



Electrochemical sensors applied to pollution monitoring: Measurement error and gas ratio bias – A volcano plume case study



T.J. Roberts^{a,b,*}, J.R. Saffell^c, C. Oppenheimer^d, T. Lurton^a

^a LPC2E, UMR 7328, CNRS-Université d'Orléans, 3A avenue de la Recherche Scientifique, 45071 Orléans, Cedex 2, France

^b Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

^c Alphasense Ltd, Sensor Technology House, 300 Avenue West, Skyline 120, Great Notley Essex CM77 7AA, UK

^d Department of Geography, University of Cambridge, Downing Place, Cambridge CB2 3EN, UK

ARTICLE INFO

Article history:

Received 2 December 2013

Accepted 27 February 2014

Available online 12 March 2014

Keywords:

Multi-Gas

Sensor response time

Pollution

Volcanic

E-nose

Electrochemical

Plume

ABSTRACT

There is an increasing scientific interest in the use of miniature electrochemical sensors to detect and quantify atmospheric trace gases. This has led to the development of 'Multi-Gas' systems applied to measurements of both volcanic gas emissions, and urban air pollution. However, such measurements are subject to uncertainties introduced by sensor response time, a critical issue that has received limited attention to date. Here, a detailed analysis of output from an electrochemical SO₂ sensor and two H₂S sensors (contrasting in their time responses and cross-sensitivities) demonstrates how instrument errors arise under the conditions of rapidly fluctuating (by dilution) gas abundances, leading to scatter and importantly bias in the reported gas ratios. In a case study at Miyakejima volcano (Japan), electrochemical sensors were deployed at both the crater-rim and downwind locations, thereby exposed to rapidly fluctuating and smoothly varying plume gas concentrations, respectively. Discrepancies in the H₂S/SO₂ gas mixing ratios derived from these measurements are attributed to the sensors' differing time responses to SO₂ and H₂S under fluctuating plume conditions, with errors magnified by the need to correct for SO₂ interference in the H₂S readings. Development of a sensor response model that reproduces sensor *t*₉₀ behaviour (the time required to reach 90% of the final signal following a step change in gas abundance) during calibration enabled this measurement error to be simulated numerically. The sensor response times were characterised as SO₂ sensor (*t*₉₀ ~ 13 s), H₂S sensor without interference (*t*₉₀ ~ 11 s), and H₂S sensor with interference (*t*₉₀ ~ 20 s to H₂S and ~ 32 s to SO₂). We show that a method involving data integration between periods of episodic plume exposure identifiable in the sensor output yields a less biased H₂S/SO₂ ratio estimate than that derived from standard analysis approaches. For the Miyakejima crater-rim dataset this method yields highly correlated H₂S and SO₂ abundances (*R*² > 0.99) and the improved crater-rim data analysis combined with downwind measurements yields H₂S/SO₂ = 0.11 ± 0.01. Our analysis has significant implications for the reliance that can be placed on 'Multi-Gas'-derived gas ratios, whether for volcanological or other purposes, in the absence of consideration of the complexities of sensor response times.

© 2014 Published by Elsevier B.V.

1. Introduction

The commercial development of low-cost, lightweight electrochemical gas sensors (e.g. as manufactured by Alphasense, CityTech, Membrapor), with low power requirements, brings new opportunities within environmental science for in-situ monitoring of atmospheric gases. The incorporation of electrochemical sensors into 'Multi-Gas' systems used for volcano monitoring has enabled a range of gases (including H₂S, SO₂, CO, H₂, HCl) to be characterised in volcanic plumes (e.g. see Roberts et al., 2012 and references therein). Temporal variations in volcanic gas composition (as identified from gas ratios) can be used to infer

changes in subsurface processes and inform long-term volcano hazard monitoring (e.g. Shinohara et al., 2008; Aiuppa et al., 2009). Measurements of volcanic gas emissions also inform the assessment of downwind plume impacts on the atmosphere and ecosystems. Recently, similar miniature electrochemical sensors have also been deployed in networks to characterise urban pollution (Hasenfratz et al., 2012; Li et al., 2012; Mead et al., 2013), using both fixed stations and mobile sensors (e.g. carried by cyclists, pedestrians and on urban tramways).

A challenge in both urban and volcanic environments is to quantify gas abundance from the sensor current or voltage output. The sensor is exposed to complex mixtures of gases whose abundances may fluctuate rapidly, due to close proximity to the pollution source(s), inhomogeneous dilution by turbulent eddies or local wind field variations affecting exposure of the sensor. The sensor itself has a finite response time, typically 10–30 s to reach 90% of signal (see Manufacturer's

* Corresponding author at: LPC2E, UMR 7328, CNRS-Université d'Orléans, 3A Avenue de la Recherche Scientifique, 45071 Orléans, Cedex 2, France. Tel.: +33 238255268.

E-mail address: Tjarda.Roberts@gmail.com (T.J. Roberts).

datasheets (Alphasense.com) and Roberts et al., 2012; Mead et al., 2013). In such a period, gas exposure to a volcanic plume at a given location may vary substantially as dictated by the source dynamics and changing wind field. Physical limitations to the time-response of electrochemical sensing devices include the rate of diffusion of species within the sensor, which can be compounded by absorption and desorption of gases from surfaces within the instrument, e.g. for HCl (Roberts et al., 2012). For miniature electrochemical sensors (~cm, <10–20 g), a relatively fast (10–30 s) response time has been achieved through novel sensor design minimising distances between the electrodes, electrolyte and gas diffusion barrier, resulting in very small, low cost and low power sensing devices. Where weight and power requirements allow, electrochemical detector sensitivity can be improved and time-responses reduced to just a few seconds by using portable (~2 kg) instruments (Interscan, Inc.) e.g. as deployed by Kelly et al. (2013) for in-situ measurements of H₂S and SO₂ alongside a UV ozone spectrometer in Redoubt volcano plume.

Determining the measurement uncertainties under complex, heterogeneous plume conditions is non-trivial if gas fluctuations occur on similar timescales to the sensor response, and particularly where cross-sensitivities also need to be subtracted in post-processing: the sensor output is a function of its time-dependent response(s) to its recent exposure to (multiple) gases whose abundances may rapidly fluctuate with time. In other words, gas ratios computed for an unvarying source will show variations (artefacts) related to the exposure time histories and sensor responses. This can be a particular issue where sensors are exposed to intermittent ‘puffs’ of volcanic plume, and if attempts are made to identify rapid fluctuations in source composition. Such measurement errors have not been considered in detail to date in volcanic gas ratios reported from Multi-Gas systems. Here, careful analysis of H₂S and SO₂ electrochemical sensor measurements of the plume of Miyakejima volcano (Japan), at both crater-rim and downwind locations (where gas abundances fluctuate to contrasting extents), are used to identify these sources of error. The focus is how finite (and contrasting) response times of the sensors can act to introduce measurement uncertainties and bias in the reported gas ratios (e.g. H₂S/SO₂) under rapidly fluctuating gas concentrations (particularly in cases where interferences are subtracted in data post-processing). Sensor response modelling and a forward ‘instrument model’ are developed to illustrate Multi-Gas instrument behaviour. Improved data analysis approaches are discussed, including sensor response modelling (Roberts et al., 2012) and an integrated data analysis method. The aim is to highlight a source of inaccuracy in Multi-Gas monitoring of volcano emissions and their reported gas ratios (e.g. H₂S/SO₂, CO₂/SO₂), and to outline methods for improved quantitative characterisation of complex fluctuating plume environments (e.g. volcanic and urban) by electrochemical sensors.

2. Electrochemical sensing of pollutant gases

An overview of the use of miniature electrochemical sensors to monitor volcanic plume gases (SO₂, H₂S, HCl, CO, H₂) and urban pollution (CO, NO, NO₂) is given by Roberts et al. (2012) and Mead et al. (2013), the former also detailing use of electrochemical sensors within in-situ (Multi-Gas) monitoring systems in volcanology (e.g. Aiuppa et al., 2005a; Shinohara, 2005; Witt et al., 2008b). Issues concerning the application of electrochemical and other miniature sensors to environmental monitoring include: calibration of sensor sensitivity (response) to the target gas, drift of baseline and sensor sensitivity, (cross-)sensitivities within complex gas mixtures, which can be a function of temperature, humidity and pressure conditions, as well as potential for competition between different species for active sites at the detector, or even poisoning of the detector, reducing sensitivity. All of these require detailed evaluation for accurate detection of gas abundances and characterization of emissions. Here, we focus specifically on measurement uncertainties that arise from the finite sensor response time

to fluctuating plume gas concentrations, as can be found in both urban and volcanic environments.

2.1. Electrochemical sensing by ‘Multi-Gas’ systems in volcanology

There is a growing interest in miniature electrochemical sensors to characterise volcanic emissions, principally through incorporation into portable ‘back-pack’ instruments or autonomous fixed stations containing multiple in-situ sensors. Such ‘Multi-Gas’ systems are increasingly providing valuable insights into volcanic degassing and complementing monitoring networks on active volcanoes. The first Multi-Gas system contained an electrochemical sensor for SO₂, alongside an infra-red sensor for CO₂, Shinohara (2005). Subsequent Multi-Gas system developments (see Roberts et al., 2012 for an overview) include additional electrochemical sensors for H₂S (e.g. Aiuppa et al., 2005a; Witt et al., 2008b) and infra-red sensors for water-vapour (Shinohara and Witter, 2005). Detection of volcanic H₂ by electrochemical or semi-conductor sensors (Aiuppa et al., 2011a; Shinohara et al., 2011a,b; Moussallam et al., 2012; Roberts et al., 2012), and HCl and CO by electrochemical sensors (Roberts et al., 2012) has also been demonstrated. Data analysis of the Multi-Gas instrument sensor output involves extraction of gas mixing ratio time-series, from which volcanic gas ratios (e.g. H₂S/SO₂, H₂/SO₂, CO₂/SO₂) can then be derived using scatter plots and linear regression. Variations in volcanic gas ratios inferred from repeated field measurements of volcanic emissions over a multi-year period or a long-term installation at the volcano crater rim can provide valuable insights into changes in subsurface magmatic and hydrothermal processes and contribute to volcano hazard assessment, e.g. Shinohara et al. (2008, 2011a,b), Aiuppa et al. (2009, 2011b), and Edmonds et al. (2013).

2.2. Data analysis methods to extract volcanic gas ratios from electrochemical sensors

The existing data analysis approach for electrochemical sensing of volcanic gases was formalized by Roberts et al. (2012): sensor output can be represented by Eq. (1), denoting the electrochemical sensor output, I (a current or equivalently a voltage signal depending on the electronic circuitry), as a function of the target gas abundance $[X]$ (in ppmv or 10⁶ mol/mol), and the sensor sensitivity s (nA/ppmv or mV/ppmv).

$$I = B + s \cdot [X] + \sum c_{s_y} \cdot [Y] \quad (1)$$

The sensor may also exhibit cross-sensitivities, c_{s_y} (nA/ppmv or mV/ppmv), to other gases of mixing ratio $[Y]$. B is the sensor baseline (nA), which may be constant or drift non-linearly with time, but is typically small compared to the ~ppmv plume gas signal, and is readily quantified during periods of negligible plume exposure. Temporal variations in the gas mixing ratios $[X]$, and $[Y]$, thus cause temporal variations in the sensor current output I , which in Multi-Gas systems is typically logged at 0.1–1 Hz. The sensor (cross-)sensitivities, s , and c_{s_y} , are determined by laboratory calibration prior to or post-field deployment.

Table 1 provides an overview of SO₂ and H₂S sensors in Multi-Gas systems deployed in volcanic plumes, their (cross-)sensitivities, and – where known – t_{90} response times to reach 90% of final sensor signal (to a constant gas abundance). Removal of interferences is critical to accurate detection and quantification of gases in complex plume mixtures. In volcanic plumes such interferences tend to be negligible for SO₂ sensors (e.g. SO₂-AF, SO₂/CF-100) that contain an integrated filter which prevents interferences from H₂S, and where potential cross-sensitivity from NO₂ is negligible given NO₂ ≪ SO₂. However, H₂S sensors (e.g. H₂S-A1, H₂S/C-50) typically exhibit cross-sensitivity to SO₂, of magnitude ~10–20% (as defined in terms of the sensor signal in ppmv target gas (H₂S) that occurs for a given ppmv SO₂ exposure). If not removed, this interference would cause substantial overestimation

Download English Version:

<https://daneshyari.com/en/article/4712386>

Download Persian Version:

<https://daneshyari.com/article/4712386>

[Daneshyari.com](https://daneshyari.com)