

Detection of Butyric Acid Concentration in Aqueous Solution Towards Intraruminal Volatile Fatty Acid Measurement

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Summary:

The use of polybutadiene thin-film coating on quartz crystal microbalance sensors is explored for measuring butyric acid concentration in an aqueous solution. Experiments show polybutadiene has a higher absorption rate of butyric acid. The fabricated sensor demonstrates an insensitivity to acetic acid and a low sensitivity to propionic acid. Therefore, progress is made towards selectively measuring butyric acid in aqueous solutions containing volatile fatty acids.

Keywords: QCM sensor, liquid sensing, butyric acid, rumen monitoring

Introduction

Methane (CH₄) is a well-known greenhouse gas with a reported potency of 20-85 times greater than carbon dioxide (CO₂). The impact of dairy, non-dairy, and other bovine species are the source of ≈22% of all global CH₄ emissions [1]. Using well-established systems, such as Green-Feed or respiration chambers, the CO₂ and CH₄ emissions can be measured. However, these external measurements don't provide complex information on the health status of the cattle. Measuring the concentration of volatile fatty acids (VFAs) in the rumen is of interest as it can be correlated to the production of CH₄, provide more comprehensive health statistics of the animal, and assist in preventing acidosis [2, 3].

Of the VFAs, acetic, propionic, and butyric acids are of most interest. However, these VFAs have similar molecular structures and are notoriously difficult to differentiate. We aim to measure these three acids in a small formfactor device capable of being swallowed by the cattle. Towards this goal we have implemented a quartz crystal microbalance (QCM) sensor. A QCM is a small and cost-effective resonator capable of measuring incredibly small quantities of molecules. By applying a thin film to the surface of a QCM, it is possible to capture molecules of interest and measure the change in mass on the surface of the sensor [4].

Materials and Methods

Prior to sensor fabrication, the presence of polybutadiene (BR) in aqueous solutions containing VFAs is investigated. Each sample has 0.05 M of a single VFA in DI water. "VFA + BR" samples

have 0.8 g of BR beads per 5 ml of solution. Measured molar concentrations of VFA samples are measured by liquid chromatography after 2 hours (Table 1).

Tab. 1: Butyric acid (Bu), Propionic acid (Pr), and Acetic Acid (Ac) molar concentration in samples.

Sample	Bu [M]	Pr [M]	Ac [M]
VFA #1	0.052	0.046	0.045
VFA #2	0.052	0.046	0.045
VFA + BR #1	0.042	0.045	0.045
VFA + BR #2	0.042	0.045	0.045

Samples with BR present show a higher absorption of butyric acid compared to the other VFAs. From this result we believe that BR coating may provide a higher selectivity to butyric acid.

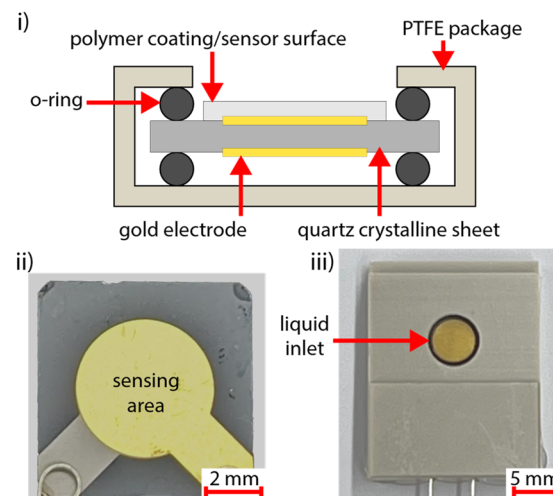


Fig. 1. i) structure of device with the positioning and composition of sensor and polytetrafluoroethylene (PTFE) packaging. ii) 20 MHz resonant QCM sensor with a \varnothing 5 mm sensing area. iii) packaged sensor.

The sensor is prepared by dissolving a solution of BR (3 wt%) and tetralin (97 wt%) and applying it to the surface of a commercial 20 MHz resonant QCM by spin coating (3000 rpm). The coated sensor is dried in a vacuum chamber at 60°C for 12 hours. The sensor is inserted into an airtight polytetrafluoroethylene (PTFE) package with the coated side of the sensor open (Fig. 1).

Experimental testing is performed inside a constant temperature chamber at 25°C. The sensor is suspended in a beaker with a magnetic stirrer to rapidly homogenize the solution (Fig. 2). Measurements were performed using a vector network analyzer (VNA) from Keysight (FieldFox n9923a).

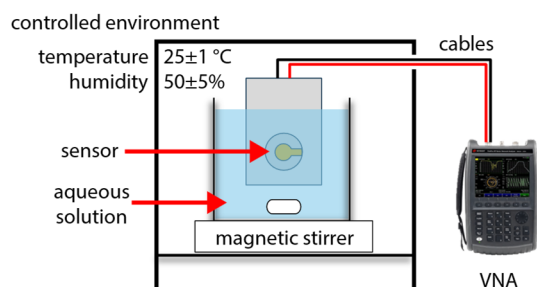


Fig. 2. Diagram of the experimental setup.

Results and Discussion

The sensor was submerged in DI water and the response to the addition of 0.05 mol/L of acetic, propionic, and butyric acids were tested.

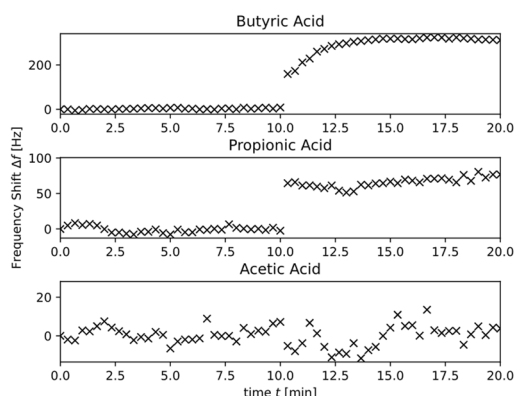


Fig. 3. Measured results from butyric, propionic, and acetic acid sample solutions. The VFA is added at 10 minutes.

The response of the sensor shows a 300 Hz change to butyric acid and a relatively insensitive response to the other VFAs of <80 Hz and <20 Hz (Fig. 3). The response to butyric acid is rapid at under 2.5 minutes and is stable after 5 minutes. The step response of butyric acid was also tested in 0.02 mol/L increments. The linear relationship between butyric acid concentration in aqueous solution can be seen in Fig. 4.

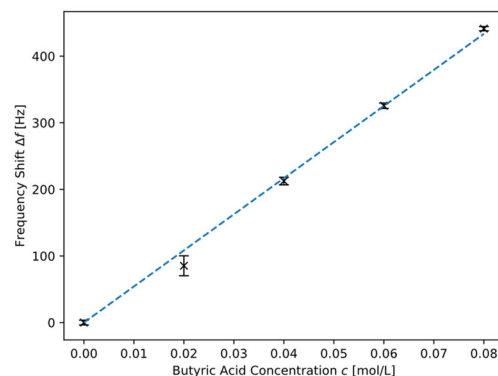


Fig. 4. Step response to butyric acid. Error bars represent standard deviation between measurements.

Systematic and human error are likely the cause of discrepancy in fig. 4. Further testing for repeatability is underway. However, these results demonstrate that a BR coated QCM is capable of selectively measuring butyric acid concentration in an aqueous solution.

Materials and Methods

A BR coated QCM is fabricated and used to measure the concentration of butyric acid in an aqueous solution. The sensor is shown to be less sensitive to propionic and acetic acid, allowing the differentiation of VFAs, a function which is not yet reliably available in such a small form-factor.

References

- [1] Z. Lei, et al., A 130-year global inventory of methane emissions from livestock: Trends, patterns, and drivers, *Global Change Biology* 28(17), 5142-5158 (2022); doi: 10.1111/gcb.16280
- [2] N. Stepanchenko, et al., Microbial composition, rumen fermentation parameters, enteric methane emissions, and lactational performance of phenotypically high and low methane-emitting dairy cows, *Journal of dairy science* 106(9), 6146-6170 (2023); doi: 10.3168/jds.2022-23190
- [3] Y. Yusuke, et al., Comparative Studies on Electrodes for Rumen Bacteria Microbial Fuel Cells, *Sensors* 23(8), 4162 (2023); doi: 10.3390/s23084162
- [4] N. Alanazi, et al., A review of quartz crystal microbalance for chemical and biological sensing applications, *Sensing and Imaging* 24(1), 10 (2023); doi: 10.1007/s11220-023-00413-w

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