

Article

# Calibration of electrochemical sensors for air pollution monitoring using the AirSensEUR box – Laboratory experiments

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**Keywords:** temperature effect; humidity effect; interference; drift.

## 1. Version

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## 2. Introduction

In the last years an increasing number of studies describing several methods for the calibration of electrochemical low-cost sensors have been published. The majority of these calibration methods by field experiments with co-location of sensor systems and reference analysers sited at Air Quality Monitoring Stations (AQMS) (references needed). Conversely, little or no laboratory experiments under controlled conditions are generally carried out. The aim of field test experiments is to establish the relationship between sensor data and reference measurements possibly taking into consideration co-variables that affects sensor responses (Reference needed) and later prediction of sensor data at other sites than the one use for calibration. Among this type of model equations used for calibration, one can distinguish between empirical (multi-)linear approaches [1] and machine learning methods

[1,2]. It has become an established technical methodology to improve the data quality of such sensor systems by co-locating them at traditional air quality monitoring stations equipped with reference instrumentation and field-calibrating individual units using various statistical techniques. Methods range from (multi-)linear regression to more complex statistical techniques, often using additional predictor variables such as air temperature or relative humidity (e.g. Spinelle et al., 2017), and occasionally data not actually measured by the sensor system itself (e.g. station observations or model output). that is data fishing, the tests in the data sheets of manufacturer can help to correctly fish.

Several laboratories studies have shown that low cost sensor are strongly affected from changes of several Variables either as cross-sensitivies (reference) or meteorological parameters, mainly temperature and humidity However, in field the variables affecting sensor measurements are not independent. Major co-linearities are common, for example between CO, NO and PM or anti-correlation between temperature and humidity. The majority of statistical tools, e. g. multilinear regression or . . . , are affected by collinearities of xs making the decision of taking into account affecting parameters very much erratic. Including type 1 and type 2, it is becoming impossible to say which parameter drives the system

The trend is towards artificial intelligence ANN and random forest seems not to be able to manage change of sampling sites De vito and Hueglin).

Is it possible to use simple deterministic model Are these model similar at the same place for several ASE. -> pre calibration set

What if we change of place? Type of site Sensitivity analysis effect of parameter variability of measurement uncertainty Best period for calibration, rolling calibration period and  $R^2$  of calibration Principle of electrochemical sensor Position of the auxiliary electrode: it remains within the electrolyte while the working electrode is exposed to air. The electrolyte is a gel Effect Are the effect temperature, relative humidity, cross sensitivities additive? Using the results of laboratory experiments, (Mueller et al., 2017) concluded that the raw signal of two NO<sub>2</sub>-B42F sensors were dependent of the rate of change of humidity with humidity changing between 40 and 60 % at rate of about Questions: should we use dynamic measurement or static for calibration, what is the rate of change of humidity in field? Add about CO<sub>2</sub> from Lewis and Hueglin

Does sensitivity change with Temperature and humidity: use design of experiment

### 3. Theory

#### 3.1. Electrochemical sensors

Amperometric gas sensors (AGS) sensors are based on electrochemical cells assuring the transfer of charges from an electrode to another which are in connection through an electrolyte phase. This electrolyte phase has to carry the cell current by enabling the transport of charge carriers in form of ions and often has to provide co-reactants (usually water, protons or hydroxide ions) to the electrode as well as to allow the removal of ionic products from the reaction site. The electrolyte can be solid [3], gel-like or organic gel as in the case of Sensoric City Technology sensors (DE) [4], liquid or gaseous electrolytes e. g. for sensors manufactured by SGX Sensortech (CH). AGSs require at least a measuring electrode and a counter electrode through which flows a current generated by the redox reaction of an analyte at the working electrode when a fixed or variable proper potential is applied to sensor electrodes. For measurement at low levels, the majority of amperometric sensors include a 3<sup>rd</sup> electrode, the reference electrode, to which a bias voltage can be applied to modify the potential of the working electrode. More recently a 4<sup>th</sup> electrode, named an auxiliary electrode, have been added to a few sensor model (e. g. the sensors manufactured by AlphaSense (UK), CityTechnology Ltd (UK) and Membrapor (CH)). The 4<sup>th</sup> electrode is used to correct for changes in sensor signal that are not induced by changes in the gaseous compound being sampled [5] + (American reference) but it accounts for changes in for example temperature and humidity of the ambient air being sampled.

In the AGSs, the reaction rate, reflected by the current,  $i_{lim}$ , at the sensing electrode, occurs for any reaction triggered by the applied electrode potential. The fundamental process for sensing an analyte by an AGS can be described in four steps: (1) the analyte diffuses to the sensing electrode. In order to achieve selectivity and/or diffusion-limited working mode this diffusion may proceed through a membrane or some other diffusion barrier. (2) The analyte is adsorbed on the sensing electrode. (3) The electrochemical reaction occurs. (4) The reaction products desorb from the sensing electrode and diffuse away [6]. Using Fick's first law and Faraday's law the following general expression for the steady state current of an amperometric sensor can be written [6]:

$$i_{lim} = \frac{nF}{R_k + \sum_{i=1}^n R_i} [C]_{gas} \quad (1)$$

where  $i_{lim}$  is the sensor output current,  $n$  is number of electrons involved in electrochemical reaction,  $F$  is the Faraday constant,  $R_k$  is the kinetic resistance of the electrochemical reaction and  $R_i$  are several resistances to the analyte diffusion at layers  $i$ . ADD the layer from Popoola, 2016 Generally a membrane is placed on top of the working electrode so that the rate of mass transport ( $R_d$ ) by diffusion and permeation through the membrane of the reactant to the electrode surface is much higher than the rate of the electrode reaction ( $R_k$ ). In fact, if  $R_k$  is much higher than  $\sum R_i$ , the rate of reaction at the electrode surface is the rate-limiting step, the limiting current,  $i_{lim}$  is controlled by the rate of the electrode kinetics. In this case, the analyte reaches the surface much faster than it is reacted, and so the concentration at the electrode surface is the same as in the gas surrounding the electrode. When operated under appropriate diffusion-limited conditions,  $i_{lim}$  is simply proportional to the concentration of the analyte [6] as shown in Equation (2). The simple relationship given in Equation (2) is valid provided that the limiting factor to the transport of charge in the sensor cell is controlled by the gas molecules diffusing to the working electrode rather than by the rate of redox reaction at this electrode. In this equation, the current,  $i_{lim}$ , is directly proportional to,  $C$ , the gaseous concentration in volume or mass concentration. This is only valid for steady concentration using the 1st Fick's law, what about 2nd law of Fick when concentration is changing?

$$i_{lim} = k[C]_{gas} \quad (2)$$

The expression for the current obeys the Faraday's law and a dynamic reaction achieving a steady-state condition in the sensor and it takes the form of Equation (3) where  $k$  represents the standard rate constant,  $F$  is the faraday constant,  $R$  is the gas constant,  $T$  is the Kelvin temperature,  $A$  is the area of the electrode,  $C$  is the concentration,  $n$  represents the number of electrons per molecule reacting, and  $R$  and  $E$  are the transfer coefficient and overvoltage of the electrode reaction, respectively. Although Equation (3) corresponds to a limited current state that is not used in this study, it shows what can be the influence of temperature in the sensor cell.

$$i_{lim} = nFkAe^{\frac{nFE}{RT}} \quad (3)$$

This process comprises a chemical reaction of the electrode as well as charge transport through the electrolyte, which can both be chemically influenced. amperometric if the current of an oxidoreduction reaction that is linearly proportional to the gas concentration is measured. The principle behind amperometric sensors is the measurement of the current-potential relationship in an electrochemical cell where equilibrium is not established. The current is quantitatively related to the rate of the electrolytic process at the working electrode whose potential is kept constant using the so-called reference electrode. The gas molecules diffuses into the sensor and the measuring electrode where a direct electron transfer takes place due to chemical reactions. These reactions produce a current proportional to the concentration of the compound [7] following the Nernst Law. Nowadays, the amperometric sensors also includes a reference electrodes, while the trend is to add a 4th auxiliary

electrode for correction of electrodes physical changes and sensor drift. Hereafter we present an evaluation of commercially available sensors for O3 and NO2.

### 3.2. Calibration of sensors

The objective is to set calibration equations that fit sensor raw current over a short calibration time interval when sensor and reference data are available. This is called calibration as in Equation (4), where  $R_i$  is the raw CO, NO, NO2 or O3 sensor data in nA or Volt that is fitted as a multilinear combination of  $C_j$ , the set of parameters that affect the sensor measurements at degree  $k$  (integer or real) and  $a_j$  the coefficients of the multilinear combination. One should note that for  $j$  equals 1,  $C_1$  is the Identity vector and  $a_1$  is the baseline or zero current, and for  $j$  equals 2,  $C_2$  is  $C_i$  the reference gas concentrations of interest while  $a_2$  is the sensitivity of the sensor for the gas compounds being monitored. For  $j > 2$ ,  $C_j$  can be called covariates.

$$R_i = \sum_{j=1}^n a_j [C_j]^k = a_1 + a_2 [C_i] + \sum_{j=3}^n a_j [C_j]^k \quad (4)$$

Subsequently the calibration is applied to compute pollutant levels outside the calibration time period using Equation (5), hereafter called prediction or inference.

$$[C_i] = \frac{R_i - a_1 - (\sum_{j=3}^n a_j [C_j]^k)}{a_2} \quad (5)$$

## 4. Materials and Methods

Materials and Methods should be described with sufficient details to allow others to replicate and build on published results. Please note that publication of your manuscript implicates that you must make all materials, data, computer code, and protocols associated with the publication available to readers. Please disclose at the submission stage any restrictions on the availability of materials or information. New methods and protocols should be described in detail while well-established methods can be briefly described and appropriately cited.

Research manuscripts reporting large datasets that are deposited in a publicly available database should specify where the data have been deposited and provide the relevant accession numbers. If the accession numbers have not yet been obtained at the time of submission, please state that they will be provided during review. They must be provided prior to publication.

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## 5. Results

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### 5.1. Subsection Heading Here

Subsection text here.

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Bulleted lists look like this:

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entry 1	data	data
entry 2	data	data

This is an example of an equation:

$$\S \quad (6)$$

Example of a theorem:

**Theorem 1.** *Example text of a theorem.*

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Example of a proof:

**Proof of Theorem 1.** Text of the proof. Note that the phrase ‘of Theorem 1’ is optional if it is clear which theorem is being referred to.  $\square$

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## 6. Discussion

Authors should discuss the results and how they can be interpreted in perspective of previous studies and of the working hypotheses. The findings and their implications should be discussed in the broadest context possible. Future research directions may also be highlighted.

## 7. Conclusion

This section is not mandatory, but can be added to the manuscript if the discussion is unusually long or complex.

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designed the experiments; X.X. performed the experiments; X.X. and Y.Y. analyzed the data; W.W. contributed reagents/materials/analysis tools; Y.Y. wrote the paper." Authorship must be limited to those who have contributed substantially to the work reported.

**Conflicts of Interest:** The authors declare no conflict of interest.

## Abbreviations

The following abbreviations are used in this manuscript:

MDPI	Multidisciplinary Digital Publishing Institute
DOAJ	Directory of open access journals
TLA	Three letter acronym
LD	linear dichroism

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**Sample Availability:** Samples of the compounds . . . . . are available from the authors.

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