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Nanoporous Gold Electrocatalysis for Ethylene Monitoring and Control

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Summary

Maintaining the quality and freshness of fruit and vegetables during transportation and storage is an important role for most postharvest industries. One way to control freshness is by carefully monitoring and regulating exposure to ethylene. By limiting exposure to ethylene the natural aging process of fresh produce is slowed down, thus prolonging its shelf life. This is especially important for organic produce where the use of chemicals for decay control is not practiced. In this paper, the performance characteristics and method of use of a new sensing approach for postharvest ethylene measurements is introduced. In this sensor, ETH-1010, oxidation of ethylene on a gold electrocatalyst produces a highly detectable and measurable amperometric signal. ETH-1010 has been packaged into a complete field portable unit. It continuously samples the air at a set flow rate, (commonly between 200 and 500 ml min^{-1}), and reports the ethylene concentration in air at a user-specified time interval. The direct contact between the ethylene molecules in air and electrocatalytic surface renders this process more sensitive and responsive than conventional diffusion-type electrochemical cells. This approach has been shown to be quite effective for continuous monitoring of cold storage rooms, where detection of lower than 10 ppm down to 10 ppb is desirable. This configuration was also used to examine the applicability of electrocatalysis for scrubbing ethylene. Results for ethylene removal have been presented in this paper where the surface reactivity on the electrocatalyst is typically between 0.1 and 0.2 μmol h^{-1} cm^{-2}. In the sensor, the high reaction rate provides high sensitivity and response time, while making it feasible to consider using electrocatalysis in a scrubbing mode for future applications.

Key words. electrocatalysis – amperometric – nanoporous gold – fruit maturity – ethylene ripening – methylcyclopropene – cold storage – controlled atmosphere

Introduction

Preservation of perishables such as fresh fruit and vegetables (FF & V) can be quite challenging due to the substantial amount of refrigeration required to prevent spoilage. In the case of FF & V, the air recirculated in the cold rooms can quickly become contaminated with ethylene gas produced by ripening fruit and vegetables. This can then lead to autocatalytic ripening of FF & V and accelerated spoilage even at ideal refrigeration temperatures. This issue is becoming progressively more critical for global trade and year round consumption of FF & V. Unfortunately, postharvest losses in developing countries account for greater than 25 % of the total fresh produce. Ethylene-related problems make up a significant portion of these losses and lead to negative economic impacts in billions of dollars every year (http://www.ars.usda.gov/research/projects/projects.htm). These losses affect growers, packers, storage houses, and distributors of FF & V. Furthermore, as the population of people living in impoverished countries continue to climb above 750 million, it is hard to ignore such enormous losses in fresh produce without running the risk of greater food security issues.

In general, ethylene-related problems are caused when high ethylene producing FF & V are placed in a storage area with highly ethylene sensitive FF & V. For example, avocados and apples are known to produce extremely high ethylene levels, even at temperatures below 4 °C. On the other hand, kiwifruit is not a high ethylene producer, but is extremely sensitive to the presence of ethylene. Kiwi should not be stored with commodities that produce significant amounts (Arpaia et al. 1985). As little as 5–10 ppb ethylene in the storage atmosphere can accelerate softening of kiwifruit without impacting other ripening processes. The result is unripe fruit that are excessively soft (Crisosto et al. 1999). Carrots produce very low ethylene at <0.1 μL kg^{-1} h^{-1} at 20 °C. However, exposure to exogenous ethylene of ~0.2 ppm and higher will induce development of isocoumarin and bitter flavour (Talcott and Howard 1999). Other examples are leafy greens, bean sprouts, broccoli, cucumbers, melons, and cut flowers where presence of ethylene results in accelerated decay and loss of quality. While separating the various fruit and vegetables may seem like a logical approach to cold storage, it is currently not practiced, partly due to insufficient knowledge about the storage condition and partly due to the apparent impracticality of isolating cold storage areas for various produces.

While long term storage of fruit and vegetables results in eventual ripening due to production and release of ethylene, monitoring of ethylene is currently not a widely adopted process in many packing houses and cold storage facilities. This is attributable to limited sensitivity and accuracy of current sensors. At or below 1 ppm detectors with sufficient sensitivity are too large and too expensive for most end-users to afford. Localization of more rapidly ripening fruit and sources of ethylene is challenged by the high cost and inconvenience in detection. Such localization could provide strategies to minimize ethylene production and to control spoilage and rapid ripening process.

Another application of the ETH-1010 ethylene sensor is for the determination of fruit maturity at harvest. This application plays a major role in determining storability, marketability, transportability, and general quality of climacteric fruit (SHEKARRIZ 2007; BLANKE 2008). A number of parameters are currently used to evaluate the maturity index of fruits and vegetables at harvest (http://www.hortresearch.co.nz/index/page/442). Examples of indices currently used for determining the commercial maturity are background skin colour, starch pattern index, and firmness. While physiological maturity determined from internal ethylene concentration (IEC) does not seem to correlate well with commercial maturity indices, it is a good indicator of storability and transportability of fruit (http://www.hortnet.co.nz/publications/science/m/mills/apple.htm). Therefore, harvest and postharvest storage and distribution decisions are more frequently based on internal ethylene concentration measurements, in addition to using the traditional indicators. Currently internal ethylene levels are measured by expert users taking a gas sample from an apple (intrusively using a core sampler or non-intrusively by collecting the ethylene outgas of the fruit) and running the sample through a laboratory gas chromatography (GC) system. This process is time consuming and expensive, limiting the number of growers and users that could benefit from this information. The US Department of Agriculture (USDA) and university agricultural extension centres play a major role in introducing and implementing more efficient and up-to-date practices into the current quality control (QC) culture within the postharvest industry in the US. The following sections provide more details on the method and device for rapid and cost-effective ethylene concentration measurement during postharvest applications.

Materials and Methods

The Electrocatalyst

At the heart of this device is a nanoporous gold electrocatalytic surface that is the primary sensing element. The basis for sensing by electrocatalytic oxidation of various analytes on gold is presented in other publications (SCHMIDT and PASTOR 1994; BURKE and NUGENT 1998). In this approach, the nano-particulate gold surface is active in adsorbing the analyte, e.g., ethylene molecules. Although gold is considered to be a noble and extremely unreactive metal, numerous reports in recent years show that atomic gold clusters ranging in size from 2 to 20 nm are highly active as heterogeneous catalysts in a number of chemical reactions (SANCHEZ et al. 1999; CORTIE and VAN DER LINGEN 2002; ASTRUC et al. 2005). Other typical catalytic metals such as platinum, palladium, nickel, cobalt, etc. have been shown to have interesting catalytic properties as nanoparticles, but these metals are already recognized heterogeneous catalysts (THOMPSON 1999). Gold in a nanoparticulate state, however, provides a new area of catalysis research, sometimes known as the "New Gold Rush."

Typically, a heterogeneous catalyst consists of a small amount of metal deposited on the surface of a metal oxide. Metal oxides such as alumina, ceria, zirconia, ferric oxide, titanium dioxide, and mixtures of metal oxides provide a support for the catalytic metal. They also provide a source/sink for oxygen in oxidation reactions. To be a catalyst, the dispersed metal must first adsorb both reactants and not significantly attract the products. This mechanism provides the pathway for bringing reactant molecules together to facilitate the reaction. Interestingly, nanoporous gold plated on a number of metal oxide substrates has attracted much attention for the catalytic oxidation of many small molecule and carbon-containing compounds. This is an important property for our consideration in that ethylene and other small molecules are attracted and adsorbed to the nanoparticle gold (GOTTFRIED 2003). This makes them ideal targets for electrochemical oxidation using our nanoparticle gold electrode cell. The successful oxidation of ethylene, propylene, ethylene glycol, formaldehyde, acetaldehyde, formic acid and carbon monoxide with air or oxygen has been reported (BURKE and NUGENT 1998).

Electrocatalytic Cell and Its Operation

The oxidation of ethylene contained in the sampled air flowing over a nanoporous gold anode, also known as a Working Electrode, provides a cell current that can be measured and used for the determination of ethylene concentrations in this sample (Fig. 1). In the present electrocatalytic cell, the gold working electrode provides electrical contact through a water and proton permeable Nafion® membrane, to the liquid chamber containing electrolyte, and counter- and reference- electrodes. Water that penetrates the Nafion membrane and wicks onto the gold surface is activated by the cell potential where it becomes the oxidizing agent for ethylene.

For sensing, the cell potential is maintained at 1.16 V vs. standard hydrogen electrode (SHE). Under this condi-

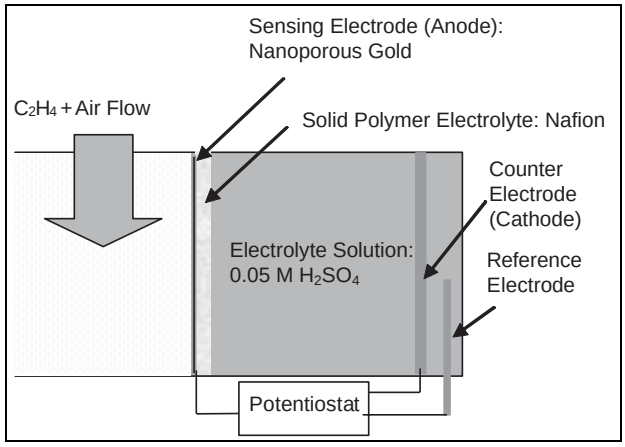


Fig. 1. Electrocatalytic reaction of ethylene on nanoporous gold catalyst.

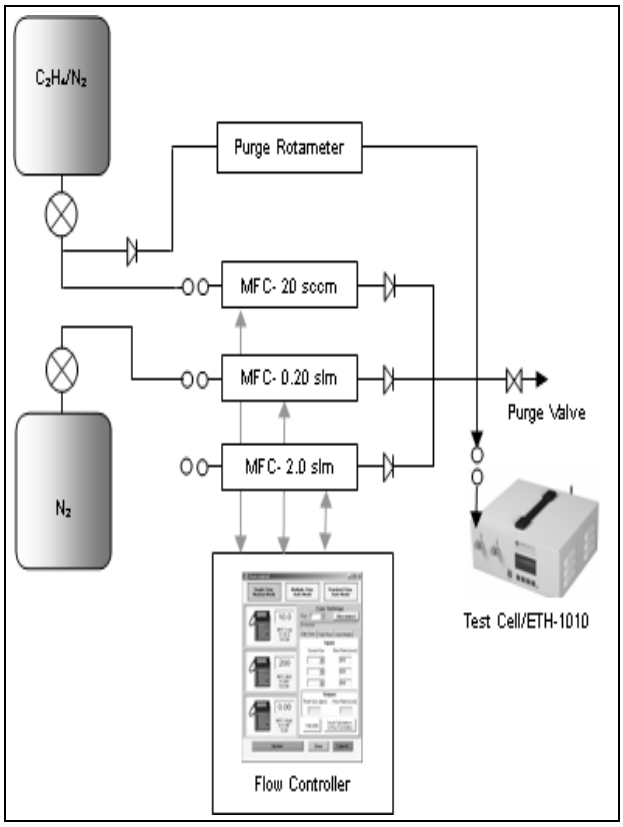


Fig. 2. The test apparatus design is aimed for easy operation and minimizing error in mixed gas.

tion, the gold electrode is stable and indirectly participates in the ethylene oxidation as an electrocatalyst. In many respects this sensing approach resembles a standard polymer electrolyte membrane (PEM) fuel cell in which the chemical energy from reaction of ethylene and water is converted to electrical energy in form of electron formation and generation of current between the cathode and anode.

Sensing Test Apparatus

To test the device performance, an experimental apparatus was assembled as shown in Fig. 2. Two gas standards, nitrogen and ethylene, were brought into contact at different ratios using precision Aalborg mass flow controllers (www.aalborg.com). The concentration of ethylene was controlled between 10 ppb to 10 ppm to within ±5 % for these studies. The flow rate through the cell was maintained at 200±5 ml min^{-1} for all the tests. The electronics for these measurements were developed internally, including the potentiostat for controlling the biased voltage while accurately measuring the current at the counter-electrode to within ±10 nA.

Reaction Rate Test Apparatus

The test setup consisted of an electrocatalytic decomposition cell, an ethylene sensing cell, and sources of ethylene and nitrogen, as shown in Fig. 3. A flow mixing system, with closed-loop control, created mixtures of ethylene and nitrogen at precise concentrations. The rate of reaction was determined from the drop in the ethylene concentration in the container.

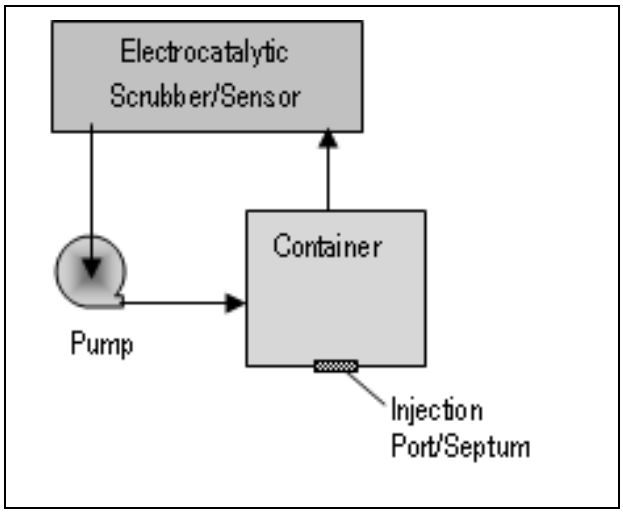


Fig. 3. Recirculating mode setup for electrocatalytic reaction rate determination. Different size containers are used in this study.

Results and Discussion

Not all Gold is Created Equal

The sensor response or sensitivity is the combined effect of analyte mass transfer, adsorption on active gold sites, oxidation reaction with water, and ion migration to counter-electrodes. Because of the serial nature of these processes, any one of them can result in signal suppression, which means a lower percentage of all molecules flowing over the electrocatalytic surface participate in producing a signal. Extensive laboratory studies show that efficient synthesis of the gold catalyst combined with proper sensing cell design play equally important roles in producing a robust and high sensitivity sensor (Gilbuena et al. 2007; Blanke 2008). Our gold electrocatalysts are synthesized using a proprietary approach involving chemical reaction and precipitation of pure gold on the surface of a polymer electrolyte membrane, namely Nafion®. The catalyst microstructural and morphological properties are affected by parameters such as gold loading, starting solution chemistry, and synthesis thermophysical conditions.

Scanning electron microscope (SEM) images of a typical gold electrocatalyst is shown in Fig. 4. These images clearly demonstrate the presence of multiple length scales to yield high performance, namely, nanoscale features provide high surface area for adsorption and reaction while micro- and meso-porous networks result in high mass transfer rates.

In average, gold loadings of 7.7 mg cm^{-2} were measured for gold deposits on the membrane with exposed dimensions of less than 10 cm^2. While all electrocatalysts were synthesized using similar gold loading, other conditions during synthesis affected the catalyst surface area and consequently in electrocatalytic response. Sensitivities ranged between 5 and 15 μA ppm^{-1} when exposed to 10 ppm standards and moderate flow rates of 500 ml min^{-1}.

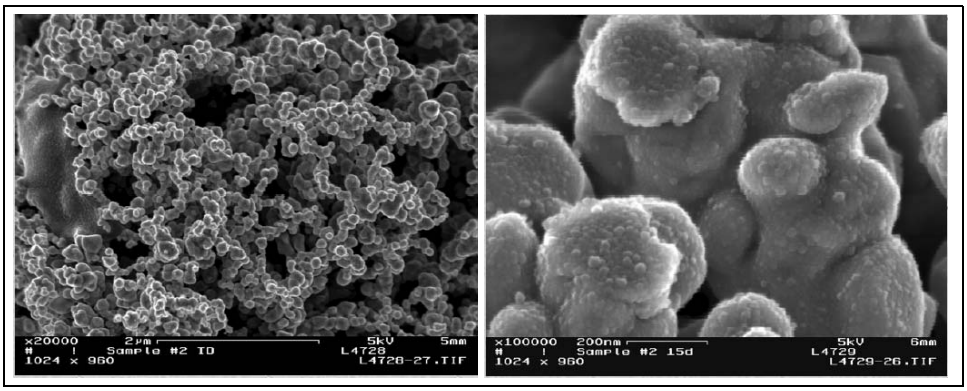


Fig. 4. Scanning electron microscope (SEM) images of nanoporous gold used as an electrocatalyst in the current sensing approach. The two images are at magnifications of 20,000x (left) and 100,000x (right) revealing features smaller than 10 nm.

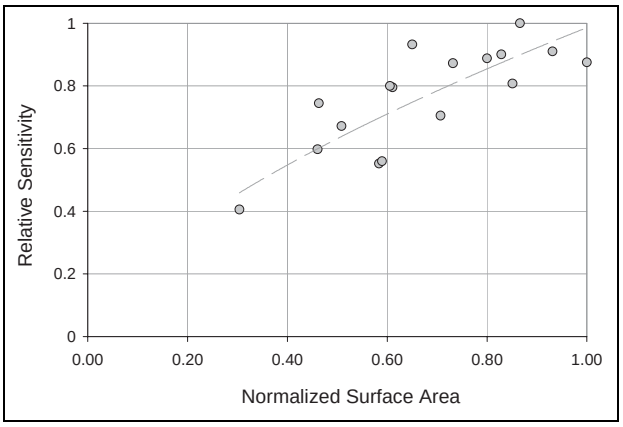


Fig. 5. Sensitivity or sensor response versus apparent surface area of catalyst.

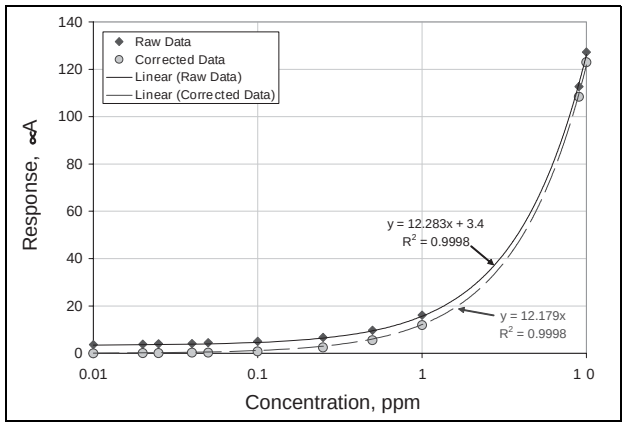


Fig. 6. Sensor linearity at low ethylene concentrations of below 10 ppm. The linear curves on a logarithmic scale provide an expanded view of small concentrations while they have exponential manifestations as shown above.

In general, the relationship between the surface area of the catalyst and the sensitivity or sensor response followed a monotonic relationship as shown in Fig. 5.

Standard Gas Measurements

A critical characteristic of a sensing device is whether or not it responds linearly over the desired operating range. Nonlinear response demands multiple-point calibration and the number of points required is a function of degree of departure from linearity. As shown in Fig. 6, the current electrocatalytic cell provides extremely linear response revealed by the trendline equations, extending to concentrations well above 100 ppm. The two graphs shown represent the raw data and the corrected data. Correction only removes the background leakage current, which shows up as a bias current in the data. Note that this particular electrocatalyst showed a response of 12.179 µA ppm^{-1}. Using the linearity property of our electrocatalytic sensor, which is typical of first order catalytic reactions, only two points are required for calibration of the device, zero and the maximum expected concentration, say 100 ppm. For better accuracy, the maximum point for calibration is selected to match the expected range of measurements, say 1 ppm for 0 to 1 ppm measurements.

Reaction Rate

Efficient electrocatalytic reaction is a critical part of the sensor. Fig. 7 shows two consecutive injections of ethylene directly into the device (see Fig. 3) such that the concentration was raised to approximately 100 ppb for each trial. By recirculating air over the electrocatalyst, the concentration of ethylene was allowed to drop through electrocatalytic decomposition. In this particular experiment, the consecutive data points were collected every 3 s, and each trial took roughly 4 min to bring the ethylene concentration to near zero. The 1/e characteristic time constant or the time it took for ethylene concentration to drop below 40 ppb was in average 1 min. Note that once a sample was injected into the device, it took between 5 and 10 s for the maximum concentration to be realized. The insert in this plot shows a magnified region of the data over a 1 min period, where the pulse-to-pulse signal fluctuation is ±5 ppb, but the 10 s average shows lower fluctuation in the results. Clearly, for very rapidly changing signal, for example near the peak shown in Fig. 7, time averaging will truncate the data. However, most real systems in postharvest applications will not undergo rapid changes in concentration and averages over 1 min should be more than adequate for signal processing and data interpretation.

When sampling the air in a closed system, both ethylene generation and destruction may be taking place simultaneously, and the total ethylene present in the system will vary according to the following equation:

$$\forall_{e,s} = \int_0^t [\dot{\forall}_{g,s}(t') - \dot{\forall}_{d,s}(t')]dt' \qquad (1)$$

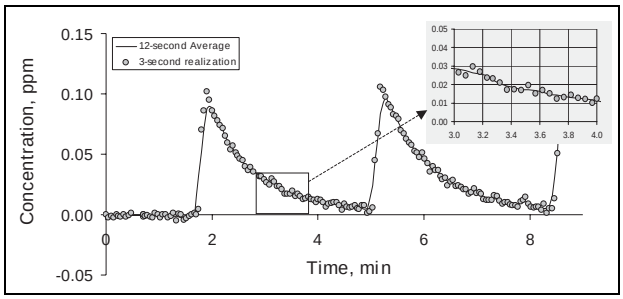


Fig. 7. Ethylene depletion within the dead space volume (20 mL) of Alpha Prototype.

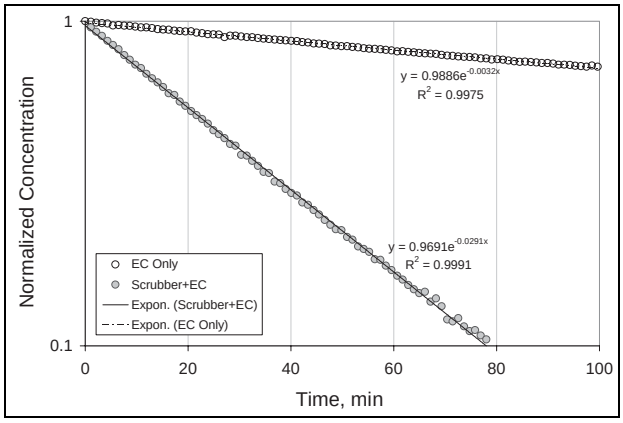


Fig. 8. Depletion rate measurements in a 4 L container with (solid symbols) and without a potassium permanganate scrubber (open symbols).

In the above equation $\dot{\forall}_{g,s}$ is the rate of generation of ethylene by the fruit or vegetables, $\dot{\forall}_{d,s}$ is the rate of scrubbing or destruction say by the electrocatalytic cell, $\forall_{e,s}$ is the volume of ethylene, and t denotes time. In a warehouse or cold storage facility full of apples, the generation rate may be quite large. In the other hand, a cold storage facility containing kiwifruit would have little to no indigenous source of ethylene other than the amount that permeates through the walls and doors, or by infiltration through ventilation system. In our model, only initial ethylene levels were considered for the purpose of sampling the air (i.e., the generation rate during sampling is negligible). In that case, the mathematical model is simplified to what is shown below:

$$C_s(t)/C_o = (1 - e^{-t/\tau}) \qquad (2)$$

C_s is the concentration at time t and C_o is the initial concentration. In the above equation τ is the characteristic system time constant, and it is defined by the interaction of the system parameters, α(catalyst rate constant in $\mu A\ ppm^{-1}\ cm^{-2}$), A (catalyst exposed surface area in cm^2), and $\forall_s$ (system volume in litre) as shown below:

$$\tau = \frac{\forall_s}{1.16x10^{-4} \cdot \alpha \cdot A} \qquad (3)$$

As evident from the above equation, smaller system volume or higher catalyst rate constant and surface area lead to faster reaction rates. This characteristic time constant is independent of the initial concentration, signifying that the percentage drop in concentration is always the same as shown in Equation (2). Referring back to Fig. 7, where the decay time constant was approximately 1 min for a system volume of approximately 20 ml, the catalyst rate constant works out to be around 0.3 $\mu A\ ppm^{-1}\ cm^{-2}$ (or roughly 0.11 $\mu mol\ hr^{-1}\ cm^{-2}$). For monitoring ethylene levels in a large storage room, such as a typical CA room, the rate of reaction of ethylene in the sensor can be ignored since the number of ethylene molecules reacted is significantly smaller than the total number of molecules present in the room. However, sampling smaller volumes may lead to a change in concentration caused by electrocatalytic measurement. In the current sensor configuration, the drop in concentration from one measurement point to the next, in the absence of ethylene generation, is simply the ratio of dead volume in the sensor to the total volume of room from which a sample is taken. Further discussion on this topic is provided in the following section in relation to Fig. 8.

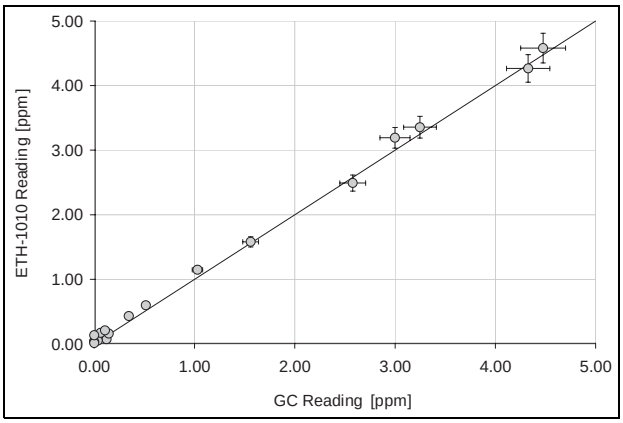


Fig. 9. Comparison of ETH-1010 measurements against gas chromatography for off-gassing of pears in RA chambers.

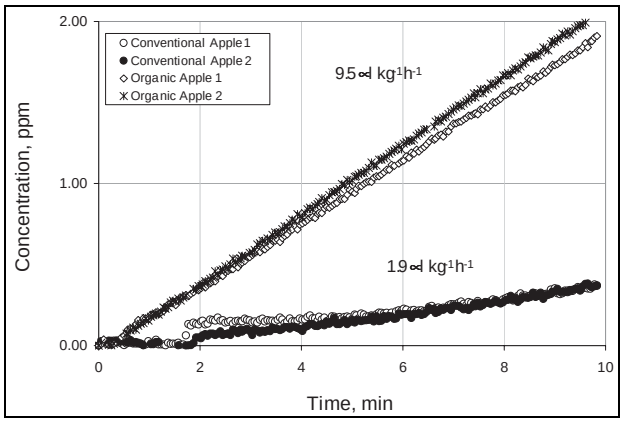


Fig. 10. Continuous sampling from a jar containing a single apple. The organic apples appeared to generate more than 9 µl $kg^{-1}\ h^{-1}$) of ethylene, or close to 5 times more ethylene than the conventional apples, possibly because they were treated with ethylene inhibitors.

Application for Scrubbing Rate Monitoring

The experimental results shown in Fig. 8 are for an experiment in which a container of approximately 4 L was used. The 200 ml min^{-1} flow was directed through a beta prototype sensor for 30 s followed by similar flow through a po-

tassium permanganate scrubber for 35 s, a total of 1.083 min cycle. This process continued for over 100 min and a data point was taken after each cycle. By injecting a 10,000 ppm gas sample into the container, the initial concentration was brought up to approximately 1 ppm and was allowed to be scrubbed out while monitoring this process with the sensor. This is evident in the slope of the two curves. While the time constant for the electrocatalytic scrubbing was linked to Equation (3), the potassium permanganate scrubber time constant, which is approximately 34 min, was related to the ratio of container volume (4 L) to the flow rate of air directed through the scrubber during each cycle (200 ml min^{-1} for 35 s). Clearly, the electrocatalytic depletion rate is roughly 10 % of that for potassium permanganate scrubber, which is 100 %.

Application in Apple and Pear Chamber Measurements

Tests were performed with various apples and pears kept in RA and CA chambers. These tests were carried out in collaboration with Dr. Jinhe Bai at the Oregon State University Experiment Station in Hood River, Oregon and Dr. Jim Mattheis at USDA-ARS in Wenatchee, Washington. For testing of pears, 18 different RA chambers were each filled with 10 pears. The air from each chamber was recirculated through our sensor while a small sample was simultaneously run through a GC. The data was then plotted for comparison as shown in Fig. 9. The very low ethylene producing pears were treated with 1-methylcyclopropene, which is an ethylene blocker. The agreement is quite good even at very low concentrations of significantly smaller than 0.5 ppm.

Another set of tests were performed for measuring the rate of ethylene production, which appears to be an important parameter for postharvest fruit quality characterization. By measuring the rate of ethylene production for various apples, one can determine the physiological maturity of fruit. This "real-time" information permits the grower to make instant decisions regarding timing the harvest as well as deciding on whether or not the fruit is storable or needs to be sold quickly. In these experiments, after placing a single apple in a sealed jar, the jar was connected to the sensor to measure the rate of ethylene build up inside the jar. Fig. 10 shows the results of our measurements for two different types of 'Fuji' apples, namely, organic vs. conventional. The results produce a very unambiguous measure of the ethylene production rate in each case, by simply using the slope of the curve at any point as a measure of the ethylene production rate.

Conclusions

In this paper, a new electrocatalytic sensor was presented where both sensitivity and response time was shown to be significantly better than standard diffusion-type electrochemical sensors. The oxidation reaction of the ethylene molecules on the surface of the nanoporous catalyst was shown to take place quite efficiently, typically between 0.1 and 0.2 μmol h^{-1} cm^{-2}. This high reactivity yields response time of better than 10 s and a sensitivity that provides the capability to measure ethylene down to 10 ppb using the current electrocatalyst configuration. Future developments could potentially provide even higher sensitivity and possibly better response times than those reported in this paper. The linearity of the sensor response provides a simple calibration operation that only requires a single point calibration at the expected range of measurement. The utility and use of this device was shown for monitoring ethylene levels during pear storage, monitoring scrubbing of ethylene in storage, and for determining the ethylene production rate of apples (or other fruit) as needed for quality control in postharvest processes.

Acknowledgements

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