Determination of Water Vapor in a Small Air Sample by a Nondispersive Infrared Gas Analyzer

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Abstract. A portable, nondispersive infrared (NDIR) gas analyzer was modified to measure the concentration of CO₂ and water vapor in small gas samples. A 2-mL gas sample was taken from a series of sealed flasks partially filled with a saturated solution of chemicals known to produce various levels of relative humidity (RH). The modified NDIR instrument quantified water vapor content by its absorption at 2.59 μm . Peak height was displayed on a strip chart recorder and a standard curve constructed. At a specific temperature, the vapor pressure (VP) and vapor pressure difference (VPD) were calculated for sweet pepper (*Capsicum annuum* L., cv. Mazurka) fruit packed in trays that were covered with plastic films having several levels of perforations. Water loss from the fruit was highly correlated with VPD inside the packages. The modified NDIR instrument has an advantage over other instruments used to measure RH because it can rapidly and simultaneously determine the concentration of water vapor and CO₂ in a single injection of a small gas sample.

Most perishable horticulture crops are subject to postharvest water loss, which causes shriveling and wilting (Hardenburg et al., 1986) and accelerates ripening, aging, and senescence (Guinn et al., 1990; Irigoyen et al., 1992; Lurie et al., 1986). The rate of water loss from a commodity is a function of the diffusive resistance of the tissue and package to the movement of water vapor, and the difference in the vapor pressure (VP) of water between the commodity and the surrounding air. Since most perishable fruits and vegetables have a high water content, it is assumed that the water VP at the surface of the fruit is the saturation vapor pressure (SVP) for water at the commodities' temperature. The vapor pressure difference, or the vapor pressure deficit (VPD), can be calculated from a knowledge of the commodities' temperature and the temperature and relative humidity (RH) of the surrounding air (Williams and Brochu, 1969). A nomogram has been devised for calculating VPD (Ryall and Lipton, 1979; Williams and Brochu, 1969). The VPD can also be calculated from RH and air temperature by using a hand calculator (Weiss, 1977). An accurate measurement of the RH is therefore very im-

portant for calculating the predicted rate of water loss in various postharvest environments.

To minimize water loss and the associated detrimental changes, susceptible fruits and vegetables should be stored at 98% to 100% RH (van den Berg and Lentz, 1978). The RH is a measure of the moisture content of air and is defined as the percentage of the maximum amount of water vapor that air will hold at a given temperature. Recently, the postharvest physiological significance of water VPD was reiterated by Lipton (1993).

Relative humidity can be measured directly with various instruments, or it can be calculated from measurements of the wet and dry bulb temperature. The accuracy of most RH measurements decreases as the RH approaches 100% (Hunter and Rowe, 1987; Woods, 1990). A combined temperature and humidity probe (model 850; General Eastern, Woburn, Mass.) has been used for monitoring RH inside a package (Shirazi and Cameron, 1992). This polymer sensor has a sensitivity of 0.1% RH, repeatability of 0.5%, and an accuracy of $\pm 2\%$ RH within 15% to 99% RH at 25 $^{\circ}\text{C}$.

Measurements of the wet and dry bulb temperatures can easily be made and used to calculate the RH in storage rooms where sensors can be exposed to a rapid flow of the atmosphere, or in containers where there is a flow of the storage atmosphere that can be diverted past the sensors. These bulky instruments cannot be used to measure the RH in small volumes where there is little or no gas flow. This limitation is especially true in small packages where permeable plastic films are

used to produce modified atmospheres to extend shelf life and maintain quality. In these packages, the commodity usually takes up most of the volume, which is often smaller than 1 L in total.

Gas samples, often only 1 or 2 mL, are commonly taken of the gases surrounding harvested commodities and analyzed for carbon dioxide, ethylene, and oxygen (Arjona et al., 1994; Saltveit, 1982). Because of its selectivity and stability, a nondispersive infrared (NDIR) spectrophotometer is frequently used to determine the concentration of CO₂ in gases. Some NDIR instruments have the option to measure water vapor simultaneously to correct for its presence in the sample. The moisture content of the gas sample can be determined by using the characteristic infrared absorption of water vapor. The moisture content of grass or hay has been measured by a moisture meter based on the water absorption band in the near infrared (1.45 μm) (Bowman, 1983).

Our study was conducted to evaluate the technique of using a NDIR gas analyzer to determine water VP in a small gas sample. The technique is then illustrated with diverse degrees of water loss from greenhouse-grown sweet bell pepper fruit that were stored in plastic containers wrapped with films of differing degrees of perforation.

Materials and Methods

Instrument modifications. A NDIR gas analyzer (model LI6262; LI-COR, Lincoln, Neb.) was originally designed for measuring CO₂ concentration in flows of air. There are two detectors specifically measuring CO₂ and H₂O. The CO₂ concentration is measured by a CO₂ detector quantifying its absorbance at 4.26 μm with a bandwidth of 0.15 μm . The original design corrects the CO₂ value by measuring H₂O vapor in the same air stream. The H₂O detector uses a filter centered at 2.59 μm with a bandwidth of 0.05 μm .

The original NDIR was designed to measure CO₂ and H₂O in a continuous air flow. We replaced the air flow with a flow of carrier gas into which the 2-mL gas sample was injected. An injection port was made from a rubber septum on a short piece of Tygon tubing attached to one arm of a Y-shaped glass tube (6.35 mm i.d.). Carbon dioxide-free air ($<10 \mu\text{L}\cdot\text{L}^{-1}$ moisture; $<1 \mu\text{L}\cdot\text{L}^{-1}$ O₂) was used as a carrier gas and regulated by a flow control unit (Model LI-670; LI-COR) to maintain a steady flow of 200 mL $\cdot\text{min}^{-1}$. The flow was divided by a Y glass tube so that one-half of the flow passed through the injector port before entering the "sample" inlet of the LI-670 flow control unit and the other half into the "reference" inlet of the flow controller. The outlets from the sample and reference were connected to the corresponding sample and reference inlets of the LI-6262 CO₂/H₂O analyzer. The difference in infrared absorption in the two detectors was measured as two peak heights and recorded on a linear chart recorder (model 285; Linear Instrument Corp., Reno, Nev.). The concentrations of H₂O and CO₂ are calculated from two separate peak heights. In estab-

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lishing the RH standard curve, only H₂O was measured. In experiments with packaged peppers, H₂O and CO₂ were measured simultaneously.

RH standard curve. Saturated solutions of six selected salts were prepared in 250-mL Erlenmeyer narrow-mouth flasks to give a range of RH. The respective equilibrium RH in the air above the six saturated solutions at 22 °C are: CuSO₄, 98%; NH₄H₂PO₄, 93%; ZnSO₄, 90%; NaCl, 75%; K₂CO₃, 43%; and CaCl₂, 32% (Rockland, 1960; Weast et al., 1983). The flasks were allowed to stand overnight at 22 °C to come to equilibrium before testing. For testing a series of six saturated solutions, the chart recorder was adjusted so that the full scale corresponded to the highest RH, i.e., slightly above that for CuSO₄. The remaining five standards were tested using the same recorder setting. At 5 or 13 °C, the series of six standard solutions was reduced to four (Fig. 1) excluding K₂CO₃ and ZnSO₄, whose RH values differ with temperature.

There were five consecutive measurements for each standard at a specific temperature. The RH above the standard solutions was measured, starting with the one of lowest RH in the series of standards, to avoid cross contamination and moisture condensation in the sample cell. The resulting peak heights were used to construct a standard curve that consisted of published RH values for the saturated solutions at the specified temperature and the corresponding measured peak heights. After calibration with a series of the standard saturated solutions at a specific temperature, 2-mL air samples were taken from cold rooms or inside the pepper packages and their RHs were determined from their peak heights according to the standard curve. Three storage rooms were maintained at 1, 5, and 13 °C. The temperatures and RH were monitored by AMWB dry/wet bulb RH sensors (Argus Control Systems, White Rock, B.C., Canada). Air samples were taken from these rooms for verifications.

Calculation of water VP. The water VP of a standard salt solution was calculated by multiplying the SVP at the testing temperature with published RH values (i.e., $VP = SVP \times RH$). The SVP can be determined at a given air temperature (Buck, 1981). The RH of each standard solution was based on published data (Rockland, 1960).

Water loss in relation to VPD. Greenhouse-grown bell pepper fruit (cv. Mazurka) were obtained from a commercial warehouse where they had been held for 6 days prior to the experiment. During the experiment, 10 fruit were placed in a plastic tray (41 × 28 × 15 cm; L × W × D) for each replication. Each tray was covered with a plastic film sealed to the container top using double-sided tape. Fruit did not touch the covering film. Four films varied in their level of perforation. An experimental polyethylene film supplied by J. Cross, Univ. of Waterloo, Ont., was 0.004% micro-perforated. Three polyolefin films from the Cryovac Division of W.K. Grace & Co., Mississauga, Ont., Canada (SM60, SM250, and SM570) had 0.2%, 0.8%, and 4% of their area perforated, respectively. There were two trays per film type. The

air temperature in the storage room was maintained at 21 °C and was monitored by a hygrothermograph (model 8368-00; Cole-Parmer, Chicago). The RH in the 21 °C room was not controlled.

After 3, 7, and 10 days, the water loss of the sweet peppers and the VP inside each container was measured. We assumed that mass loss due to respiration was negligible and thus equated loss in mass with loss of water. Fruit mass was measured by initially weighing the fruit, and then periodically weighing the fruit plus the tared container to the nearest gram. The SVP was calculated by Buck's formula (Buck, 1981). The VP of a gas sample was measured with the modified NDIR gas analyzer described above. The VPD was calculated as the difference between SVP and VP. The percent water loss in fruit after 3, 7, and 10 days of storage was correlated with the calculated VPD.

Statistical procedures. The RH was regressed against the peak height for the construction of the standard curves by using general linear model of SAS statistical system (SAS Institute, 1985). The SAS statistical package was also used in correlation analysis.

Results and Discussion

Standard curves (RH vs. peak height). Standard curves were constructed for the series of saturated salt solutions held at 5, 13, and 22 °C (Fig. 1). A series of saturated solutions at 22 °C was measured twice. The first series consisted of six solutions, but the second series involved only those with the lowest three humidities. These two series were measured on separate days. The readings were repeatable, and they were combined as a single standard curve. All three standard curves were linear, but their slopes and intercepts differed. For a specific

salt solution at a specific temperature, the standard deviation of peak heights was normally <4% of its mean ($n = 5$). When additional air samples were taken from cold rooms at 1, 5, or 13 °C, the RH values obtained by using NDIR were within 3% of those determined by a dry/wet bulb humidity sensor. This study illustrated that the moisture content can be determined in a 2-mL gas sample injected into a modified NDIR gas analyzer. The RH of the sampled atmosphere can then be calculated from the temperature of the atmosphere and the moisture content as quantified from its peak height (Fig. 1). The measured peak heights for a specific RH were very reproducible, with a relative standard deviation <4% (i.e., standard deviation divided by the mean; $n = 5$).

Combined standard curve (kPa vs. peak height). Each RH value for the air above the standard saturated solutions shown in Fig. 1 was converted into a water VP and a combined regression line was constructed (Fig. 2). The linear relationship between VP and peak height indicated that the VP of a small gas sample could be determined from the peak height within the experimental range of 5 to 22 °C. The VP of the sampled atmosphere can be calculated from its temperature and RH (Fig. 2). Contrary to the RH, which is dependent on temperature, the VP of a gas sample can be determined from the peak height regardless of air temperature.

Water loss as a function of VPD. The percent water loss of pepper fruits was positively correlated with the VPD inside the film containers (Fig. 3), with resulting r^2 of almost 1 on days 3, 7, and 10 ($P \leq 0.01$). The levels of VPD were created by the differing degree of film perforation. Differences in water loss among peppers in the films were apparent within 3 days of storage. The ability of these films to protect peppers against water loss

Fig. 1. Three standard curves relating relative humidity (RH) of saturated salt solutions and peak height determined by using a nondispersive infrared (NDIR) gas analyzer. A series of saturated salt solutions were held at 5, 13, and 22 °C overnight before 2-mL gas samples of the head space were injected.

Fig. 2. The combined standard curve between vapor pressure (kPa) and peak height determined by using a nondispersive infrared gas analyzer. All the values of kPa were converted from the RH values shown in Fig. 1. Symbols are the same as in Fig. 1.

depended on their degree of perforation. The CO_2 concentrations in the atmosphere around the fruit ranged from $486 \mu\text{L}\cdot\text{L}^{-1}$ (control, unwrapped) to $7,275 \mu\text{L}\cdot\text{L}^{-1}$ (tray covered with micro-perforated film).

The physiological significance of VP and VPD is illustrated in the film experiment (Fig. 3). The percent water loss is a function of VPD. If the days of storage were taken into consideration, the water loss per kPa per day for each of the three sampling dates were very

similar; the loss was 1.27%, 1.30%, and 1.30% for storage periods of 3, 7, and 10 days, respectively. The similarity of these three values indicates that the rate of water loss of pepper fruits was relatively constant between day 3 to 10. This study also illustrates the direct relationship between water loss of perishable produce and its surrounding VPD. The water loss was measured with a sample unit of 10 fruit. Therefore, variation in water loss among individual fruit was not tested in this study.

Fig. 3. The relationship between water loss of greenhouse-grown sweet bell pepper fruits and the vapor pressure deficit (VPD). Three regression lines represented the 3-, 7-, and 10-day sampling dates during storage.

The modified NDIR gas analyzer is an excellent research tool because it is easy to set up and operate, is rapid, and uses only a small ($\approx 2 \text{ mL}$) air sample to simultaneously measure the content of both H_2O and CO_2 . Samples of $< 2 \text{ mL}$ moist air were tested with satisfactory results. The limitations of using a smaller sample size become apparent at low moisture content and low temperature, or both. The peak height from the chart recorder can be calibrated to read in either RH at a specific temperature or in VP units (kPa). In practice, there was very little delay between injections and little drift in the baseline recorded on the chart recorder. The ability of this instrument to simultaneously determine H_2O and CO_2 in a single injection within 30 to 60 s makes it suitable for processing many samples.

Our NDIR method is especially suited for analyzing the small gas volume commonly taken for CO_2 analysis in postharvest studies. It is also excellently suited for studies with film-wrapped packages of fruits and vegetables, since taking small gas samples is relatively nondestructive to the wrapping film. Other available techniques, such as the dry/wet bulb hygrometer and the polymer sensor, are too bulky or too costly to be used in package studies. Polymer sensors are smaller in size, but they have to be attached to a package and costs can be high when multiple sampling is necessary (Adam and Pritchard, 1994).

In summary, the four advantages of our technique are the small sample size ($< 2 \text{ mL}$), the simultaneous measurements of CO_2 and water vapor, the quick response, and the lack of moisture condensation in the sample cell. The usefulness of the technique was illustrated with water loss in bell peppers that were stored in containers covered with films of unequal perforation.

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