Evaluation
MacView® Ethylene Analyser

For use in horticultural settings

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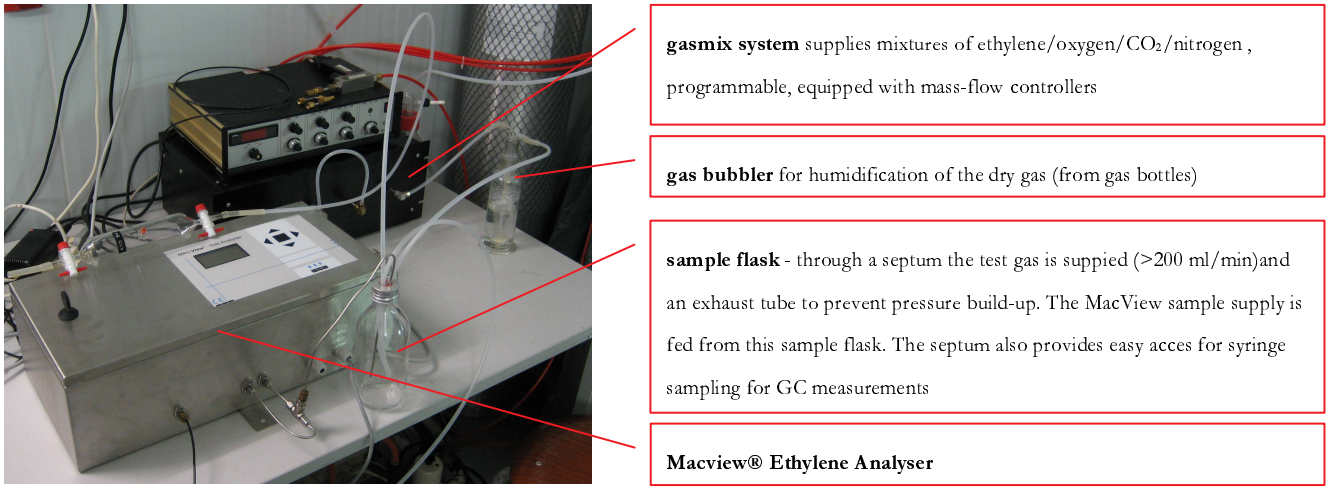
1 Introduction

The MacView® Ethylene Analyser is a measuring device for determination of ethylene concentrations in air.
In order to evaluate the suitability of this analyser for use in horticultural settings like in cold stores or Controlled Atmosphere storage rooms (CA, ULO), AFSG, a part of Wageningen UR, has done a independent screening of the accuracy and the stability of the apparatus in a range of circumstances common in horticultural practice. The evaluation is accomplished in 2007-2009. In the last stage manufacturer Environmental Monitoring Systems BV (EMS) has made certain technical developments for optimising use in horticultural practice. The original analyser (momentarily in use for storage of flower bulbs) with a range of 0-2000 ppb has been modified with a range of 0-100 ppm especially for use in storage of fruit.

2 Methods

In 2007-2009 a number of tests were performed to check if the sensor has sufficient sensitivity for measuring ethylene and if the distinguishing capability for detection of ethylene is sufficient under conditions commonly encountered in horticultural stores (such as differences in relative humidity, Controlled Atmosphere conditions, cross sensitivity etc).

The analysers have been tested under strictly controlled circumstances. The signals of the analysers have been regularly checked with ethylene measurements on a calibrated gas chromatograph (GC) and tests were performed with calibrated gasses. Through a software controlled system which controls through mass-flow controllers the amount of oxygen, carbon dioxide gas, nitrogen and ethylene in a gas mix, the test gas is supplied to a sample flask of 1.5 l trough a gas bubbler (in case of humidifying the gas mixture) through a septum. The septum also provides passage of the sample supply of the MacView® Ethylene Analyser and a outlet hose to prevent rise in pressure.



Measurement setup of a MacView® Ethylene Analyser connected to a gas mix supply system

The used flow rate was 1000-2500 ml/min, at least more than 3x the suction speed of the analyser in order to prevent suction of "false air". The whole installation was placed in a temperature controlled cold store. The temperature for most experiments was set to 20°C. Regularly the ethylene concentration in the sample bottle with septum was determined by taking a sample with a 2.5ml syringe and analysing this in the GC.

Sensitivity, response time

The minimum detection limit of ethylene is determined in clean air with several concentrations of ethylene until approximately 2 ppm. Through increasing and decreasing concentrations memory

effects are determined. The response and regenerating time are determined by pulsed application of ethylene.

Interference with ambient conditions

The effect of changes in ambient conditions (temperature, relative humidity, carbon dioxide, oxygen) on the response and the selectivity of the sensor is determined in a surrounding with approximately 1000 ppb ethylene (20 ppm with the tests with the 0-100 ppm range analyser). The response time and regenerating time are also determined by pulsed ethylene application. After the experiments the sensitivity of the sensor in clean air is determined once again.

Variables :

- O_2 : range of 0-21%
- CO_2 : range of 0-10%
- T : temperature profiles between 0 and 40°C
- RH : low (dry gas,< 10%) and high (>95%)

Cross sensitivities

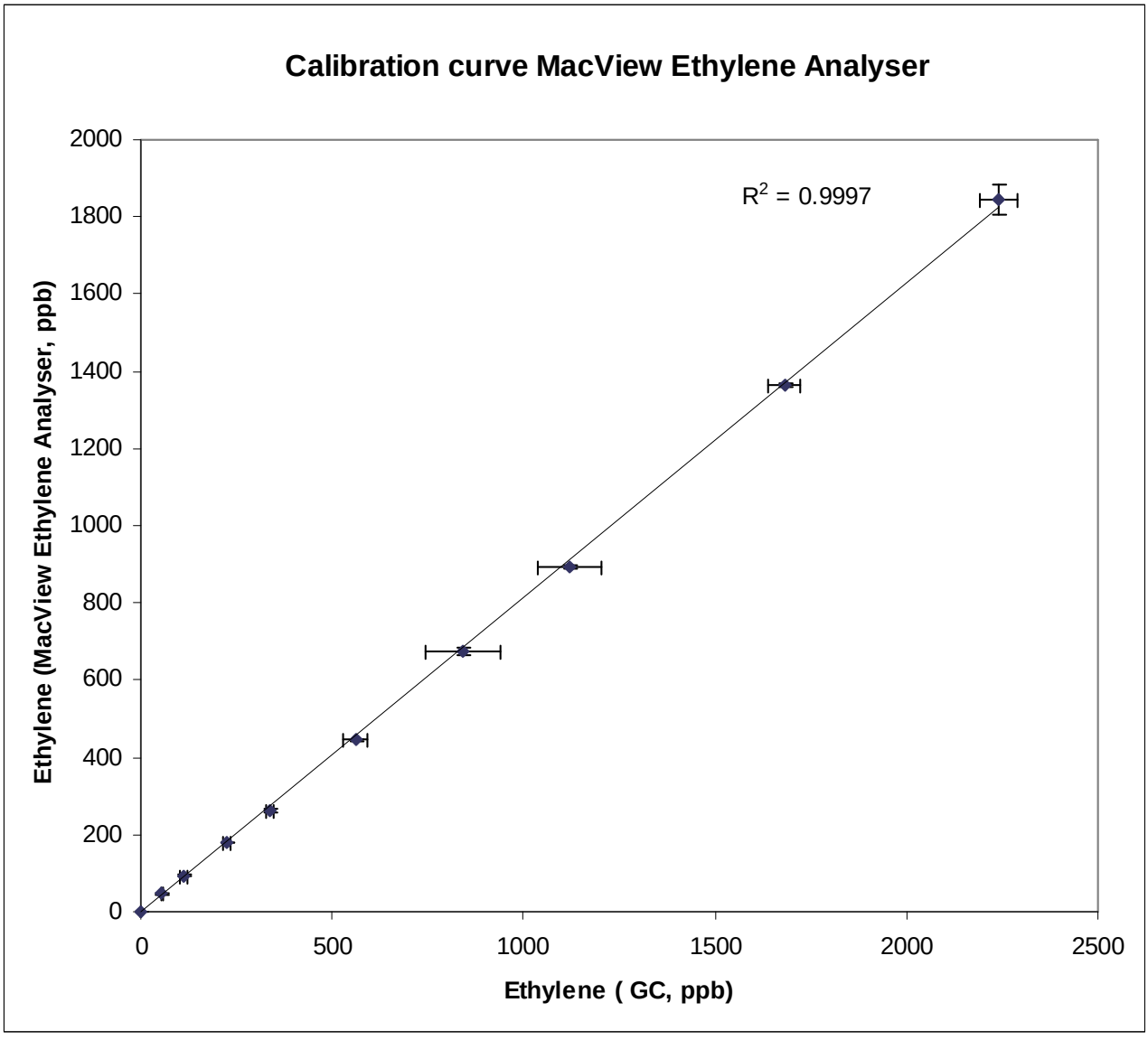
A number of tests have been performed to get an impression of the cross sensitivity with other gasses present in the fruit conserve stores and specifically alcohol (ethanol). The presence of alcohol can occur through processes of fruit rot but also under influence of low oxygen through fermentation. By adding a series of low concentrations of ethanol to the gas bubbler, several concentrations of ethanol are added to the gas stream. The influence of ethanol on the ethylene measurements is determined through measuring the ethanol and ethylene concentrations in the sample flask using gas chromatography and comparing this with the results of the analyser.

Also a short test is performed with aromatic apples. The cross sensitivity of the analyser in such a complex mixture is determined. In this test 15kg of apples are put in a 70 l container and flushed with 1 l/min from the gas mix system. The outlet air was led through the sample flask to the analyser.

3 Results and discussion

Sensitivity and accuracy

In the tested range up to approximately 2500 ppb ethylene the MacView® Ethylene Analyser has a outstanding linear response (see chart). The detection limit of the used gas chromatograph is approximately 15 ppb. The analyser can measure lower concentrations but the reliability of these measurements could thus not be determined with our equipment. This means that the analyser has a detection limit lower than 15ppb which is outstanding.

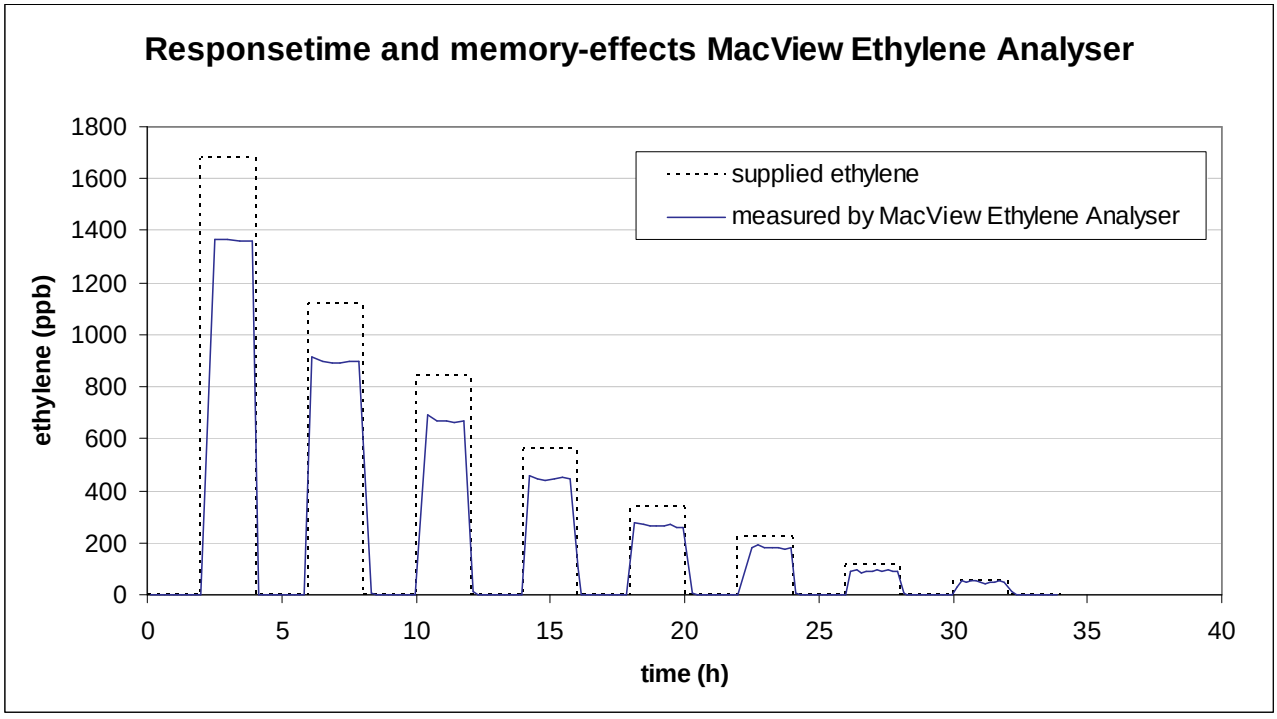


The deviation of the values of the analyser compared to the ethylene gas chromatograph values are a consequence of the calibration settings of the analyser. Considering the linear

character of the response this is no problem but a question of a small adjustment of the settings of the analyser, see also point 13 of the conclusions about the outstanding stability of the calibration. Given that the settings for the calibration of the MacView® Ethylene Analyser during the test period have not been altered frequently, the deviation between offered and measured concentrations is sometime's visible in the next diagrams. At the last tests the calibration settings where correct. After this the agreement between the analyser and the gas chromatograph was almost completely 1 on 1.
The variation between the measurements of the same concentration is similar to the GC equipment for evaluation of the analyser (% standard deviation < 1%).

Response time and memory effects

The MacView® Ethylene Analyser has no continuous measurement signal. The apparatus sucks continuous and analyses a sample every 10-15 minutes. This seams the major limitation in the response time. After a strong change in ethylene concentration the sensor reacts at once at the next measurement and is rather stable, see chart.

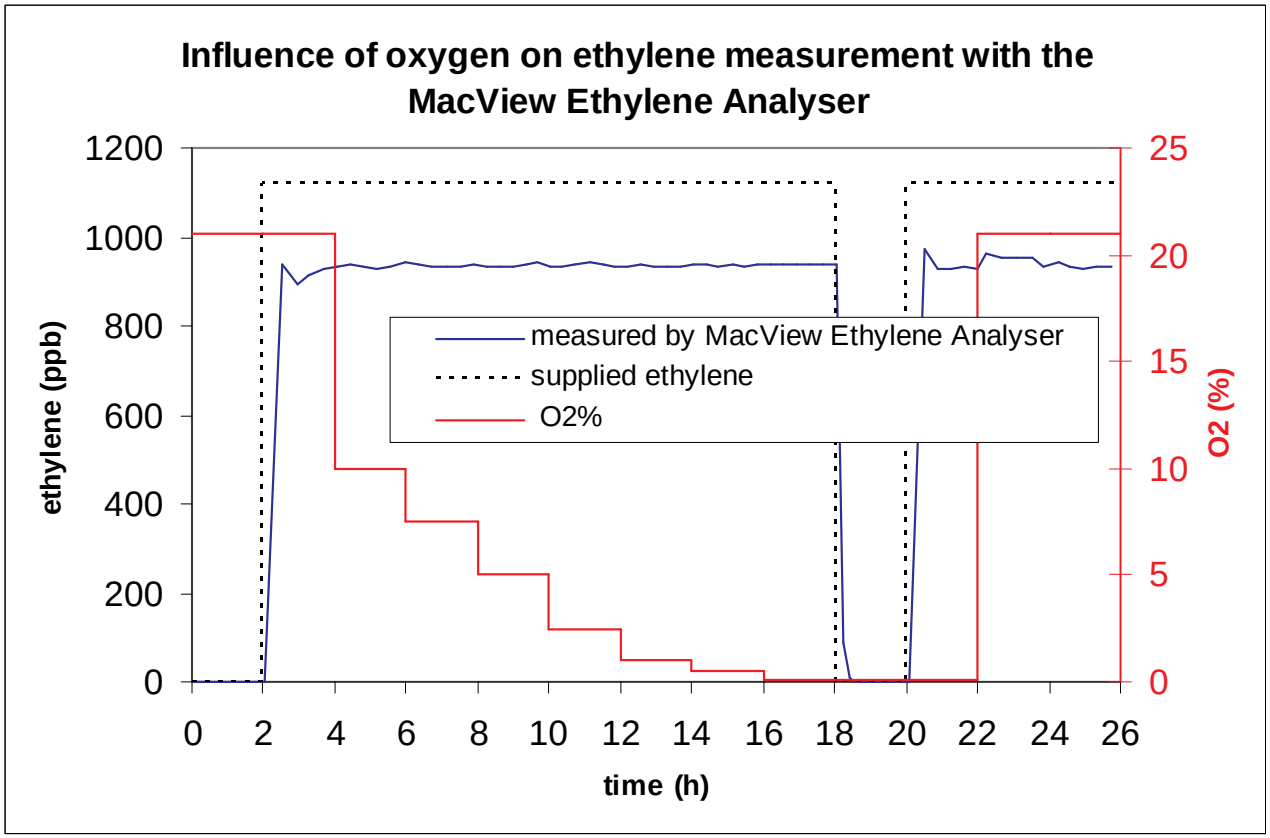


As also shown in the chart, ethylene is offered to the sensor in pulses of two hours succeeded with 2 hours of clean air. The offered ethylene concentrations in this example decreased from 1700 to 50 ppb. The analyser followed this pattern almost exactly. When exposed to longer periods of the same concentration (for days) the analyser gives a very stable signal. At earlier tested ethylene sensors long recovery periods were required to get a stable signal after a strong concentration change (tricky memory effects), or the sensor signal tended to drift slowly. This analyser does not show this kind of problems, even after a period of months of use the response showed to be reproducible.

Influence oxygen (O_2), carbon dioxide (CO_2), relative humidity (RH) en temperature

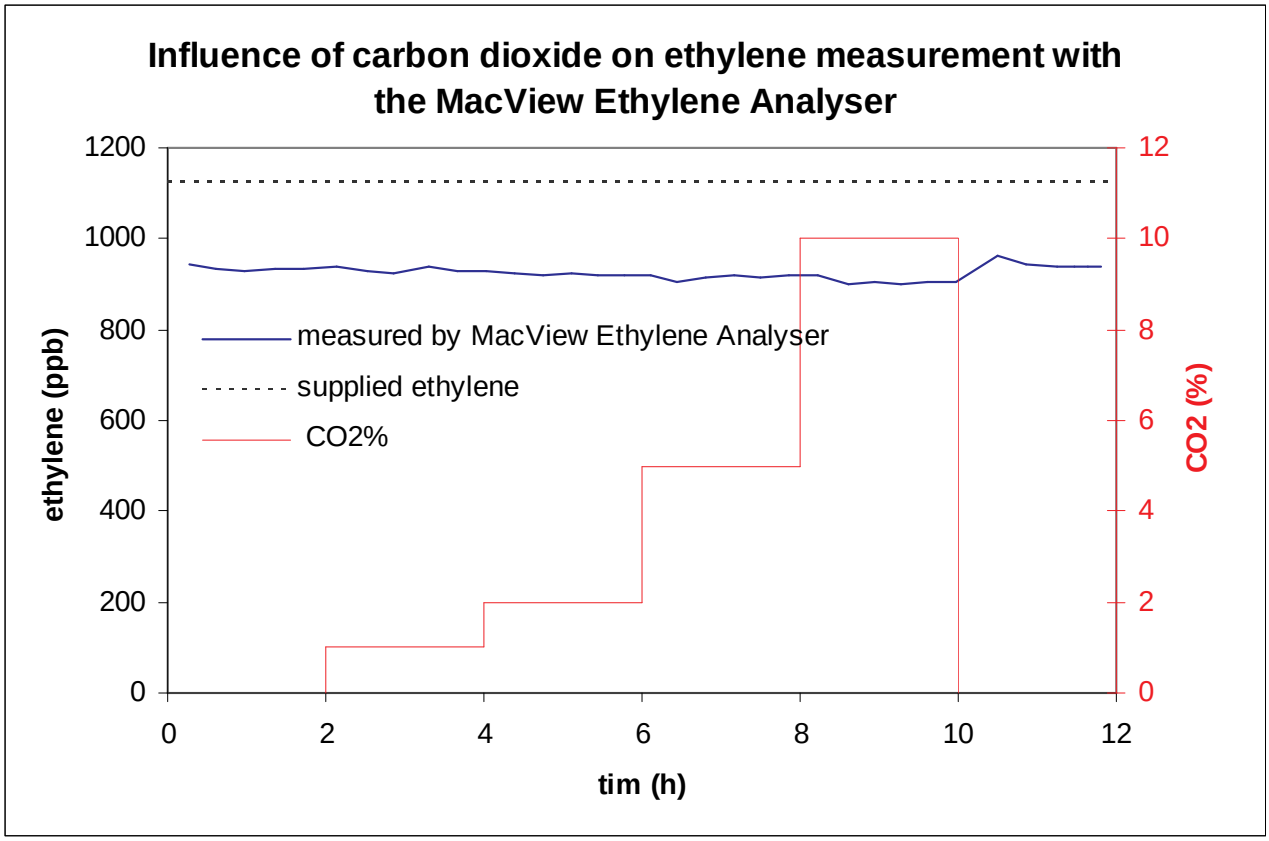
Because in storage rooms for horticultural produce the circumstances for oxygen, carbon dioxide, relative humidity and temperature can vary al lot, it is of importance to know if these variables can disturb a reliable ethylene measurement by the analyser. Especially in Controlled Atmosphere storage which is in use for storage of fruit, often severely lowered oxygen and elevated (high) carbon dioxide concentration occur.

In the next diagram is shown that the measurement of ethylene by the analyser is not noticeable influenced when an oxygen concentration in a range of 21 and lower is added, the signal stays stable.



When after 18 hours the ethylene concentration immediately is lowered to zero, it shows also immediately in the response of the analyser while changes in the oxygen concentration give hardly or no change in the analyser measurement.

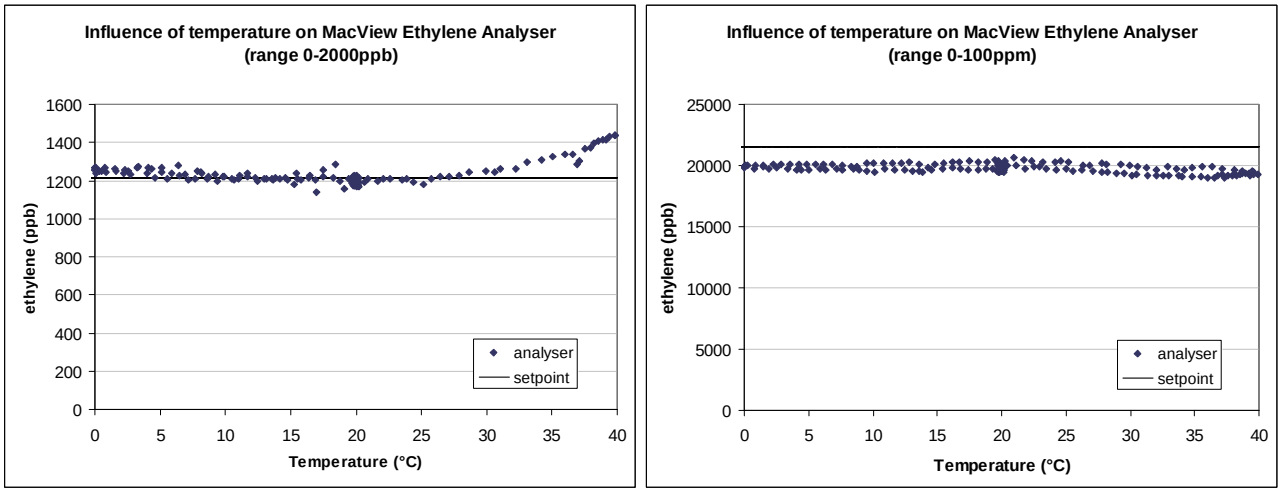
A similar test is performed for carbon dioxide with concentrations of 0 to 10%. There is a slight influence: at 10% CO_2 the response of the analyser is approximately 3.5% lower than at 0% CO_2. This is no obstacle for use of the analyser in horticultural practice because it is only a slight sensitivity and the carbon dioxide concentration during storage is in most situations not higher than 4% and stable. Next diagram shows the hardly visible influence of CO_2.



Temperature

Fluctuation of ambient temperature hardly influences the operation of the MacView® Ethylene Analyser. In comparison with measurements at constant temperature the deviation of the measurements rises from <1% to >2%.

At higher environment temperatures than 28°C the temperature of the internal sensor block rises above setpoint which causes the measurement of the low range analyser (0-2000 ppb) to rise strongly (+13% at 40°C). At the analyser with the range 0-100 ppm it has no effect. Attention to the correct positioning of the analyser (taking local environmental temperature fluctuations into account and/or increasing the setpoint temperature of the internal sensor block are possibilities for uncomplicated measurement at higher temperatures than 28°C.



In these graphs the effects of different temperature profiles between 0 and 40°C are collected. Most measurements are carried out at 20°C, this gives a direct picture of the deviation in the values at constant temperature.

Relative Humidity

The influence of the relative humidity on ethylene measurement is tested through leading very dry gas (direct from gas bottles) directly or through a gas bubbler (high humidity) to the analyser. The relative humidity of the gas to be measured has no noticeable influence on the values of the MacView® Ethylene Analyser. Measurements at RH>95% and <10% gave identical results. There is no expectation for limitation of use in horticultural settings because of the (much) smaller range in RH fluctuations observed in horticultural practice in general.

Cross sensitivity Ethanol

By adding a series of low concentrations of ethanol to the water in the gas bubbler, several concentrations of gaseous ethanol are added to a gas mixture with ethylene. The influence of the ethanol concentration on the ethylene measurement is determined through measuring the ethanol and ethylene concentrations in the sample flask using gas chromatography and compare these with the analyser results.

The MacView® Ethylene Analyser has limited cross sensitivity for ethanol. Addition of up to 1 ppm ethanol gives no measurable effect, at 10 ppm ethanol the 0-2000 ppb range version analyser gives a signal increase of 6% at 1 ppm ethylene. The version with range 0-100 ppm shows no influence at a measurement of 20 ppm ethylene when 10 ppm ethanol is added to the gas stream. In horticultural practice the ethanol concentrations are generally always lower than 1 ppm, so there is no expectation for ethanol cross sensitivity problems in measurement of ethylene.

Cross sensitivity Apple aroma

A short test is performed with aromatic apples (cultivar Kanzi) for determination of the cross sensitivity in a complex mixture. In this test 15kg of apples are put in a 70 l container and flushed through for two weeks with 1 l/min from the gas mix system. The outlet air was led through the sample flask to the analyser. Although the outlet air had a distinct smell of aromatic apples, it did not result in an increased response of the analyser. Addition of extra ethylene was registered correctly. In this complex matrix containing various esters and aldehydes there was no measurable cross sensitivity and the ethylene concentration was always determined accurately by the analyser.

Measuring in horticultural settings

The tests covering a range of relevant concentrations of oxygen, carbon dioxide, different levels of Relative Humidity and alcohol, aromatic apples and the first experiences with application in practice show that measurement in horticultural settings is perfectly possible without problems or interference from complex gas mixtures.

Nevertheless, it can not be excluded that in specific situations cross sensitivity for in particular very high concentrations of volatile substances could occur. Think of interference with on-site chemical postharvest treatments, or the use of high concentrations of cleaning liquids etc. During normal operation in horticultural settings these cross sensitivities will have no effect.

High doses of aggressive substances can damage the analyser. The manufacturer's advice is to contact him or switch the analyser off before using high (smelling) concentrations of insecticides or cleaning liquids. Specific gasses can be detected as abnormal (for instance Actellic for control of flower bulb mite, this can trigger a rinsing cycle to protect the analyser).

In case of new or different applications or uncertainty about the measurement values a verification measurement with the GC can exclude if in these specific situations unbiased measurement is performed.

4 Conclusions

From this evaluation the following is concluded:

1. In mixtures of pure nitrogen, oxygen and carbon dioxide the MacView® Ethylene Analyser has a linear response in the range from 0 to 2500 ppb and a detection limit lower than the GC in use (<15 ppb). The variation between measurements of the same concentration is comparable to the used GC equipment for evaluation of the analyser (<1% standard deviation)
2. The MacView® Ethylene Analyser does not produce a continuous measurement signal. The apparatus samples continuously but analyses a sample once every 10-15 minutes. This is the main limitation in response time. After a strong change in ethylene concentration the sensor reacts at once at the next measurement and is stable fast. There are no "memory effects" observed.
3. The MacView® Ethylene Analyser gives a very stable signal after long periods (weeks, months) of exposure to the same concentration. There is no or hardly any signal drift. Even after months of use the response remains reproducible.
4. Oxygen (O_2) in the range of 21 to 0% has a limited influence on the response of the MacView® Ethylene Analyser.
5. Carbon dioxide (CO_2) in the range of 0 to 10% has a very limited influence on the response of the MacView® Ethylene Analyser. Up to 5% CO2 there is no measurable influence on the measurement of ethylene. At 10% CO2 the response on 1ppm ethylene is 3.5% lower than with no CO2. Because it is only a slight sensitivity and the carbon dioxide concentration during for instance CA storage is most of the time not higher than 4% and almost stable, there is no expectation for limitation of use in horticultural settings.
6. The relative humidity (<10->95%RH) of the measured gas has no influence on the response of the MacView® Ethylene Analyser.
7. No interaction between oxygen, CO_2, RH and temperature on the measurement values was observed.
8. The MacView® Ethylene Analyser has a very limited cross sensitivity for ethanol. At 1 ppm ethanol no influence was observed. A 10 ppm ethanol the 0-2000 ppb range version responded with an increased signal (6%) at 1 ppm ethylene. The 0-100 ppm range version showed no influence at a measurement of 20 ppm ethylene when 10 ppm ethanol was mixed in the gas stream. In horticultural practice the concentrations of ethanol are almost always much lower than 1 ppm so no problems with this limited cross sensitivity when measuring ethylene are to be expected.
9. The test with apples as performed in this evaluation did not show any influence of a distinct smell of aromatic apples on the measurement of ethylene with the MacView®

Ethylene Analyser. The first measurement experiences in practice in Controlled Atmosphere storage of Conference pears also pose no problems.

10. The tests with a broad range of relevant temperatures, oxygen, carbon dioxide and relative humidity levels, alcohol, aromatic apples and the first practice experiences show that measurements in horticultural practice is possible without problems or interferance with reigning conditions.
11. The MacView® Ethylene Analyser has diagnostic software which generates error messages if there are technical measuring problems (for instance obstruction of the sample tube, over range, application of Actellic, etc.) which strongly increases the practical reliability.
12. The MacView® Ethylene Analyser is easy to use, can be connected directly to most common control systems and is capable of directly switching external equipment. Measurement data are stored in the MacView® Ethylene Analyser and can easily be read or monitored with the provided software.
13. Regular calibration by users is not required due to the long lasting stability. The suppliers of ethylene calibration mixtures deliver an analysis certificate with an accuracy of +/- 5%. In these tests one has compared the calibration gas of EMS and AFSG. The differences amounted up to 8% , this is the major source of deviation between the measurement values of the analysers and the GC. When corrected for this phenomenon the difference between the GC and the analysers was always very limited (<2%).

Final conclusion :

The MacView® Ethylene Analyser is perfectly suitable for the measurement of ethylene in horticultural settings