Ethanol	H_2
Individual Model	11.3	11.1
Batch wise Calibration Model	15.7	17.5
Class Reference Model	39.4	55.1

TABLE X. MAXIMAL ANALYSIS ERRORS IN % FOR SENSOR S2

Maximal Analysis Errors in %	Ethanol	H_2
Individual Model	14.8	13.1
Batch wise Calibration Model	19.3	13.3
Class Reference Model	44.5	17.4

TABLE XI. MAXIMAL ANALYSIS ERRORS IN % FOR SENSOR S3

Maximal Analysis Errors in %	Ethanol	H_2
Individual Model	14.2	12.4
Batch wise Calibration Model	14.2	13.9
Class Reference Model	34.5	17.1

It can be clearly seen that in all considered cases the analysis results obtained by the batch wise calibration model are very close to the best possible analysis results.

VI. CONCLUSION

Using the calibration procedure ProCal2.0, the very time consuming and expansive calibration of batch wise fabricated sensor elements can be reduced almost by the factor of 3. ProCal2.0 is able to determine the class reference chip, which best represents the chips of the batch and can exclude outliers, i.e, chips which cannot be calibrated with this procedure. It was shown that the calculated signal patterns are close to the sampled signal patterns and the analysis errors using this calibration model are very close to the best possible ones using the very time-consuming individual model, but dramatically better than those using the class reference model.

The same procedure can also be applied for cost effective and time saving recalibration.

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