Atmospheric Environment 147 (2016) 330–343

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Development of a baseline-temperature correction methodology for electrochemical sensors and its implications for long-term stability

Olalekan A.M. Popoola*, Gregor B. Stewart, Mohammed I. Mead, Roderic L. Jones

Department of Chemistry, University of Cambridge, Cambridgeshire, UK

HIGHLIGHTS

- Temperature correction of low cost air quality sensors.
- Developed a robust baseline-temperature correction methodology.
- Methodology shown to be reproducible for different gas species.
- Temperature corrected data show good agreement with reference instrument.
- Long term gain/sensitivity of sensors not affected by meteorology.

ARTICLE INFO

Article history:
Received 16 May 2016
Received in revised form
10 October 2016
Accepted 14 October 2016
Available online 14 October 2016

Keywords:
Air quality
Electrochemical sensors
Long-term measurements
Nitric oxide
Carbon monoxide
Baseline-temperature correction

ABSTRACT

Recent studies have shown that (three-electrode) electrochemical sensors can be utilised for air quality monitoring and exposure assessment. The long-term performance of these sensors is however, often limited by the effects of ambient meteorological parameters on the sensor baseline, in particular temperature. If electrochemical (EC) sensors are to be adopted for air quality measurement over extended periods (months), this effect must be accounted for. Recent long-term, ambient measurements of CO, NO and NO_2 using EC sensors have revealed that temperature (and relative humidity (RH)) had an effect on the baseline which was more pronounced in the case of NO sensors with coefficient of determination, R^2 of 0.9 when compared to CO and NO_2 with $R^2 < 0.2$. In this paper we present a correction methodology that quantifies this effect (referred to here as fitted baseline), implementing these correction on the EC measurements. We found that EC sensors corrected for baseline-temperature effect using the method describe in this paper show good agreement when compared with traditional reference instrument. The coefficient of determination R^2 of 0.7–0.8 and gradient of 0.9 was observed for baseline-temperature corrected NO compared to $R^2 = 0.02$ prior to baseline-temperature correction. Furthermore, the correction methodology was validated by comparing the temperature-baseline with proxy temperature compensating measurements obtained from the fourth electrode of a set of novel four-electrode electrochemical sensors. A good agreement ($R^2 = 0.9$, with gradients = 0.7–1.08 for NO and $0.5 < R^2 < 0.73$ for CO) was observed between temperature fitted baselines and outputs from the fourth electrodes (also known non-sensing/auxiliary electrode). Meanwhile, the long-term stability (calibrated signal output) of temperature-corrected data was evaluated by comparing the change in sensor gain to meteorological parameters including temperature, relative humidity, wind speed and wind direction. The results showed that there was no statistically significant change in sensitivity (two-sided *t*-test, $p = 0.34$) of the temperature-corrected electrochemical sensor with respect to these parameters (over several months). This work demonstrates that using the baseline-temperature correction methodology described in this paper, electrochemical sensors can be used for long-term (months), quantitative measurements of air quality gases at the parts per billion volume (ppb) mixing ratio level typical of ambient conditions in the urban environment.

Abbreviations: EC, electrochemical; WE, working electrode; AE, the auxiliary electrode; LAQN, Local Air Quality Network; SNAQ-Heathrow, sensor networks for air quality at London Heathrow airport; CCC, Cambridge City Council; DTG, Digital Technology Group; AURN, the UK Automatic Urban and Rural Network; CHL, chemiluminescence analyser.

* Corresponding author.
E-mail address: oamp2@cam.ac.uk (O.A.M. Popoola).

http://dx.doi.org/10.1016/j.atmosenv.2016.10.024

1. Introduction

Health effect of air quality gases such as carbon monoxide (CO), nitric oxide (NO) and nitrogen dioxide (NO_2) is well documented. As part of the European Union (EU) air quality directive, member nations are required to monitor air quality gases in area where levels are predicted to exceed limits set by the body (EU directives 1998, 2009). Routine monitoring are carried out using reference technique which are based on established techniques such as chemiluminescence used for NO, NO_2 monitoring and dispersive infra-red for CO. While these techniques have been shown to be highly sensitive with high temporal resolution, they are very expensive to install and run, requiring routine maintenance, and highly secured locations. This limits the number of monitoring stations that can be setup, thereby limiting spatial air quality data coverage.

Air quality is highly heterogeneous in space, to better understand the chemistry and exposure studies it is important to have good spatial information on air pollutants. Recent work has shown application of low-cost electrochemical sensor nodes in air quality network studies (Mead et al., 2013; De Vito et al., 2009). These sensor nodes measure CO, NO and NO_2 in addition to ambient temperature. While using short term studies (hours) have demonstrated the reliability of these sensor nodes in capturing temporal and spatial variability in air quality, long term (days to weeks) deployments for air quality assessment have proven to be much more challenging. Measurements from the latter are affected by the diel variations in ambient temperatures which affect the baselines of the measured pollutant a situation which is not experienced in the former. Although sensor manufactures tend to provide temperature/RH dependent data (Alphasense, AAN), these are however not sufficient enough to account for the additional problems encountered in operating these sensors in real world (see details in Section 3.5). In order to utilise electrochemical sensor nodes as indicative techniques for air quality assessment, it becomes imperative to develop a baseline-temperature correction methodology to account for the change in baseline resulting from variations in ambient temperature.

The work presented in this paper explains the methodology developed to address this problem through quantitative extraction and correction of temperature-dependent baseline effects.

1.1. Electrochemical sensors

Most of the works presented in this paper are based on the use of three-electrode electrochemical sensors. The four electrode electrochemical sensors are only included in this work to validate the baseline correction methodology.

1.1.1. Three-electrode electrochemical sensors

The main electrochemical sensor nodes used in this work utilise CO-AF, NO-A1 and NO_2 A1 electrochemical sensors manufactured by Alphasense Ltd, UK. They are made of three electrodes: working (sensing electrode), counter electrode and reference electrode. These electrodes are in contact with an electrolyte made of highly concentrated sulphuric acid via a wetting filter. As with all electrochemical cells, current is generated by the flow of electrons resulting from the reduction-oxidation (redox) reaction occurring at the electrode-electrolyte interphase. Oxidation/reduction half reaction of the target gas occurs at the working electrode (WE), while the counter electrode completes the redox reaction by reducing oxygen or oxidising water molecules. Electrochemical reactions are governed by Nernst equation which relates the natural logarithm of the ratio of the activities of the oxidant and reductant to temperature, number of moles of electrons involved in the reaction, temperature, Faradays constant and the cell potential. This type of electrochemical cell is referred to as potentiometric cell. However, if the active electrode is maintained at a constant voltage, then the electrochemical cell is said to be operated as an amperometric cell, in which case the current generated by the redox reaction is related to the concentration of the target gas (Stetter and Li, 2008). The reference electrode is used to anchor the WE at a stable potential, this is achieved by connecting it to the WE via a potentiostat (Fig. 1).

1.1.2. Four-electrode electrochemical sensors

More recently Alphasense have developed a novel four-electrode electrochemical sensor which were used in a recent project involving the deployment of sensor networks for air quality at London Heathrow airport (SNAQ-Heathrow project) (Popoola et al., 2013). The additional electrode in this new sensor called the auxiliary electrode (AE) is similar in design material as well as arrangement to the WE. However, the AE is not in contact with the target gas. It therefore provides useful information on the effect of ambient condition mostly temperature on the output of WE. In this work, raw EC data refer to the mixing ratio equivalents of the currents recorded at WE while AE outputs are mixing ratio equivalents of baseline-temperature dependence of WE. As part of the validation section for the baseline-temperature correction method, the fitted baseline presented in this work will be compared to AE outputs. The particular sensors used in the work presented here were the CO-B4 and NO-B4 sensor from Alphasense.

1.2. Electrochemical sensor nodes

Details of the mobile electrochemical sensor nodes used in this work have been reported (Mead et al., 2013). In summary, each sensor node is made up of three-electrode electrochemical sensor measuring CO, NO and NO_2. Each node also has temperature sensor as well as GPS and GPRS module for position/time and data transmission. The temporal resolution of the data is 5 s and all sensor nodes are powered by main power supply throughout the duration of the deployment.

1.3. Fundamental temperature effects on electrochemical sensors

The electrochemical sensors used in this study are designed to work as amperometric devices, configured in such that the output current is limited by the diffusion of gases into the sensor (Mead et al., 2013). In this mode of operation, the overall current is the summation of the current that results from diffusion across four regions, namely: the electrolyte–electrode, membrane, gas space

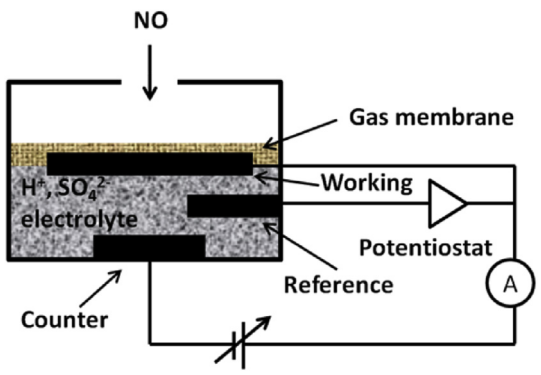

Fig. 1. Schematic of an amperometric NO electrochemical gas sensors showing the basic components including three electrodes, electrolyte and gas membrane.