Evaluation of MACView® Portable Ethylene Postharvest Gas Analyser

Independent test of suitability and performance for use in horticultural settings

July 2017

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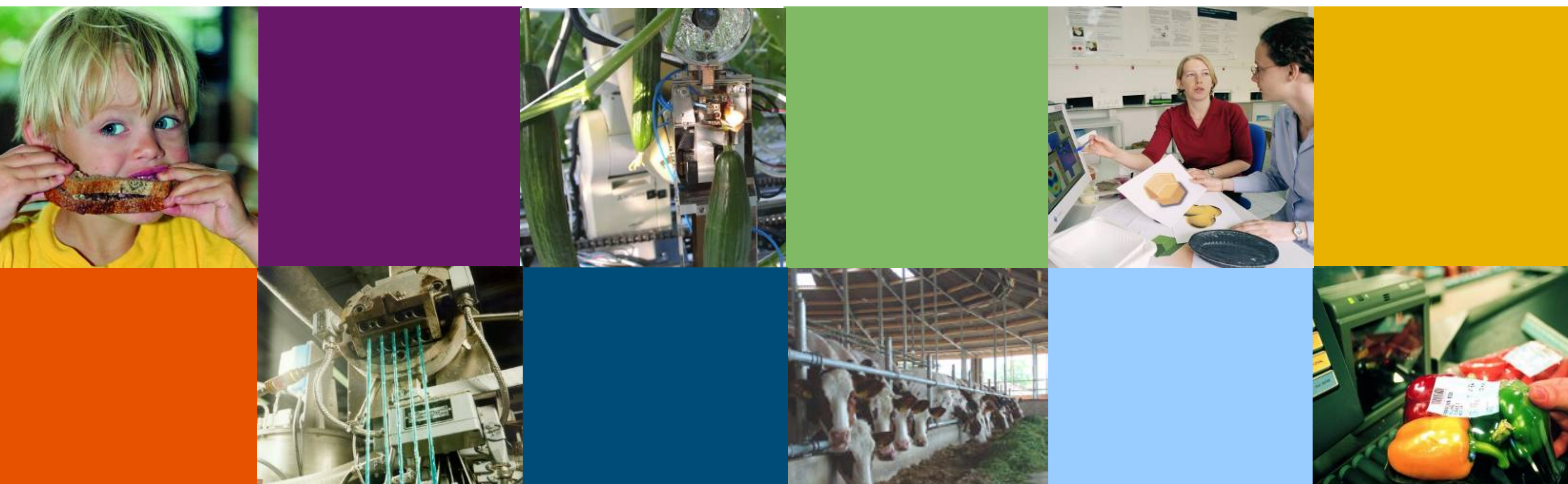
Report 1753



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Content

1 Introduction

In many horticultural settings, monitoring ethylene (ISO name ethene) concentrations can give produce information related to product quality. Many sensors are on the market, but often they show limited sensitivity and/or specificity for ethylene, or sensors are cross-sensitive to other interfering gases resulting in false readings. A practical, precise and sensitive sensor which is not sensitive for conditions or gases commonly found in horticultural settings could be a valuable tool to monitor and manage ethylene sensitive produce such as kiwifruit etc. during postharvest life. Interfering conditions can be temperature, water vapour (Relative Humidity) and gases such as oxygen, CO_2, ethanol (fermentation product of plant materials), and fruit volatile organic compounds (VOC's).

According to its producer, the MACView® Portable Ethylene Postharvest Gas Analyser (indicated as PHGA from hereon) is an easy to operate device that can measure ethylene concentrations, and also oxygen and CO_2 in horticultural settings.
The PHGA is produced by Environmental Monitoring Systems (EMS) B.V., St. Annaland, Netherlands. EMS requested WFBR for an *independent* test on the suitability and performance of the PHGA in horticultural settings. By a series of tests under controlled conditions, sensitivity and cross sensitivities for a range of factors were determined:

- Ethylene concentrations ranging from 1 ppb and up were tested.
- Effects of oxygen and/or CO_2, Relative Humidity and temperature on ethylene measurements were assessed
- Ethylene measurement in storage air of kiwifruits and effect of plant fermentation product ethanol on ethylene measurements (potentially cross reacting volatiles) were also assessed.

This report gives an overview of the test set-up, results and conclusions.

2 Methods

2.1 MACView® Ethylene Portable Postharvest Gas Analyser (PHGA)

A MACView® Portable Ethylene Postharvest Gas Analyser (indicated as PHGA from hereon), range 0-5000 ppb ethylene, capable of also measuring oxygen and carbon dioxide, was tested by Wageningen Food & Biobased Research (WFBR) in the period May-June 2017 for its suitability to be used in horticultural settings. Results were acquired via a web based portal *(http://www.mymacview.com) of EMS*.

2.2 Measurement set up

A measurement set up was constructed enabling the PHGA to sample test gas from a gas stream without pressure build-up. The gas stream was made from pure gases (N_2, O_2 and CO_2 and certified standard gas (1017 ppb ethylene, balance N_2, Linde Gas Benelux BV). A gas mixer consisting of programmable multiple range mass-flow controllers was used to create a flow of 300 ml/min, which was transported using 1/8" tubing to a nearby climate room set at 1°C and 90% humidity for most tests. By raising the temperature in the measurement room, the effect of temperature on PHGA performance was tested. These harsh conditions for most electric devices was chosen to show robustness of the PHGA. The gas stream was passed through a gas wash bottle with demineralized water to humidify the gas stream to approx. 99%, verified with a calibrated humidity sensor. The PHGA autonomously samples about 100 ml/minute continuously, and by releasing the rest of the gas stream through a ¼" tubing, pressure build up was prevented.

2.3 Verification of ethylene measurements

Ethylene was monitored and verified using a calibrated photoacoustic laser detector (ETD300, SensorSense)(Cristescu, Persijn et al. 2008). This is a sensitive and ethylene specific device measuring every 5-10 seconds, enabling to monitor ethylene concentrations in time very accurately (theoretical resolution 0.3 ppb).

The detector was placed in a lab adjacent to the cold store in a stable environment at 22°C. Gas was drawn continuously with a sample pump (approx. 3 l/h), from the ¼" tubing after the PHGA (see set-up schematics figure later on). Water vapour and CO_2 were removed from this gas stream using

(chemical) scrubbers to prevent interference of these gases on ethylene measurements of the ETD-300. See *2.1.5 Schematics of test set up for evaluation of the PHGA ethylene sensor.*
Ethylene concentrations were sometimes additionally verified by withdrawing 2.5 ml samples and injecting them into 200 µl sample loops of a gas chromatograph (Shimadzu model 17A, equipped with a GS-Gaspro column backflush configuration and a FID detector).
The GC was calibrated using certified standard gas (1017 ppb ethylene, balance N2, Linde Gas Benelux BV).

2.4 Verification of oxygen and CO_2 measurements

In this 1/4"outlet also a calibrated oxygen/CO_2 sensor (Checkmate II, Dansensor, Denmark) was sampling 15 seconds every 5 minutes at a rate of about 20 ml/minute to verify PHGA oxygen and CO_2 readings. Exit flow was over 50 ml/minute at all times to prevent suction of "false air". See also *2.1.5 Schematics of test set up for evaluation of the PHGA ethylene sensor.*

2.5 Schematics of test set up for evaluation of the PHGA ethylene sensor

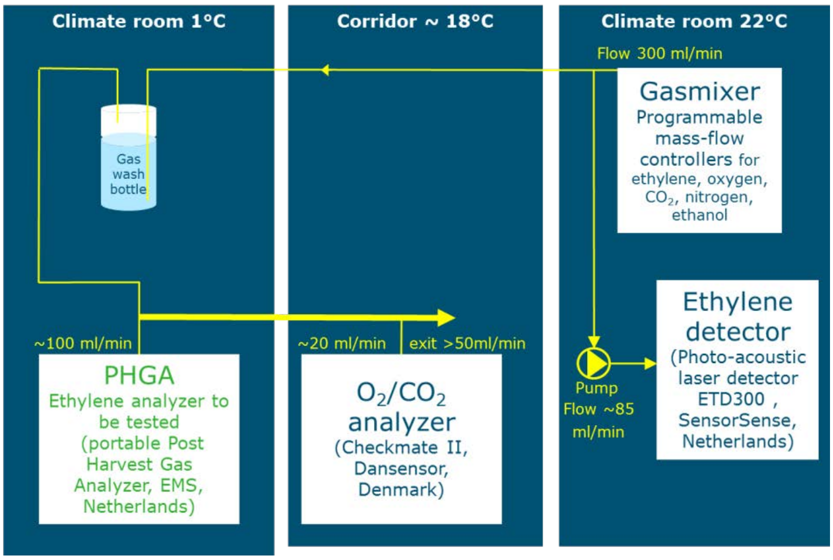

Figure 2-1: Schematics of test set up for evaluation of the PHGA ethylene sensor. This set up was used to test ethylene sensitivity and response to oxygen, CO_2, humidity, ethanol and temperature.

Below some pictures of the equipment used.

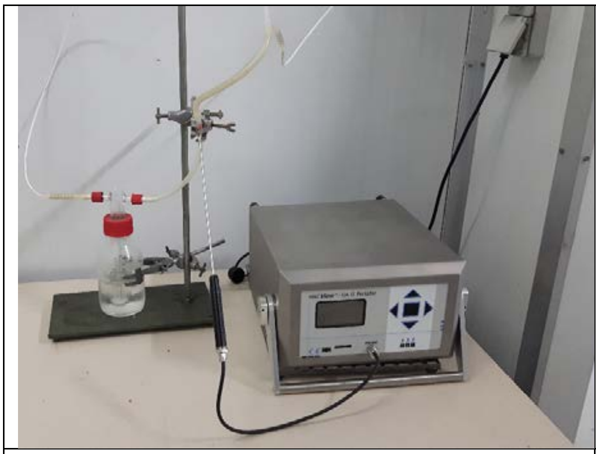

Figure 2-2: MACView® Ethylene Postharvest Portable Analyser in the test set up in a 1°C /90%RH climate room. Test gases were humidified using a gas wash bottle to create high humidity of the gas to be measured.

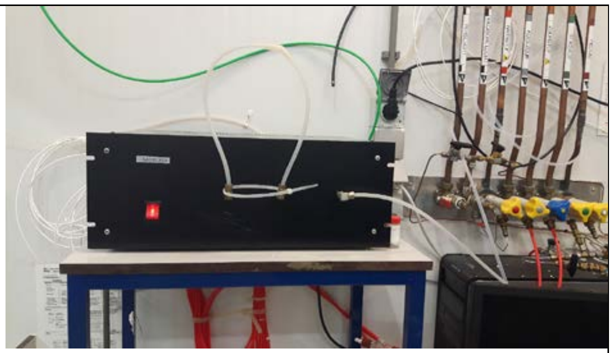

Figure 2-3: Programmable Gas mixing system enabling automated flushing of a sequence of ethylene, oxygen and carbon dioxide concentrations.

Figure 2-4: Checkmate II (Dansensor) Oxygen/CO_2 sensor used for verification of the on board PHGA Oxygen/CO_2 sensors

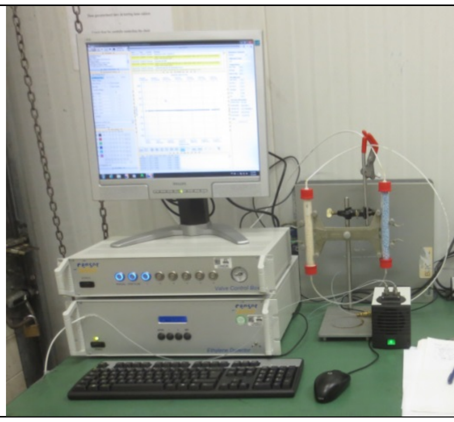

Figure 2-5: Photoacoustic ethylene detector ETD-300 (SensorSense) used for verification of PHGA ethylene measurements

The ETD data are used as validation of the PHGA results for ethylene, the Checkmate II data are used for oxygen and carbon dioxide results of the PHGA.

2.6 Measurement series

In several sessions the gas mixing system supplied the PHGA in the set up with a range of gas conditions/ concentrations, each for a period (=step) of 2 hours before switching to the next step. See next table for details:

	step	ethylene (ppb)	O2 (%)	CO2 (%)	ethanol (ppb)	T (°C)	RH (%)
ethylene series A		0	21	0	0	1	high (99%)
0-300 in 5 steps	1	30	21	0	0	1	high (99%)
	2	50	21	0	0	1	high (99%)
	3	100	21	0	0	1	high (99%)
	4	200	21	0	0	1	high (99%)
	5	300	21	0	0	1	high (99%)
ethylene series B		0	21	0	0	1	high (99%)
0-30 in 5 steps	1	1	21	0	0	1	high (99%)
	2	2	21	0	0	1	high (99%)
	3	5	21	0	0	1	high (99%)
	4	10	21	0	0	1	high (99%)
	5	30	21	0	0	1	high (99%)
O2-series A	1	30	21	0	0	1	high (99%)
0-21%	2	30	15	0	0	1	high (99%)
	3	30	10	0	0	1	high (99%)
	4	30	5	0	0	1	high (99%)
	5	30	3	0	0	1	high (99%)
O2-series B	1	30	2	0	0	1	high (99%)
0-2%	2	30	1	0	0	1	high (99%)
	3	30	0.8	0	0	1	high (99%)
	4	30	0.4	0	0	1	high (99%)
	5	30	0.2	0	0	1	high (99%)
O2-series C	1	30	2	5	0	1	high (99%)
0-2% in 5%CO2	2	30	1	5	0	1	high (99%)
	3	30	0.8	5	0	1	high (99%)
	4	30	0.4	5	0	1	high (99%)
	5	30	0.2	5	0	1	high (99%)
CO2-series A	1	30	21	5	0	1	high (99%)
0-5%	2	30	21	4	0	1	high (99%)
	3	30	21	3	0	1	high (99%)
	4	30	21	2	0	1	high (99%)
	5	30	21	1	0	1	high (99%)
CO2-series A	1	30	2	5	0	1	high (99%)
0-5% in 2%O2	2	30	2	4	0	1	high (99%)
	3	30	2	3	0	1	high (99%)
	4	30	2	2	0	1	high (99%)
	5	30	2	1	0	1	high (99%)
RH series	1	30	21	0	0	1	~75%
	2	30	21	0	0	1	~88%
	3	30	21	0	0	1	high (99%)
Cross-reactivity ethanol		30	21	0	~400	1	high (99%)

To test the sensitivity of the PHGA for effects of relevant **relative humidities**, gas wash bottles containing saturated salt solutions of NaCl and KCl were used and demineralized water only, at 1 °C resulting in %RH of 75% (NaCl) , 88% (KCl) and 99% (demineralized water)(Greenspan 1977).

By heating the entire climate room from 1°C to 30°C at 2°C/h while measuring a low concentration of ethylene (30 ppb), the **effects of temperature** on the PHGA were determined. This was done in normal air at high RH (99%).

2.7 Cross reactivity testing

To create ~400 ppb of **ethanol** (universal plant fermentation metabolite) a gas wash bottle was filled with 23.1 µl ethanol/l demineralized water, resulting in the desired concentration in the gas stream at 1°C. This procedure was used and verified extensively in the past, but at this time a Gas Chromatograph to check final ethanol concentration was not available.

To test **cross reactivity with kiwifruit volatiles**, two batches of approx. 20 kg of kiwifruit (unripe, very firm) and somewhat ripened and softer by storage at higher temperature, were placed in 550l containers with water locked lids. These containers were placed in the 1°C climate room and flushed with ethylene-free air using mass flow controllers at 500 ml/minute. In order to generate maximum concentration of possibly cross reacting kiwifruit volatiles (VOC's), in one test the containers were closed for 16 hours prior to flushing/measuring.

Figure 2-6: Setup of kiwifruit tests

Figure 2-7: The containers were flushed continously for initial tests. Later a test was done with closing a container without flushing overnight to generate an environment with maximal kiwifruit volatiles before measuring ethylene

Figure 2-8: PHGA test setup for kiwifruit: a pump draws air through a KMnO4 filled cuvette and feeds mass flow controllers flushing each one of two 550l containers filled with kiwifruits. Measurements were done on the air expelled from the containers. Also visible are the gas wash bottles with saturated salt solutions equilibrillating at 1°C to create various levels of Relative Humidity.

3 Results

3.1 Results raw data

The MACView® Portable Ethylene Postharvest Gas Analyser (PHGA) is equipped with a display to read out results on the device. It is also possible to monitor results through a web portal, enabling remote checking of the device while measuring on location. Below a graph of a selected part of the test period generated from the portal:

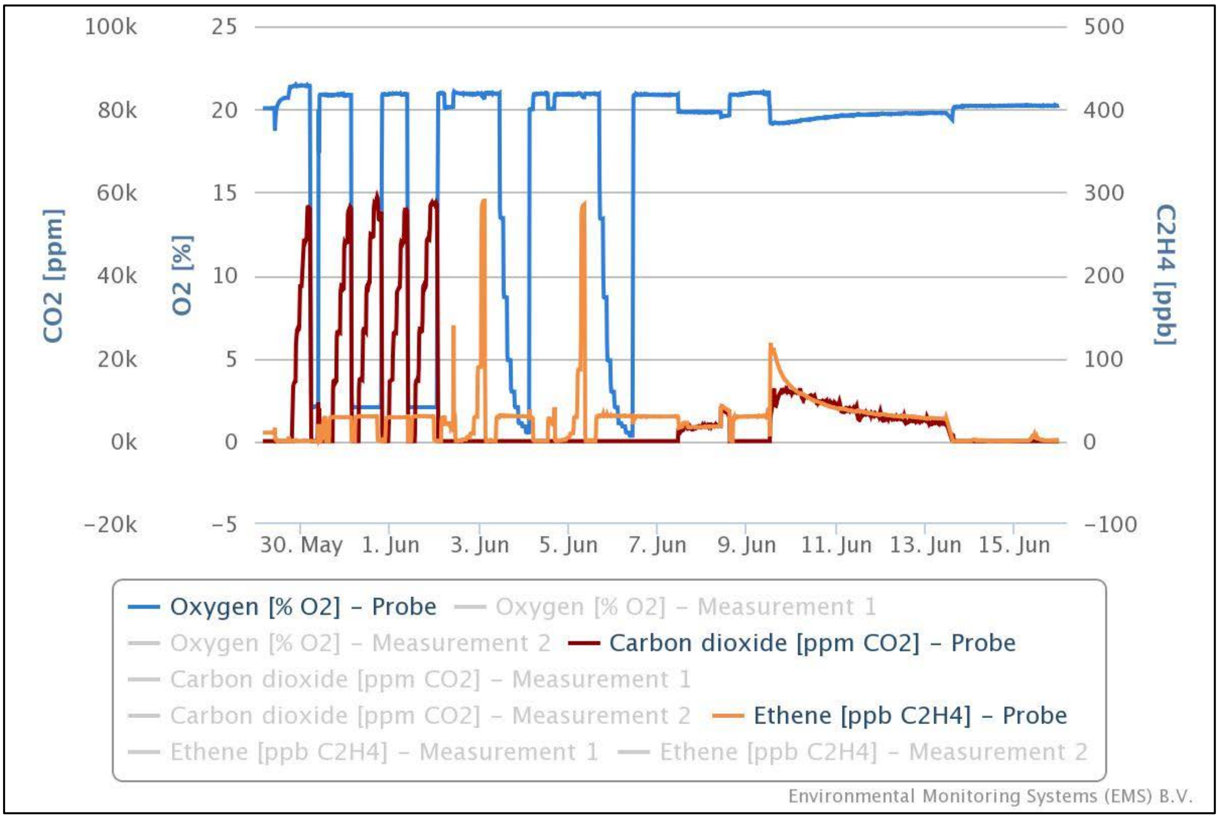

Figure 3-1: Overview of PHGA-results of the test period from the web portal (http://www.mymacview.com) of EMS. It shows periods of stable ethylene concentrations while varying CO_2 or oxygen levels, series ethylene concentrations and cross sensitivity tests with kiwifruits.

The PHGA has a 15 minute measurement cycle, so 4 readings for ethylene, oxygen and carbon dioxide per hour. The long length of the tubing feeding the sensors in the climate room resulted in an approximately 10 minute delay before equilibrium was reached after selecting a new gas mixture. In general, response time of the PHGA was mainly limited by the 15 minute sample interval, often the first reading after a concentration change was not fully stable yet. Stability proved to be very good over long periods of time if a stable gas mixture was supplied.

The ethylene measurements of the devices used for verification, the photoacoustic laser detector ETD-300 were every 5-10 seconds, but also here response time to new gas mixtures was approx. 10 minutes due to tubing lengths and scrubber volumes.

The raw data of the ETD-300 is usually corrected for zero offset, which has been done manually. The set values/set points are processed by mass-flow controllers of the gas mixing system, resulting in indicative values since these mass flow controllers were not precisely calibrated. The ETD data are used as validation of the PHGA results for ethylene, the Checkmate II for oxygen and carbon dioxide.

3.2 Ethylene sensitivity

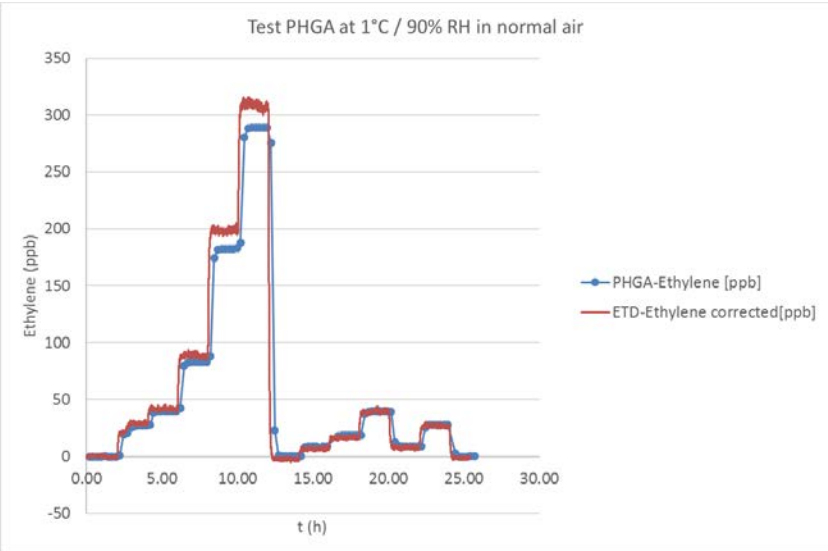

Figure 3-2: Typical raw data test result graph. Ethylene concentrations run with intervals of two hours per concentration. Pattern of ethylene concentrations in time coincide very well.

From each of the 2 hour intervals in which the various concentrations of ethylene were supplied, approx. the last 90 minutes of data (to make sure the new gas condition was stable at sensor level) were averaged and standard deviation was calculated. Results of various runs with normal air is presented below:

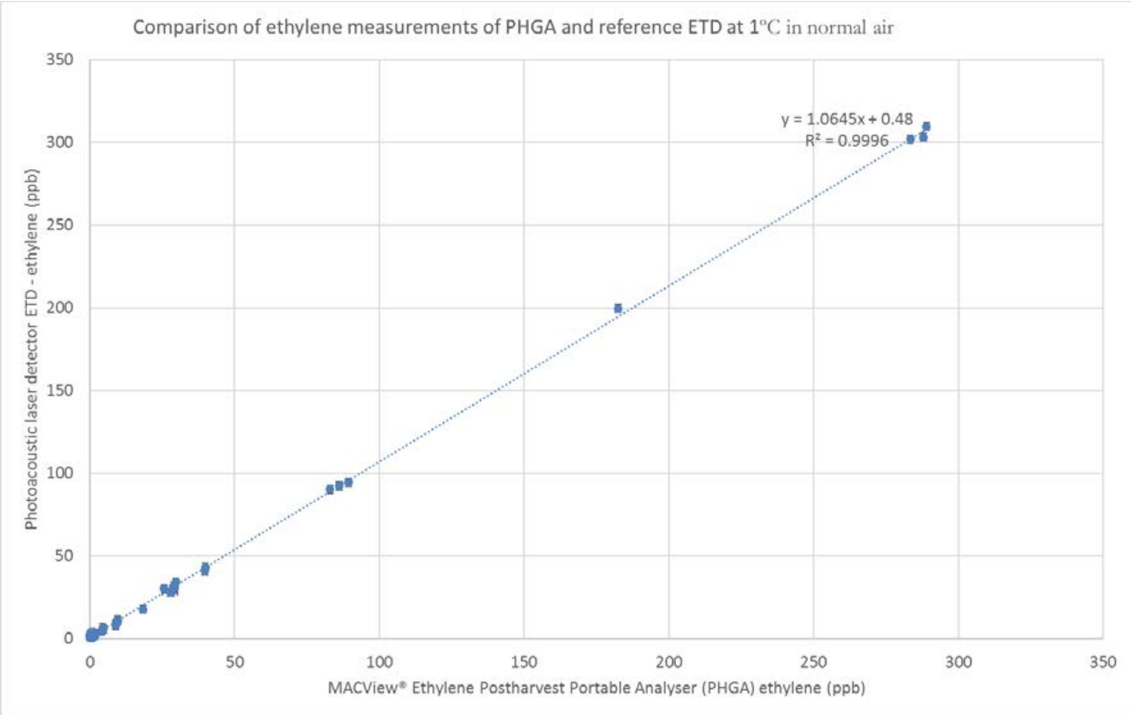

Figure 3-3: Results of multiple tests with averaged values over 90 minutes including standard deviations (shown but small). On average, standard deviation of PHGA was 0.24 ppb, ETD 1.05ppb.

The deviation of the 1:1 response (slope inclination 1.0645) can be explained by result of difference in calibration gas used to calibrate the two analyzers which were both calibrated by the respective suppliers. The certified calibration gases often have a 5% tolerance.

Focussed on the lower range ethylene concentrations resulted in raw data like the next graph:

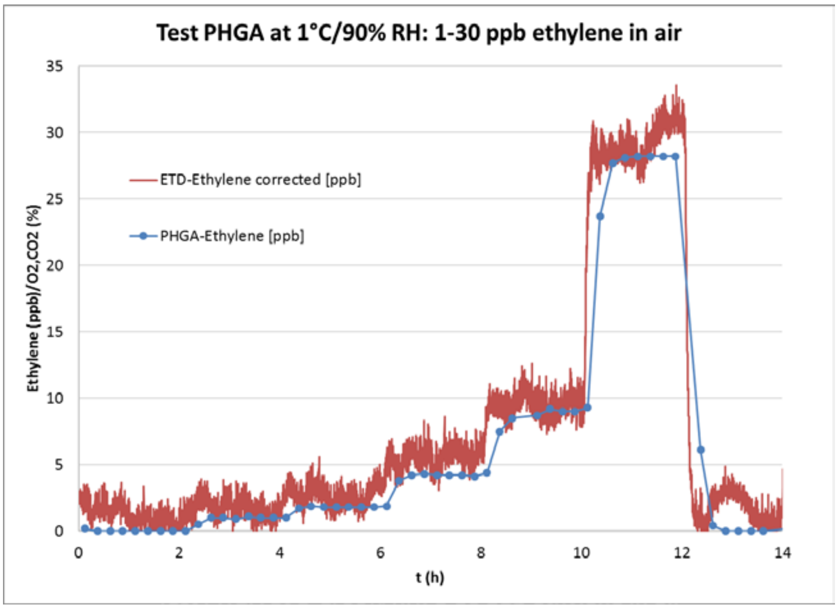

Figure 3-4: In general, at low concentration levels, the PHGA results showed much clearer compared to the reference measurement with the ETD due to reduced variability between measurements.

If results are averaged over the last 90 minutes after a change in concentration and standard averages for the measurements are added, the plot looks like the graph below:

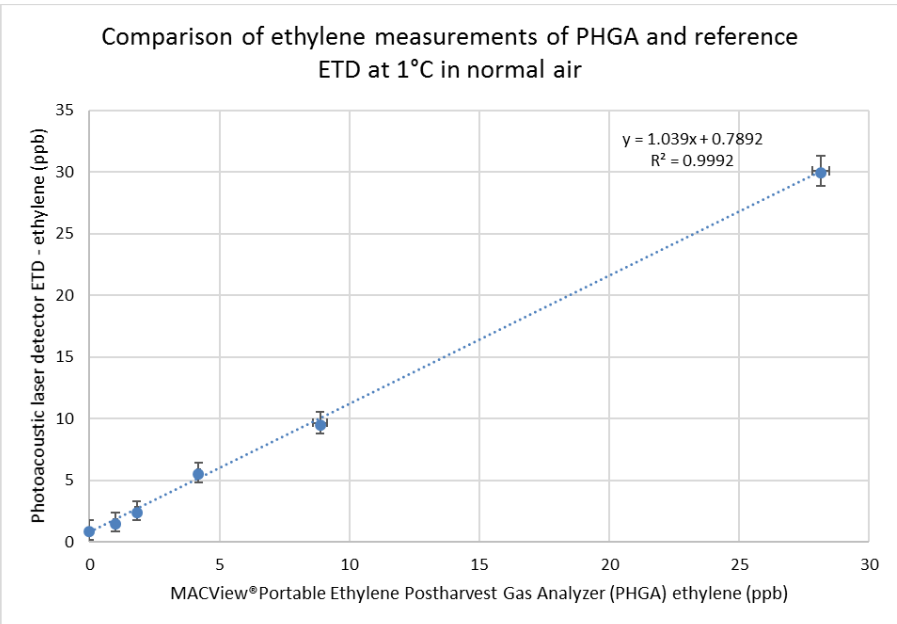

Figure 3-5: Results of low range ethylene tests with averaged values over 90 minutes including standard deviations. On average, standard deviation of PHGA was 0.12 ppb, ETD 1.13 ppb.

3.3 Effects of CO_2 and oxygen

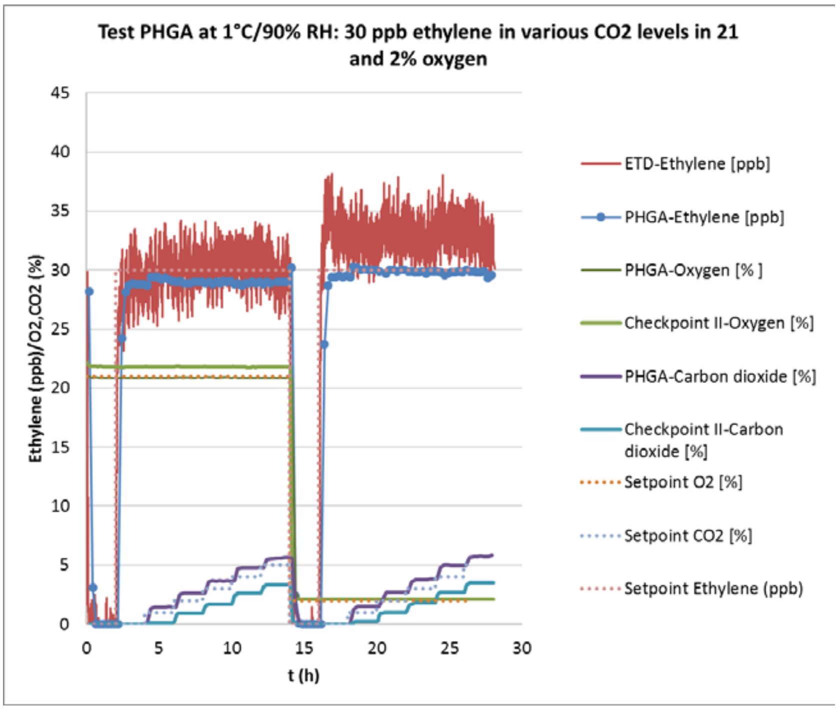

Figure 3-6: Raw data of test results of effects of oxygen and carbon dioxide on ethylene measurements.

No clear visible effect of oxygen and carbon dioxide on ethylene measurement is seen for the PHGA. At 2% O_2 the ETD shows about 2.5 ppb higher values than at 21%, see also table below. Oxygen data correspond very well with the Checkmate II data. For CO_2 values the Checkmate II seems to be relatively lower than the CO_2 set point and the PHGA data fits closer to the CO_2 set point. The difference is presumably a calibration issue.

Values of ethylene measurement averages and standard deviations for the range 0-5% CO_2, measurements at 21 or 2% oxygen are given below.

	PHGA	ETD
ethylene average (ppb) @ 2% O_2	29.86	30.74
ethylene standard deviation (ppb) @ 2% O_2	0.12	1.19
ethylene average (ppb) @ 21% O_2	29.20	28.19
ethylene standard deviation (ppb) @ 21% O_2	0.09	1.37

PHGA shows very low standard deviations (~0.1 ppb) compared to the reference ETD (~1.3 ppb).

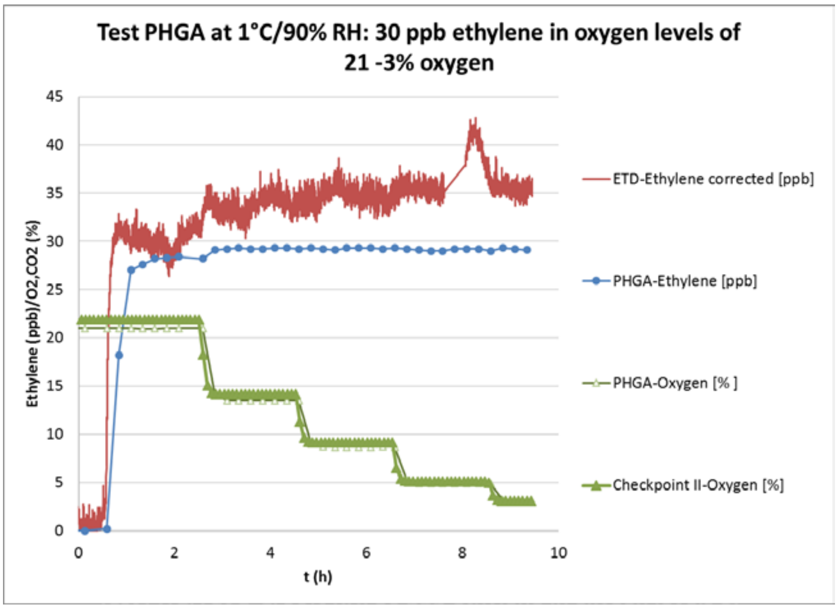

Figure 3-7: Raw data test results of impact oxygen levels on ethylene measurements.

PHGA data seem much more consistent towards set points at lower oxygen levels than the ETD data. Also here no clear visible effect of a range of oxygen on ethylene measurement is seen for the PHGA. *At lower oxygen concentrations the ETD gives an overestimation of ethylene concentrations.*

3.4 Effect of Relative Humidity

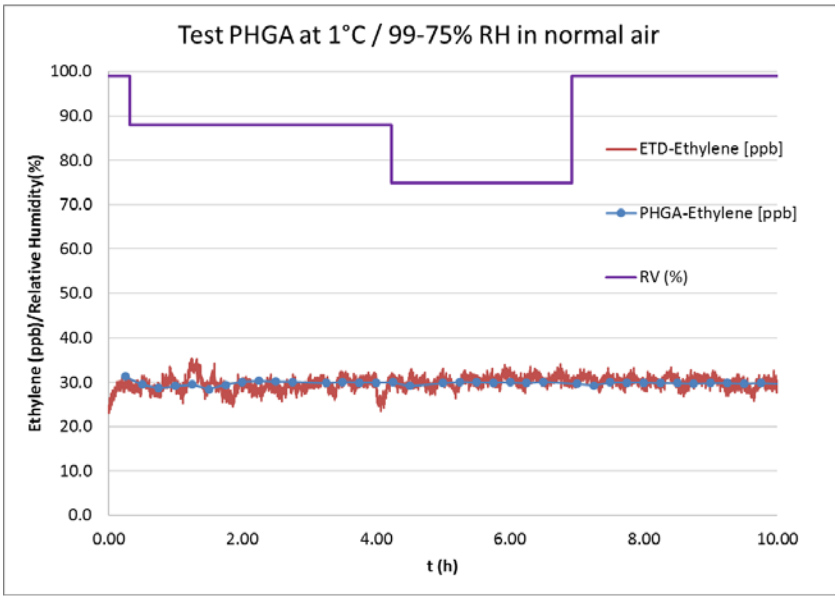

Figure 3-8: Raw data of test results of measurements of 30 ppb ethylene in air at high (99%) to lower (88 and 75%) relative humidity.

No effects of RH on ethylene measurements were observed in this range of 75-99% RH.

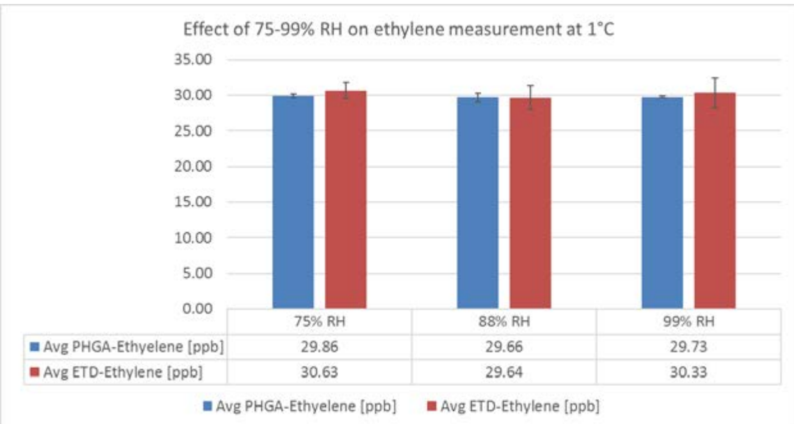

Figure 3-9: Comparison of averaged ethylene concentrations + standard deviations between PHGA and ETD

PHGA: 29.8 +/- 0.34 ppb
ETD: 30.2 +/- 1.62 ppb

3.5 Effect of Temperature

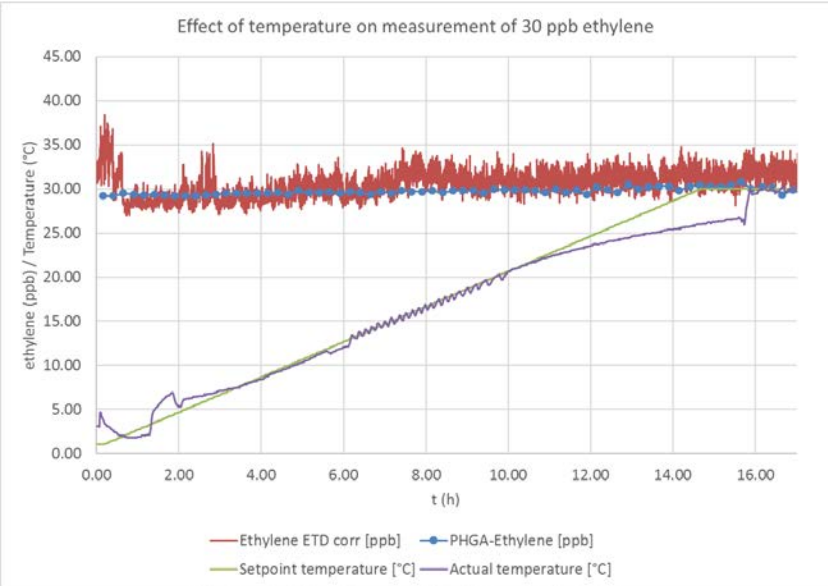

Figure 3-10: No practically relevant temperature effects on measurement of 30 ppb ethylene were observed

By heating the entire climate room from 1°C to 30°C at 2°C/h while measuring a low concentration of ethylene (~30 ppb), the **effects of temperature** on the PHGA were determined. After 11 hours, the heating capacity of the climate room proved to be insufficient to raise the temperature according to set point, after 15.5 h a heater was added to the room to raise the temperature to 30°C.

No practically significant temperature effects on measurement of 30 ppb ethylene (in air, RH 99%) were observed, over the 1-30° C range, overall values were:

	PHGA	ETD
ethylene average (ppb)	30.0	30.6
ethylene standard deviation (ppb)	1.5	1.5

3.6 Cross reactivity of ethanol

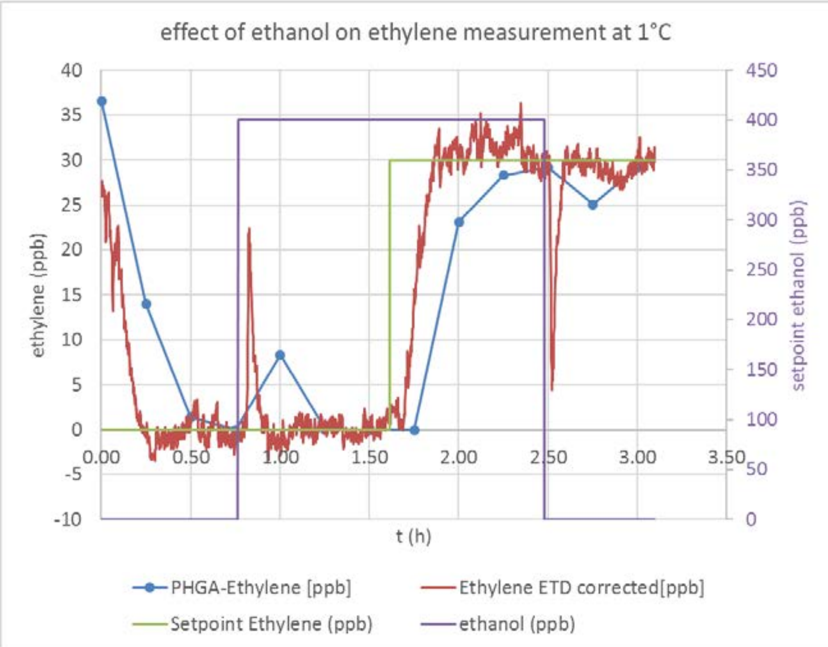

Figure 3-11: Effect of 400 ppb ethanol without and with 30 ppb ethylene

No practical relevant cross reactivity of PHGA ethylene measurement at relatively high concentration of ethanol could be observed.

The spikes in the ETD signal at t=0.8 and 2.6 translate also in higher resp. lower values in the proceeding PHGA measurement, indicating a real but unintended change of ethylene concentration due to changing of the gas wash bottles containing ethanol during the test. After these spikes values returned to expected values the next measurements.

3.7 Effects of kiwifruit volatiles

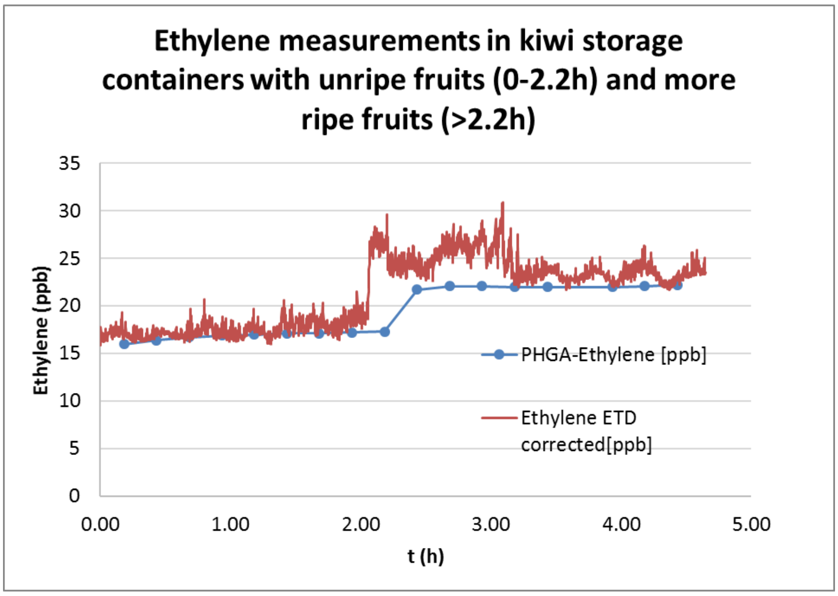

Figure 3-12: Data of test results of ethylene measurements of stored kiwifruits at 1°C in normal air. Before t= 2h, a container with firm, unripe kiwifruit was measured, after 2h a container with softer/riper kiwifruits was selected for measurements.

Flush rate of the 550l containers containing approx. 60kg of kiwifruits was 500 ml/minute, which was started >24h prior to this test, resulting in stable values for both containers during the test:

		PHGA ethylene (ppb)	ETD ethylene (ppb)
Average	unripe kiwifruits	16.8	17.5
	riper kiwifruits	22.0	24.2
Standard deviation	unripe kiwifruits	0.4	0.8
	riper kiwifruits	0.1	1.6

Extra reference measurements using a calibrated gas chromatograph did not add extra information (standard deviations > 5 ppb on the gas chromatograph (GC)): the tested PHGA was more sensitive than the reference GC used. Standard deviations of PHGA were < 0.4 ppb for the PHGA and > 0.8 ppb for the reference ethylene measurement using the ETD.

In a second test the container with riper kiwifruits was left closed overnight (16h) to increase concentrations of kiwifruit-related volatiles that could possibly lead to cross reactivity with the PHGA. After this, this container was flushed with 500 ml/h ethylene-free air, and gas was sampled from the outlet to the PHGA, ETD-300 and Checkmate II for ethylene and reference measurements.

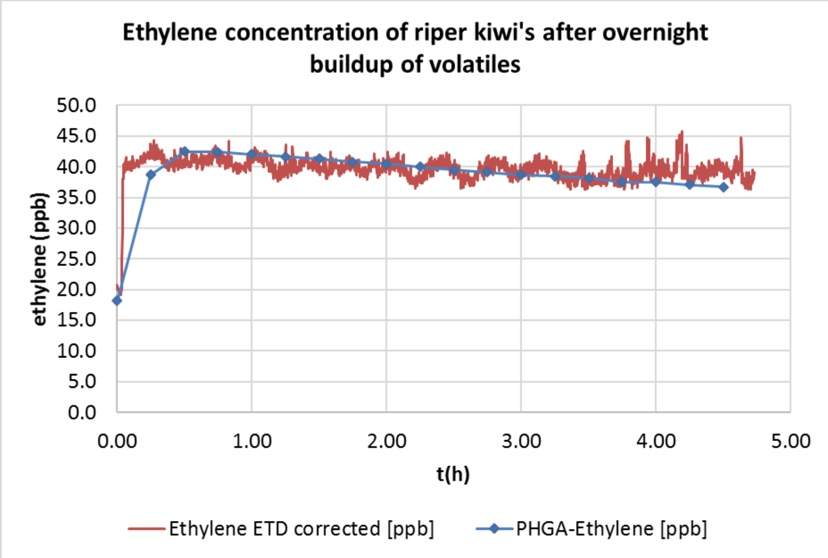

Figure 3-13: No overestimation of ethylene by the PHGA was observed in air from kiwifruit, indication no signs of cross reactivity. The decrease of the ethylene concentration in time is the effect of flushing 500 ml/h after the accumulation period prior to testing.

Average values and standard deviations of the period 0.5-4.5h:

	PHGA-Ethylene [ppb]	Ethylene ETD [ppb]
average ethylene (ppb)	39.6	39.6
Standard deviation ethylene (ppb)	1.9	1.4

Here the standard deviation is relatively large: due to the decreasing value in time due to flushing of the kiwifruit container rather than measurement variation itself.

4 Conclusions

The test results for the sensitivity, stability and specificity of the MACView® Portable Ethylene Postharvest Gas Analyser (PHGA) are very good.

The reference ethylene measurements using the photoacoustic laser detector ETD-300 are much more frequent (6-12 measurements per minute) than the PHGA (15 min per measurement). In these tests ETD stability and sensitivity at low ethylene levels were less than the PHGA.

Concluding from these test we found that the PHGA:

- was easy to operate and to collect and remotely monitor data
- did function without problems for a period of several weeks at 1ºC and 90% humidity, even during/after periods of high condensation on the device
- during the testing period in this study (2 months), no changes in calibration were required and no changes in stability or sensitivity were observed
- can detect low levels of ethylene (1-300 ppb) at 1°C and at high humidity levels accurately
- resolution of 1 ppb was realized
- showed no effects of oxygen (range 21-0.2%) or carbon dioxide (0-5%) or interactions thereof on ethylene measurements at a low level (30 ppb) at 1°C.
- showed no effect of temperature of measurement environment (1 to 30°C) on ethylene measurements at a low level (30 ppb).
- showed no effects of variation in Relative Humidity in the range from 99-75% on ethylene measurements at a low level (30 ppb) at 1°C.
- showed no effects of 400 ppb ethanol on ethylene measurements at a low level (30 ppb) at 1°C.
- showed no cross reactivity of ethylene measurements with kiwifruit volatiles, not in a flow-through equilibrium-situation nor after overnight accumulation of kiwifruit-volatiles.
- requires 15 minutes per measurement. Depending on the timing, after a change of sampling point or gas, the first measurement value is often not stabilized yet.

From these tests we conclude that the MACView® Portable Ethylene Postharvest Gas Analyser is suited for precise and reliable measurement of ethylene in horticultural settings, even at low temperatures and high humidity, and without special skills or requirements. This makes the MACView® Portable Ethylene Postharvest Gas Analyser an excellent practical device for monitoring ethylene in storage and logistics of ethylene sensitive products such as kiwifruits.

References

Cristescu, S. M., et al. (2008). "Laser-based systems for trace gas detection in life sciences." **92**(3): 343-349.

Greenspan, L. (1977). "Humidity fixed points of binary saturated aqueous solutions." Journal of research of the national bureau of standards **81**(1): 89-96.

Acknowledgements
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