

# A High Sensitivity Continuous Ethylene Monitoring Device for Postharvest Applications

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**As a fruit ripening hormone, ethylene gas is effective at greater than 0.1 ppm. There are significant costs associated with ignoring the ethylene gas produced by (or surrounding) fruit at the various stages of postharvest. In this paper, a new approach for postharvest ethylene sensing is introduced, in which electrocatalytic oxidation of ethylene molecules on the sensor produces an amperometric signal. The electrochemical sensor developed by Fluid Analytics, ETH-1010, has been packaged into a complete field portable unit. It continuously samples and monitors the ethylene in air at a specified flow rate, commonly between 100 and 500 mL/min. The direct contact between the molecules in air and electrocatalytic surface renders this process more sensitive and responsive than conventional diffusion-type electrochemical cells. The detection threshold for our sensors has been better than 100 ppb, although a detection threshold of 10 ppb and better have also been developed and tested with this device. The overall system for this sensing approach is relatively simple and requires few components, thus providing a very cost effective gas monitoring system. This paper describes the method of detection of ethylene and applications of the current device.**

Availability of high quality fresh fruits and vegetables is now year round, thanks to improved packaging, storage technologies, and rapid global transportation (Sloan, 1996). Fruit maturity at harvest plays a major role in determining storability, marketability, transportability, and general quality of fruit. A number of parameters are currently used to evaluate the maturity index (<http://www.hortresearch.co.nz/index/page/442>). Examples of indices currently used for determining the commercial maturity are background skin color, starch pattern index, and firmness. While physiological maturity determined from internal ethylene concentration (IEC) does not seem to correlate well with the 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, the harvest and postharvest storage and distribution decisions are more and more 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, which limits the number of growers and users that could benefit from this information. The following sections provide more details on the method and device for rapid and cost-effective ethylene concentration measurement during postharvest applications.

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## Materials and Methods

**GOLD ELECTROCATALYST.** At the heart of this device is a nanoporous gold electrocatalyst as the primary sensing element. The basis for sensing by electrocatalytic oxidation of various analytes on gold is covered in other publications (Burke and Nugent, 1998; Schmidt and Pastor, 1994). In this approach, the nano-particulate gold surface is active in adsorbing the analyte, e.g., ethylene molecules. Scanning electron microscope (SEM) images of a typical gold electrocatalyst are shown in Fig. 1. These images clearly demonstrate the presence of multiple length scales to yield high performance, namely, nanoscale primary particles and features provide high surface area for adsorption and reaction, while micro- and meso-porous networks result in high mass transfer rates.

**ELECTROCATALYTIC CELL OPERATION.** The oxidation of ethylene contained in the sampled air flowing over a nanoporous gold anode (working electrode) provides a cell current that can be measured and used for the determination of ethylene concentrations in this sample (Fig. 2). In the current electrocatalytic cell, the gold working electrode provides electrical contact through the Nafion® membrane, to the liquid chamber containing electrolyte, and to 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 the analyte.

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

**TEST APPARATUS.** To test the performance of the device, an

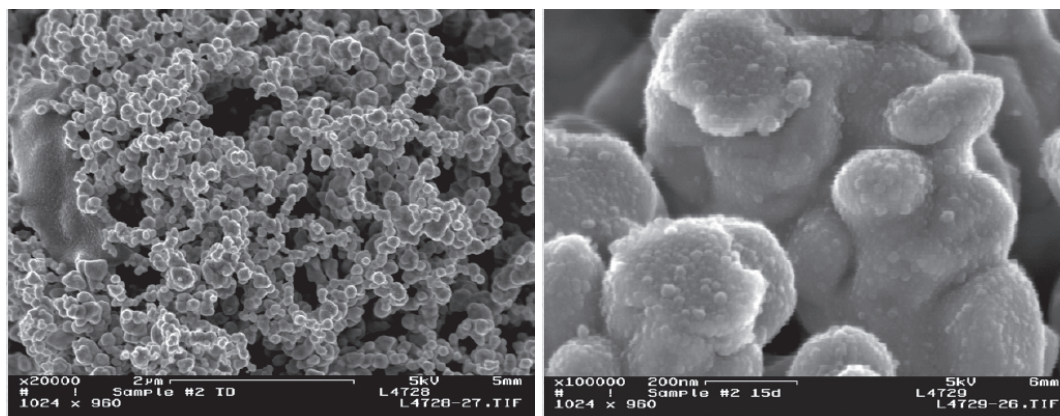


Fig. 1. Scanning electron microscope (SEM) images of nanoporous gold used as an electrocatalyst in the current sensing approach. The two images are at magnifications of 20,000× (left) and 100,000× (right), revealing features smaller than 10 nm.

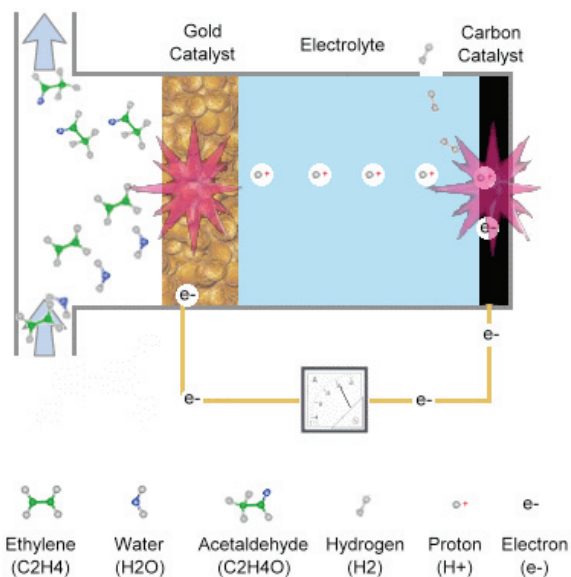


Fig. 2. Electrocatalytic reaction of ethylene on nanoporous gold catalyst.

experimental apparatus was assembled as schematically shown in Figure 3. Two gas standards, nitrogen and ethylene, were brought in contact at different ratios using precision Aalborg mass flow controllers ([www.aalborg.com](http://www.aalborg.com)). The concentration of ethylene was controlled between 10 ppb to 10 ppm to within  $\pm 5\%$  for these studies. The flow rate through the cell was maintained at  $200 \pm 5$  mL/min 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  $\pm 10$  nA.

## 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 signature suppression, which means a lower percentage of all molecules moving past the electrocatalyst surface participate in producing a signal. Extensive laboratory studies show that efficient synthesis of the

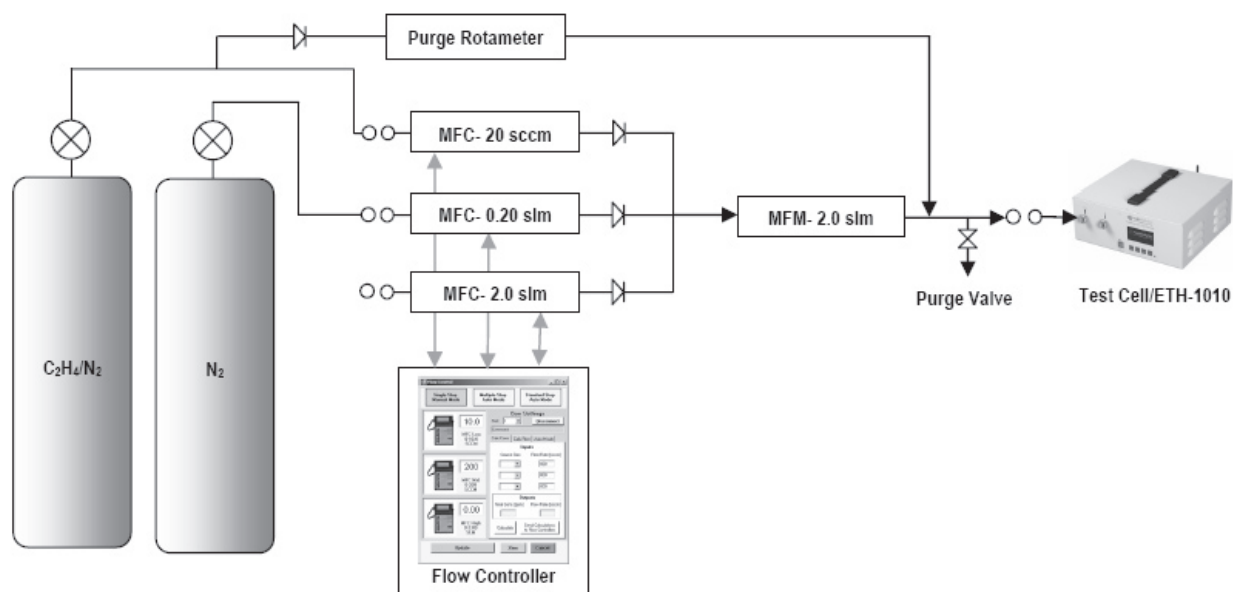


Fig. 3. The test apparatus design is aimed for easy operation and minimizing error in mixed gas.

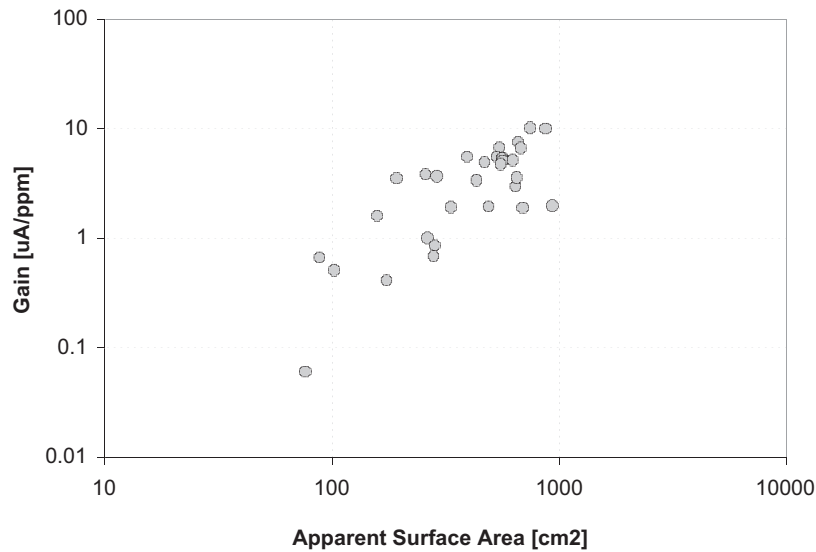


Fig. 4. Impact of gold electrocatalyst active surface on sensor sensitivity.

gold catalyst combined with proper electrochemical cell design play the key role in producing a robust and high sensitivity sensor (Gilbuena et al., 2007).

Our gold electrocatalysts are synthesized using a proprietary approach involving mixing two different solutions containing gold 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 temperature. In average, gold loading is 7.7 mg·cm<sup>-2</sup> measured by the amount of gold initially used for synthesis, and most of which was deposited on the membrane. While all electrocatalysts were synthesized using similar gold loading, other conditions during synthesis affected the catalyst surface area and consequently in electrocatalytic response.

Gold electrode thickness and the size of gold nano-granules comprising the gold deposit are parameters that control the amount of surface for adsorption and coverage by ethylene. As

shown in Figure 4, there is a strong correlation between active surface area, measured using a cyclic voltammetry approach, and sensor sensitivity or gain, determined from measuring ethylene concentration versus its amperometric response. By controlling various parameters during synthesis, we are able to consistently obtain high active surface area of greater than 500 cm<sup>2</sup> and, as a result, high gains greater than 2 µA/ppm.

**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 Figure 5, the current electrocatalytic cell provides extremely linear response, which extends to concentrations well above 100 ppm. Using this inherent 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. To obtain higher confidence in our

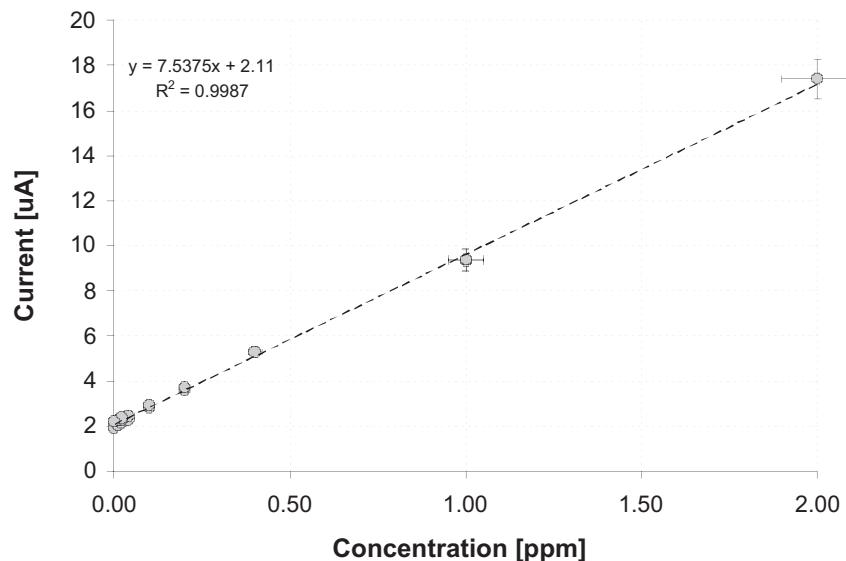


Fig. 5. Sensor linearity at low concentrations.

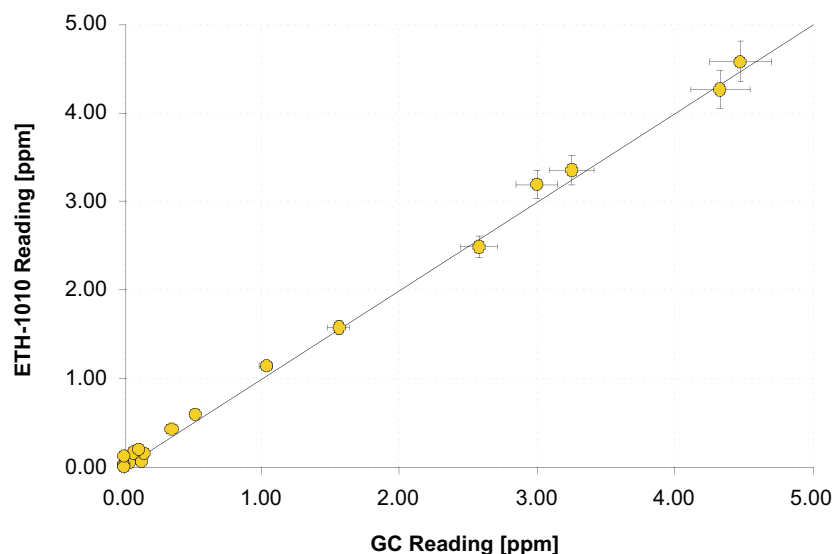


Fig. 6. Comparison of ETH-1010 measurements against gas chromatography for off-gassing of pears in RA chambers at OSU Experiment Station in Hood River, OR.

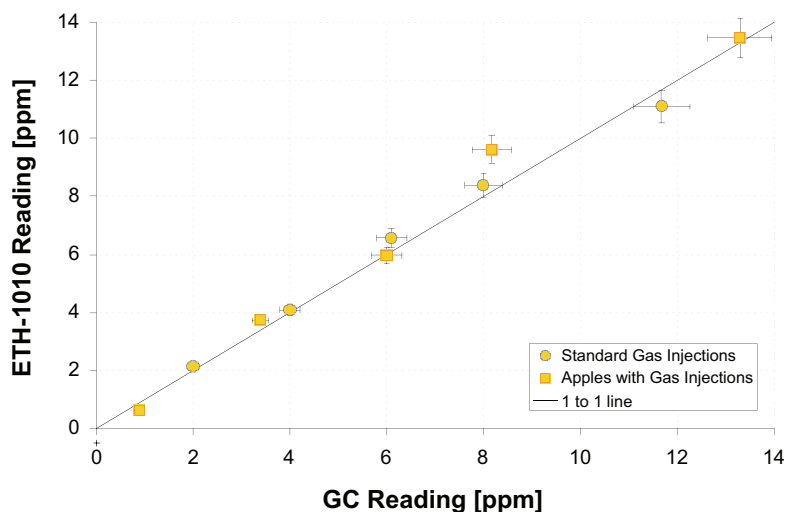


Fig. 7. Comparison of ETH-1010 measurements against gas chromatography for off-gassing of pears in CA chambers at USDA-ARS in Wenatchee, WA.

readings, the calibration point was set to 10 ppm for most of our tests.

**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 Jinhe Bai at the Oregon State University Experiment Station in Hood River, and Jim Mattheis at USDA-ARS in Wenatchee, WA. 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 were then plotted for comparison as shown in Figure 6. 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.

Similar tests were performed at USDA-ARS Tree Fruit Research Laboratory in Wenatchee, WA. Three different CA

chambers, each with an empty volume of 151 L, were used. Two of the chambers contained 50 'Braeburn' apples and one chamber was kept empty as control. In order to simulate the humidity condition in the apple-containing chambers, moist paper towels were maintained in the control chamber. The measurement process included two GC samples that were taken before and after the ETH-1010 measurements with our electrochemical sensor. Careful measures were taken to minimize the reading differences between the two GC samples for each run. The tests started with the chambers filled with the apples and allowed to sit under the recommended CA conditions for more than 24 h. The gas composition was maintained at 1.0% O<sub>2</sub>, 5% CO<sub>2</sub>, and 94% N<sub>2</sub> and the temperature was kept at 1 °C. Since the background ethylene was low, additional ethylene gas was injected into the chamber in order to make quick comparison between the GC and fluid analytics ethylene sensor at the CA conditions. The ethylene injections were performed every 15 min at increments of 3- to 5-ppm using a

14,680 ppm ethylene standard, followed by a 0.5 ml sample tested in a HP 5880A GC with flame ionization detector, continuous sampling through the ETH-1010 sensor, and again followed by a second GC sample. As shown in Figure 7, the data from both empty chambers as well as those taken from chambers full of apples show agreement with GC results within  $\pm 5\%$ , indicating little to no interference from other volatile gases.

### Conclusions

In this paper, we described an electrochemical approach for detection of ethylene molecules in air. The approach is based on directly exposing a nanoporous gold catalyst to sample air, where adsorption and reaction of ethylene provides a measure of its concentration in air. Properly synthesized nanoporous gold electrocatalysts is the most prominent component of the current electrocatalytic sensor. We have shown a good sensitivity to

ethylene at levels of well below 100 ppb and good agreement with measurements was obtained using a standard GC in realistic and relevant postharvest conditions.

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