Postharvest S02 – 02 oral IHC Monday afternoon 4:30 pm (Leon Terry, chairperson)

# Gold Nanoparticles and Sensor Technology for sensitive Ethylene Detection

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## ABSTRACT

A new electrocatalytic sensor for measurement of gaseous ethylene ($C_2H_4$) concentration in air is presented. The measuring principle is based on ethylene oxidation on a gold-Nafion anode with weak sulphuric acid used as the electrolyte. The small ethylene molecules are trapped in the pores of the nanoporous gold matrix and partly consumed to produce the signal proportional to their concentration in air. The high surface area of the nanoporous gold catalyst renders high sensitivity and fast response in detection of ethylene in air making it particularly suitable for postharvest or plant physiology applications. In the current study, the accuracy was 96-98% with a SD of 0.05-0.15 ppm $C_2H_4$ and a variation coefficient of 0.5-2%, when the calibration gas of 8 ppm $C_2H_4$ was measured after calibration. The measuring range of the device is 0 -50 ppm $C_2H_4$ with an accuracy of ±5% of reading and displayed resolution of 1 ppb. For a 30 sec measurement, the instrument draws a ca. 150 ml gas sample and appears suitable for measurement of individual fruit in an open or closed gas system, for continuous sampling or single gas samples. Temperature, humidity, $CO_2$ (option) and another gas or ethylene analogue like MCP (option) are displayed concomitantly. The reproducibility of the values was 93% with 3 subsequent measurements of a variety of fruits. The unit can be operated on mains or built-in battery providing up to 8 hours operation and weighs 4.5 kg. This makes it portable for *in-situ* ethylene measurement after calibration with an external gas supply and is elegant alternative to ethylene determination in a 10 ml sample from head space of jar after hours of accumulation by gas chromatography.

## INTRODUCTION

In the past, ethylene was primarily measured with stationary equipment in laboratories associated with fruit stores e.g. for apple, avocado, pear and kiwi, but also onion and potato. The most common devise was a gas chromatograph (GC) with a flame ionisation detector (FID) (Table 1). GC-FID requires calibration gas, nitrogen to use as carrier gas delivered from a cylinder or bottle, mains power and an integrator for data assessment (e.g. Saltveit, 1999). However, mobile measurements *in situ*, where ethylene is produced have been hampered by the lack of a portable unit that is sensitive and responsive enough to provide meaningful measurements. Some examples of application areas that would benefit from such a unit are study of plants in response to stress (e.g. Kong et al., 2008), banana ripening, flower stimulation in Bromeliaceae, long distance transportation of fruit, vegetables and flowers on trucks or ships, and environmental and air quality monitoring.

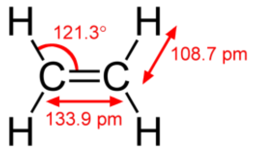
**Table 1:** Typical devices used for ethylene detection

| **Device** | **Price in Euros** | **Typical resolution [ ppb ]** |
|---|---|---|
| Standard electrochemical sensors | € 1,500 – 2,000 | 100 |
| GC with FID | € 20,000-40,000 | 50 |
| Laser spectroscopy | € 15,000-25,000 | 0.1 – 1 |
| Photo- thermal detection (PTD) | € 40,000 | 0.5 |
| Photoacoustic (PA) | €40,000-60,000 | 0.006 |
| *New gold nanocatalyst sensor* | *€ 10,000* | *2-5* |

Equipment for ethylene detection ranges from the low-cost sensor without calibration function to the photoacoustic technology that requires high effort for stability and gas cleaning. The current nanoporous gold electrocatalytic sensor combines both a relatively high resolution with intermediate price range (Table 1). This sensor has recently become commercially available as an off-the-shelf instrument, as will be discussed later in this paper.

## MATERIALS and METHODS

### Ethylene Interaction with Gold Nanoparticles



Ethylene is a colourless and odourless gas, which has no known effect on human beings. Ethylene is a naturally occurring gas, associated with plants under stress and fruit maturation in horticulture. The relatively small and simplest alkene, ethylene molecules consist of four hydrogen atoms associated with a carbon atom each (http://en.wikipedia.org/wiki/Ethylene). Their characteristic double or 'π-bond' is a prerequisite for this new nanotechnology gas detection system. The 'inert' gold molecule does not react with most other compounds and hence fulfils a great role in human health from tooth fillings to artificial knees. Below a particle size of ca. 100 nm, the properties of nanoparticle gold radically change and their extremely large surface area contributes to their high reactivity (Fig. 1); nanoparticles have high affinity for ethylene molecules resulting in strong physical adsorption of ethylene onto the nanoparticle matrix, thus increasing the residence time for oxidation of carbon double bonds (Humboldt, 1994; Cortie and van der Lingen; 2002). 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 (Shekarriz, 2007). In the current configuration, the 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.

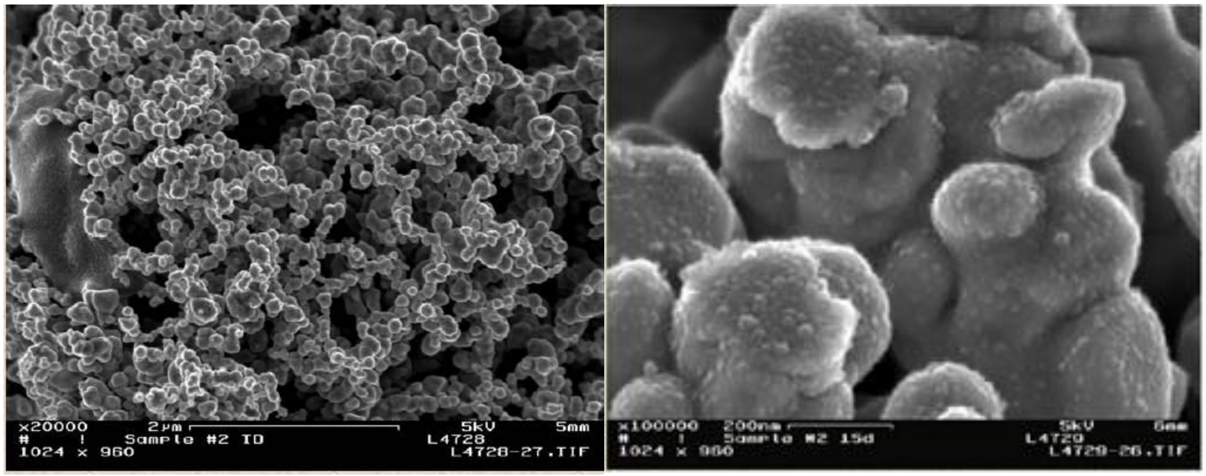


**Fig. 1:** Scanning electron micrographs of gold nano particles (magnification x20k-left and x100k -right; with permission from Shekarriz and Allen, 2008).

## Electrocatalytic Cell and Its Operation

The interaction of the ethylene $\pi^*$ bonds with the metal donor sites result in strong complexation and adsorption of ethylene onto the surface of gold catalyst (Gottfried, 2003). This unique interaction limits the interaction to unsaturated hydrocarbons, the most strongly adsorbing species being ethylene molecules. It's been shown that saturation coverage can be as high as 3.1 monolayers of ethylene adsorbed onto the gold surface both through physisorption (low coverage) and chemisorption (high coverage). The amount adsorbed (i.e., coverage) is a function of the partial pressure of the analyte in the air stream. The adsorbed ethylene reacts with water at the "triple-phase boundary" where gold, electrolyte (oxidizing agent), and ethylene (reducing agent) are all present (Carrette et al. 2001). The protons (cations) released from the reaction travel through electrolyte-saturated Nafion membrane, migrate through the electrolyte, and collect electrons from the surface of the counter electrode to form hydrogen molecules (Fig. 2).

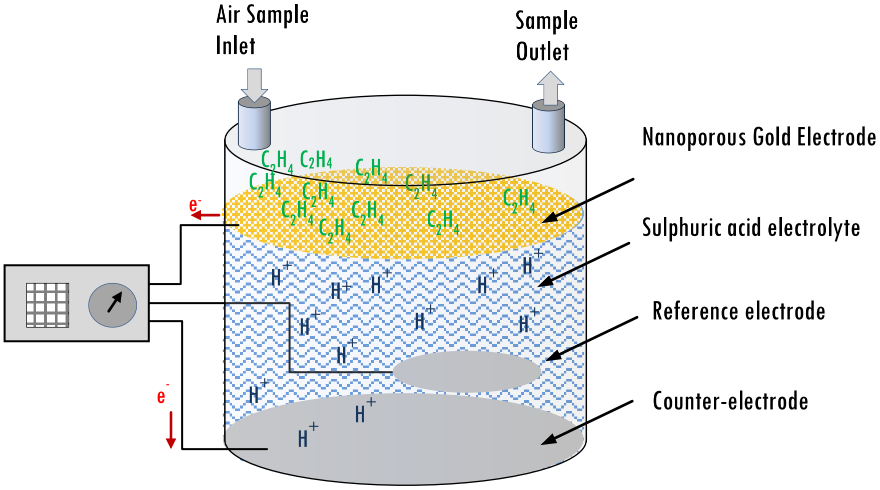


**Fig. 2:** Schematic of the measuring process with the gold nanoparticle-plated anode, cathode and sulphuric acid as electrolyte.

The amperometric signal generated is directly proportional to the number of analyte molecules that adsorb and oxidize on the surface of the working electrode (Dean, 1979).

$$C_2H_4 + H_2O = CH_3CHO + 2H^+ + 2e^- .$$

As shown in Fig. 3, the sensor is packaged in a fashion that it can be carried into the field for field measurements. The striking similarity of the MCP and ethylene molecule also enables MCP detection with the same technology; this could be realised e.g. by a dual channel unit with one channel for ethylene and one for MCP.

**Fig. 3:** The ethylene analyser sold under the trademark CI-900 by CID Bioscience (LEFT) Fruit or leaf chamber can be attached to the device for field measurements of ethylene (RIGHT); www.cid-inc.com.

## Care and Calibration

During the warming-up phase, the unit automatically calibrates its zero by employing dried, ethylene-free gas from the built-in drying and potassium permanganate columns. The potassium permanganate has a limited life and has to be replaced on a regular basis. The replacement components can be obtained from the supplier or can be maintained on a regular basis by the end-user, provided that the protocols given by the manufacturer are closely followed. The sensor technology allows calibration from a standard gas cylinder with 1- 10 ppm $C_2H_4$ with a user-selectable option of choosing the calibration gas concentration on the front panel of the device. Although the overall calibration is kept for several days to weeks, the manufacturer recommends calibration before each use for highest accuracy (Fig. 4) and leaving the unit switched on (Blanke, 2008) to maintain the sensor element at the equilibrium condition with the environment.

**Fig. 4:** Calibration setup, which may consist of the standard calibration bottle or the calibration setup provided by the manufacturer (ABSOGER SAS and supplier CID Bioscience).

# RESULTS

## Sample application: Ethylene efflux from stored fruit

Ethylene efflux was measured in the laboratory – in a similar way to using a traditional gas chromatograph for measuring the fruit metabolism in a respiration chamber (Fig. 5). With the continuous, real-time measurements of the nanoporous gold sensor, the steps of gas accumulation, injection into the column and calculation of the time efflux were eliminated. In a closed gas circuit or within an open environment, continuous measurement mode of the sensor provides one reading per minute (or at a user-selectable interval) without waiting for ethylene to accumulate in the head space, and then inject a sample into a GC.  Using this approach, the trend in ethylene accumulation from which the rate of generation of the ethylene within that space can be determined, as shown in Figure 6.  The new versions of the analyser provide an option for automatic determination of the fruit ethylene production rate with every reading.

**Fig. 5:** Left: Closed gas circuit employed to measure real-time continuous ethylene efflux from fruit like avocado; the postharvest gas sensor displays all four, ethylene, CO2, temperature and humidity; Right: Continuous in situ measurement in a grading facility with the sorting lines.

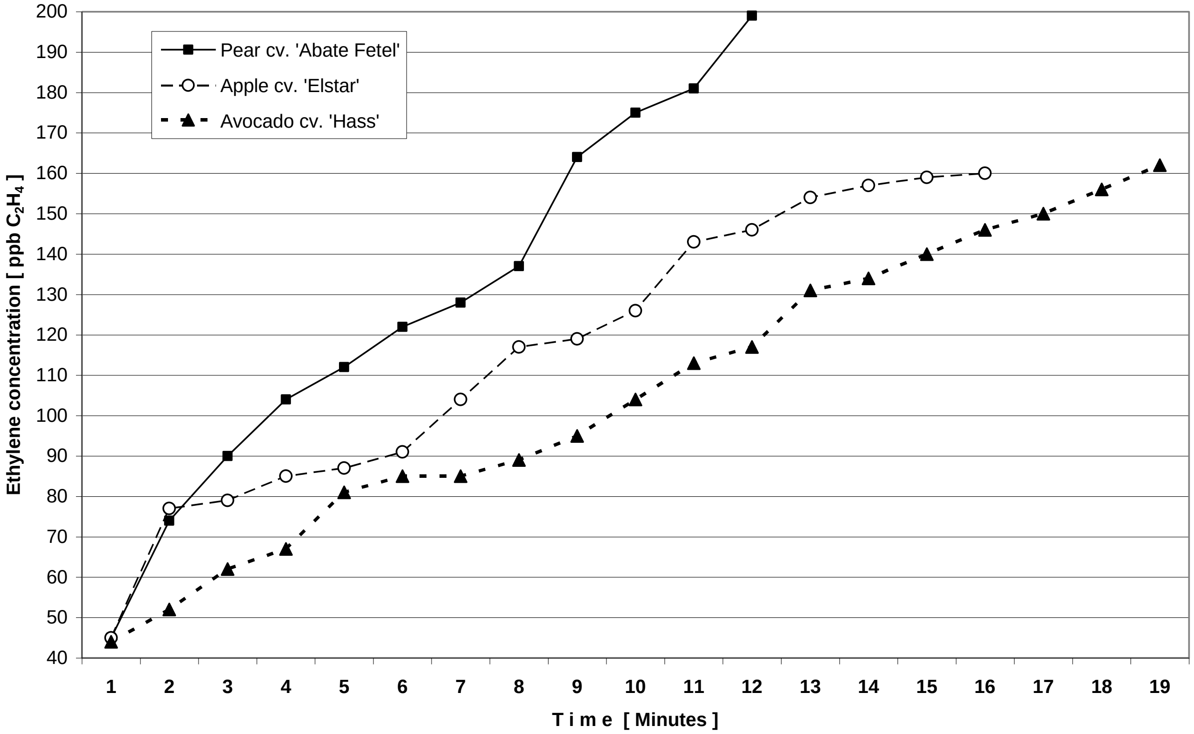


**Fig. 6**: Measurement of ethylene efflux from apple, pear and avocado during shelf life with an. immediate response within a minute, measured with fruit enclosed in a jam jar in a closed gas circuit.

In a separate experiment, the sensor was tuned to measure the 1-MCP molecules without interference from ethylene or other molecules. The sensor was connected to a 29-L chamber and sufficient concentration of 1-MCP (obtained from Agrofresh Corporation, Springhouse, PA) to create an initial concentration of 4-ppm in the chamber. The analyser was calibrated at that concentration and was allowed to measure the rate of decay of 1-MCP within this chamber. The result of this test is shown in Figure 7 in a time decay plot, where the vertical axis is the concentration of 1-MCP in a logarithmic format and the horizontal axis is time. Note that the decay rate is approximated quite well by an exponential decay function, where the decay rate is a function of the concentration at any point in time. This type of measurement establishes the utility of this device for verification of the concentration of 1-MCP molecules in cold storage facilities that apply 1-MCP for prolonging storage life of products such as apples.

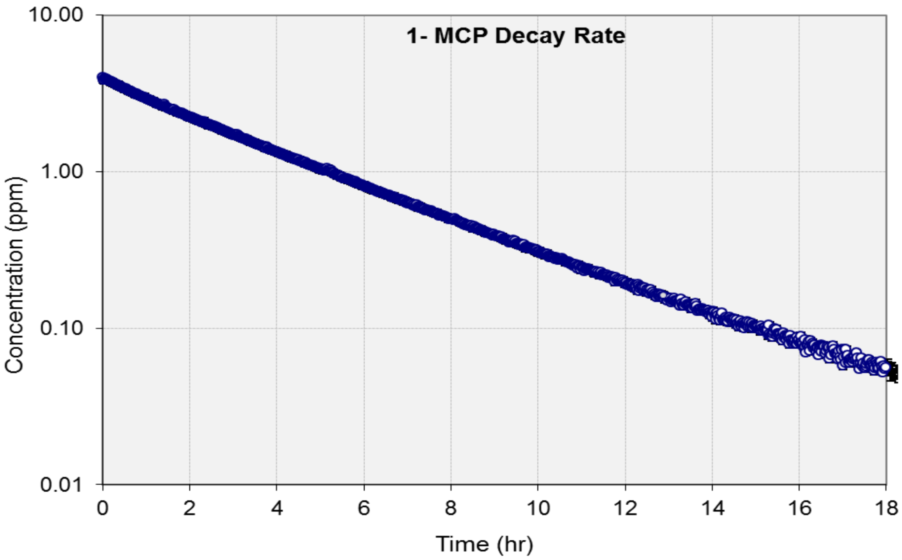


**Fig. 7:** Measurement of the rate of exponential decay of 1-MCP in a closed 29-L container.

## In situ ethylene measurements

Ethylene concentrations were measured *in situ* in the apple supply chain (Fig. 8). Ethylene concentrations changed along the apple supply chain. While ethylene was essentially absent with values less than 11 ppb $C_2H_4$ from the CA (controlled atmosphere) store with long term fruit storage, it had accumulated in the RA (regular air) cold store with cv. Elstar over 4 months to ca. 5 ppm $C_2H_4$ (Fig. 8). In the grading facility with the sorting line, ethylene accumulated to 0.5 ppm $C_2H_4$, while the concentration in the wooden bins with side vents was 72 ppb.

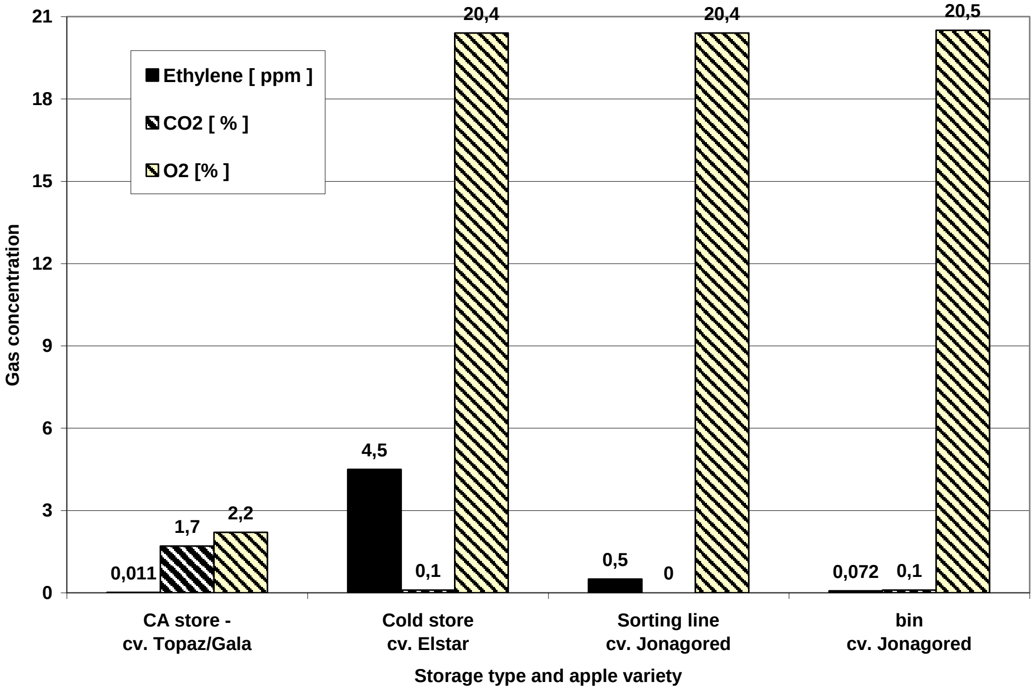


**Fig. 8:** Ethylene concentrations throughout the apple supply chain.

## CONCLUSIONS

The current sensor using electrocatalysis and nanotechnology is a new and promising technology for affordable detection of ethylene, which will enable research in areas where ethylene could not be measured before due to lack of portable, sensitive, and near real-time measurement equipment. Future research and application will show and reveal more details of this fascinating new technology.

## ACKNOWLEDGEMENT

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