

Developing Low Concentration Acetic Acid Sensors for the Museum Sector

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Abstract

There is a demand for affordable acetic acid sensors for the heritage sector, capable of detecting parts per billion concentrations (ppb), to enable wide spread museum monitoring of this compound. This paper demonstrates the potential for lead oxide coated quartz crystal microbalances (QCMs) to sense such concentrations of acetic acid. The prototype QCM sensor unit recorded a gradual increase in mass over time in the presence of ~216 ppb of this species, due to the formation of lead acetates. Furthermore, as the sensor's response to changes in relative humidity produced a step change in mass, the sensor's response to acetic acid should be separable from that caused by water vapour fluctuations.

Key words: Acetic acid, Museums, QCM, nano materials, gas sensing

Introduction

Acetic acid has been detected inside museum display cases and linked to artefact degradation [1]. For a general museum collection, guideline concentrations of less than 100 ppb are stated [2]. However, current monitoring methods available to museums are too costly, require expert knowledge and/or have high levels of uncertainty. Low cost, accurate acetic acid sensors are required for the heritage sector, which would enable wide spread monitoring of this compound in museums and allow data driven preventative conservation to be performed.

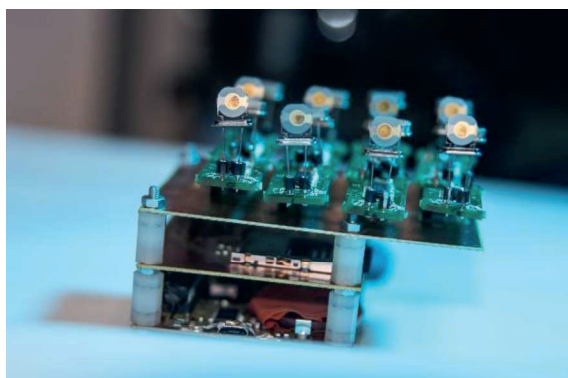


Fig. 1. Handheld QCM data logger with eight lead oxide coated sensors.

QCMs coated in lead have been previously used to detect corrosive environments in museums [3]. However, as lead forms a thin layer of lead oxide on its surface over time, an increase in mass can be observed even in clean air. Furthermore, as this process is dependent on humidity, it is difficult to isolate and quantify the response due to acidic vapours.

This paper investigates the sensitivity of lead oxide coated QCMs towards acetic acid and their interference from water vapour. It is postulated that they will have greater stability in clean air and reduced cross-interference from water, compared to lead. Furthermore, the use of small particles, as opposed to a continuous surface, deposited onto QCMs is hypothesised to increase the sensitivity of the sensor.

Samples

Lead oxide particles were synthesised according to Yousef et al [4]. Dynamic light scattering established the powder was polydisperse, with particle sizes ranging from the nano to the micro scale. X-ray diffraction and Raman Spectroscopy confirmed the product was lead oxide, predominantly the orthorhombic form.

HC49, uncanned, 10MHz AT-cut crystals with gold electrodes measuring 4mm in diameter, with an 8mm quartz backing plate were used in this study, obtained from Quartztec Ltd.

A 0.3mg/ml suspension of the synthesised lead oxide powder was prepared in a 50:50 blend of water:glycerol. A volume of 6 μ l was pipetted centrally onto both sides of the gold electrodes on the QCMs. They were then dried in an oven at 150°C for 1 hour, 300°C for 30 minutes and then 450°C for 1 hour. After drying, the resulting frequency loading was approximately 10 kHz.

Experimental methods

Custom built electronics were developed to infer the frequency difference between a coated and uncoated QCM, based on previous research performed by Agbota et. al [5]. The resulting system can monitor the outputs for up to eight QCMs, logging the data to an SD card. The handheld, battery operated device is shown in Figure 1.

The QCM data logger was utilised to monitor the change in frequency of eight coated QCMs during exposure in the lab over the course of 12 days. The temperature and relative humidity was recorded using an EL-USB-2-LCD data logger (EasyLog).

Lead oxide coated QCMs were also exposed in NPL's Tunable Rapid Atmospheric Controlled Environment (TRACE) facility at 54% RH and 19°C. A FlexStream™ Gas Standards Generator (Kin-Tec) with an acetic acid permeation tube was used to introduce a known concentration of acetic acid into the exposure chamber. The concentration was calculated from knowledge of the permeation rate and flow rate of the diluent scrubbed air and was estimated to be 216 ppb.

Exposure of lead oxide coated QCMs

Lead oxide coated QCMs showed a response to changes in relative humidity – shown in Figure 2. The frequency tracks the humidity change, which is postulated to be water absorbing and desorbing from the lead oxide coating.

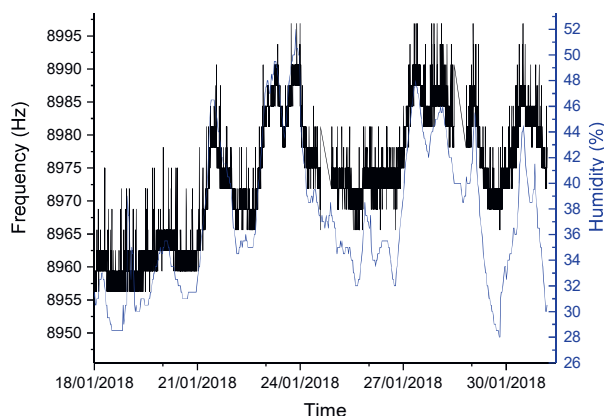


Fig. 2. Coated frequency change during exposure to fluctuating humidity.

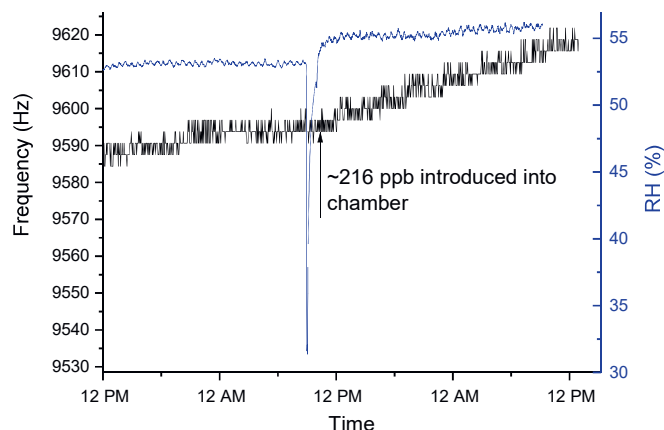


Fig. 3. Coated frequency change during exposure to acetic acid

When the coated QCMs were exposed to 216 ppb acetic acid at 54% RH, a change in gradient was observed – shown in Figure 3.

The gradient change during acetic acid exposure was 0.86 Hz/hr, whereas the gradient prior to acetic acid introduction was approximately 0.45 Hz/hr. This suggests a limit of detection of approximately 100 ppb, which is a commonly suggested guideline for museums [2].

As the device showed a response to humidity, this will need to be monitored during exposures, however, it is common for museums to monitor RH. Furthermore, as the type of response was different from that observed due to the presence of acetic acid, it is postulated that the influences of the two factors will be separable.

References

- [1] L. T. Gibson, C. M. Watt, Acetic and formic acids emitted from wood samples and their effect on selected materials in museum environments, *Corrosion Science* 52, 172–178 (2010) doi: 10.1016/j.corsci.2009.08.054.
- [2] PAS 198: Specification for managing environmental conditions for cultural collections. The British Standards Institution, 2012.
- [3] T. Grøntoft et al. Pollution monitoring by dosimetry and passive diffusion sampling for evaluation of environmental conditions for paintings in microclimate frames. *Journal of Cultural Heritage* 11, 411–419 (2010); doi: 10.1016/j.culher.2010.02.004
- [4] R. Yousefi et al. Synthesis and characterization of single crystal PbO nanoparticles in a gelatin medium, *Ceramics International* 40, 11699–703 (2014); doi 10.1016/j.ceramint.2014.03.180
- [5] H. Agbota et al. Remote assessment of cultural heritage environments with wireless sensor array networks. *Sensors* 14, 8779–8793 (2014); doi:10.3390/s140508779