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Detection of gaseous ethanol by the use of ambient temperature platinum catalyst

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Abstract

An ethanol sensor system is build and tested by means of a platinum in-line catalytic converter on ambient temperature, which acts as a zero reference with an electrochemical sensor, sensitive to ethanol. The system is selective to ethanol and proposed to measure ethanol gas concentrations from fruit. The system's performance was investigated regarding sensitivity and cross sensitivity for several volatile organic compounds (VOCs) commonly emitted by fruit (e.g. apples). The ethanol gas sensor system was tested with fruit samples in a test facility close to a storage environment.

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1. Introduction

Monitoring of fruit especially apples (Malus domestica) by ethanol gas measurement will provide useful information of natural decay and is an important signal for determination of the oxygen shortage during the storage under ultra-low oxygen/controlled atmosphere (ULO/CA) conditions to prolong lifetime [1,2]. Since the invention

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of DCS [3] and there corresponding proposed automatic control with ethanol sensors [4], there were no sensors or methods which were able to measure reliable ethanol concentrations inside a fruit storage on ppbv levels without negative influence of cross-sensitivities.

The systems described have, due to the low vapor pressure of ethanol at storage temperatures of 1°C, a lack of sensitivity and selectivity, and are not able to detect ethanol at the ppbv concentrations required [5,6]. The aim is to detect metabolic changes in the fruit during the aging process and to detect oxygen shortages during storage in ULO/CA conditions during long term storage. The novelty of the ethanol gas sensor system in Fig 1. lies in the combination of an electrochemical ethanol sensitive gas sensor with a selectively operable in-line heterogeneous platinum catalytic converter on ambient temperature (35°C) that allows for the selective removal of alcohols for zero-reference measurements. The system alternately switches the ethanol gas stream between the measurement line and the zero reference line, while calculating the difference of the 2 signals. This unique combination results in a highly selective and sensitive ethanol detection system. The platinum heterogeneous catalytic converter acts as a zero or sensor baseline reference which removes small alcohols from the gas stream without affecting other VOCs inside the gas stream. The catalytic process which is still active under ambient temperatures converts ethanol in different parallel and separated pathways to CO2, water, ethyl acetate and possible other reaction products. Although the electrochemical sensor remains sensitive to humidity, temperature and certain other volatiles than ethanol, the results show that the ethanol response from the detection system matches with GC-MS reference data. A big contribution is the ambient catalytic effect of the Pt catalyst. Because the composition of the gas stream is not changed by thermal changes, causing shifts in RH or temperature. A detection limit of several ppbv of ethanol is possible in ULO/CA conditions. An investigation of cross sensitivity was then performed by setting up a reference system simulating the volatiles of apples by means of a setup with permeation ovens. After these tests the system was investigated in a test facility with real fruit, simulating an environment in which apples were exposed to low oxygen. A reference system of thermal desorption GC-MS was connected to verify and compare the results.

2. Materials, methods and measurement procedures

2.1. Application setup of the ethanol reference with GC-MS

Several ethanol gas sensor systems were prepared (EMS B.V. Netherlands) in a measurement system with analyser capabilities with temperature controlled stability and calibration options. Corrections on the sensors and analyser system had been made as well as an understanding of the humidity influence is investigated and optimized. The ethanol gas sensor systems were calibrated with 1000 ppbv ethanol mixed by MFC's from a 1490 ppbv calibration gas bottle of ethanol in synthetic air (Scottgas). After the 2 point calibration of 0 ppbv and 1000 ppbv the ethanol sensor systems were exposed to different ethanol gas concentrations by mass flow controllers for linearization checks. The linearization was parallel checked by TD-GC-MS. (TD Markes Airserver, GC Agilent 7990A and MS 5975C). The TD-GC-MS was calibrated on concentrations of 1490 ppbv, 1000 ppbv, 500 ppbv and 100 ppbv of ethanol. Exposure of ethanol to the ethanol gas sensor system was done in the order from low to high, 50 – 100 – 500 and 1000 ppbv and vice-versa from high to low of the same concentrations. The gas stream was humidified with a humidified air mixture. The output of the electrochemical gas sensor was connected directly to the injection port of the thermal desorber. Measurements were parallel done and automatically synchronized.

2.2. Application setup with interfering gasses

Several possible gasses of interest classified as interference gasses in fruit related applications were used to investigate the reaction of the ethanol gas sensor system and to investigate cross sensitivity. The gasses that were used in different concentrations diluted with air composition coming from 5 different permeation ovens (Type EMS B.V. Netherlands) were acetaldehyde, toluene, methanol, ethyl acetate and methyl acetate. The ovens were filled and maintained on an isothermal temperature and before and during the measurement gravimetric measured.