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MODIFIED HUMIDITY PACKAGING

OF FRESH PRODUCE

By

Ahmad Shirazi

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Food Science and Human Nutrition

ABSTRACT

MODIFIED HUMIDITY PACKAGING OF FRESH PRODUCE

By

Ahmad Shirazi

High humidity is responsible for development of microorganisms on many fresh produce items packaged in polymeric films. The generally recommended levels of 85 to 95% RH's for storage of fresh fruits and vegetables are aimed to restrict microbial spoilage while conserving moisture from produce.

The feasibility of controlling in-package relative humidity (IPRH) at recommended levels using compounds possessing Type III sorption isotherm behavior was studied. It was demonstrated that IPRH can be controlled to predetermined levels. IPRH was found to be a function of chemical structure of the compounds and the ratio of chemical to fruit mass. Ten grams of sorbitol, xylitol, sodium chloride, potassium chloride and calcium chloride maintained stable RH's of approximately 75, 80, 75, 85 and 30%, respectively in closed packages containing one mature green tomato fruit at 20° C for up to 48 days.

A method was developed to study the kinetics of water loss from fresh produce and water sorption by package components. This method allows relatively rapid and accurate measurement of rates of water loss or gain by the system components over a wide range of controlled humidities and temperatures. An inverse relationship was generally found between the maintained IPRH and the water absorption capacity for the chemicals. For example, one gram of each sorbitol and potassium chloride absorbed about 0.4 and 0.08 g water.hr⁻¹ at 85% RH and 20° C while the corresponding IPRH values with a single fruit were 75 and 85%, respectively.

Increasing quantities of chemicals absorbed water vapor at higher rates but with a nonlinear pattern due in part to physical limitations of dispersion when larger quantities of compounds were used.

Prediction information was developed for controlled humidity packaging of tomato fruit. Information of this nature can be developed for other fruits and vegetables and directly utilized for application of controlled humidity packaging systems. To my mother,

wife, and children;

and in memory of my father

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INTRODUCTION

Modified atmosphere packaging (MAP) has been a useful method for prolonging the shelf life of fruits and vegetables. It has come a long way since its emergence in the 1930's. Presently, there are several models available for optimization of package parameters for a number of fruits and vegetables.

Most polymeric films utilized in MAP have low water vapor transmission rates relative to transpiration rates of fresh produce. This difference in rates leads to nearly saturated conditions within produce packages. The excessively high in-package relative humidity can cause condensation and, at least in the case of some produce items, favor microbial spoilage. Such problems have limited the usefulness of MAP. A variety of approaches have been taken to overcome these problems, including the reduction of humidity within the package. However, most of these approaches have had limited success, if any at all.

A new concept for regulation of humidity within the packages, Modified humidity packaging (MHP), is introduced utilizing the unique water sorption properties of compounds possessing Type III isotherms. A method for relatively rapid determination of the transpiration rates of small fruits and vegetables was developed and used to analyze the kinetics of MHP systems.

LITERATURE REVIEW

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LITERATURE REVIEW

Modified Atmosphere Packaging (MAP): A Historical Overview

Controlled atmosphere storage was developed in England around 1918 by Franklin Kidd and Cyril West (2). It basically involved lowering of O_2 and increasing CO_2 levels in airtight produce storage rooms in order to suppress respiration rate and thereby extend fruit storage life. An alternative approach for reaching lowered O_2 and increased CO_2 has utilized polymeric films and in general is called MAP.

Cellophane was the first continuous film, produced by a Swiss chemist in 1911. Production of cellophane started in 1923 in Buffalo, N.Y. and then, other films: polyethylene, polystyrene, polyvinyl chloride, etc were introduced and replaced the use of paper and waxed paper because of their much greater resistance to moisture transfer (24).

Studies started in the 1930's using polymeric films to extend the shelf life of a variety of fruits and vegetables showed films to be effective primarily by controlling the weight loss. However, problems such as condensation, mold growth, off-flavor, and physiological breakdown of produce needed to be overcome (4, 5, 6, 57, 67). Other studies stressed the value of polymeric films for maintaining a beneficial atmosphere around fruit during storage (17, 28, 71).

In 1946, it was shown that most films used for packaging of fresh produce did not allow sufficient diffusion of oxygen to supply the needs of even slow-ripening vegetables at 10° C (45). In such cases, the high CO_2 and low O_2 concentrations developed in the packages were pernicious to the produce (56). Thus perforation of film packages was suggested (8, 45). Studies with perforated packages showed a limited success. For example, Eaves (15) described a method for the maintenance of modified atmosphere (MA) in plastic packages for the storage of fruits. His studies with apples in perforated and CO_2 -scrubbed packages showed the possibility of maintaining desirable gas concentrations at 0° , 3° to 5° and 21° C.

Tomkins (65) stated that films were normally 2 to 5 times more permeable to CO_2 than to O_2 . He also stated that perforation of the films, though a simple way of changing permeability, made them equally permeable to O_2 and CO_2 in addition to weakening them. Meanwhile, several studies (20, 26, 41, 47, 53, 54, 59, 60,) proved that it was possible to prolong the storage life of produce by the use of nonperforated sealed films. In 1962, a method of estimating the respiration requirements (film permeability requirements) for various varieties of apples, sizes of containers, and storage temperatures was presented (62). The method could provide basic data for package film specifications that were not previously available.

Jurin and Karel (34) studied respiration rates of apples as a function of oxygen concentration and determined the effect of CO_2 concentrations on this relationship and estimated the critical concentrations of O_2 and CO_2 that result in the onset of anaerobic respiration. Then they used the obtained relations for graphical prediction of steady state concentrations of the stated gases in sealed packages of apples. Their work was later applied to predict and control

the desired atmosphere in packages of green bananas with limited success (35).

Veeraju and Karel (69) developed a formula which, based on the ripe produce requirements for 0_2 and $C0_2$ concentration inside a package, designate the necessary 0_2 and $C0_2$ permeability of the film to be used. Their experimental results were in close agreement with the predicted values.

Tolle (63) referred to several investigations and a variety of techniques and stated that polymers and copolymers could be satisfactorily made to fit any need. He developed a mathematical procedures for optimizing the packaging parameters of post climacteric apples.

Nichols and Hammond (43) proposed an equation applicable to several films to describe the relationship between the equilibrium CO_2 concentration at $18^{\circ}C$ and the permeability of the films for mushrooms. However, he did not find the relationship to hold at another temperature, possibly due to the uncertain values for the O_2 and CO_2 permeabilities.

Unlike many other researchers, Henig and Gilbert (31) assumed variable respiration quotients and presented a computerized solution for the differential equations relating to the simultaneous and interacting processes of respiration and permeation which take place in the dynamic system of produce package. Their proposed method and computer solution provided a rapid way of predicting equilibrium concentrations of 0_2 and CO_2 . Their experimental results were in good agreement with the predicted values. Hayakawa et al. (30) modified Henig and Gilbert's model and developed a new mathematical equation for simultaneous gas

exchange (transient or steady state) of a fresh produce package. They used the formulae for estimating the O_2 and CO_2 concentrations at equilibrium state plus the time values needed to obtain these concentrations in fresh tomato or banana packages. In the case of time values and O_2 exchanges, the estimated and experimental values were in fair agreement. However, great differences were observed between the estimated and the experimental values for CO_2 exchanges.

Deily and Rizvi (14) developed analytical formulae for simulating transient and equilibrium state gas concentrations of fresh peaches packaged in polymeric films which could also be solved for optimization of packaging parameters. They found a good agreement between experimentally determined time values for concentrations of O_2 and CO_2 and those calculated using analytical formulae. They also checked the validity of the derived equations by developing retail packages of various polymeric films which had different O_2 and CO_2 transmission rates. However, optimum packages could not be created since polymeric film meeting the calculated O_2 and CO_2 transmission rates was not commercially available.

One other example of optimization of in-package gas concentration is the work of Prince (46) who utilized simple mathematical equations describing the respiration rate and film permeability to predict equilibrium O_2 and CO_2 concentrations in a tulip bulb package and verified the predictions by packaging trials. Also, Cameron et al. (10) achieved optimum O_2 and CO_2 concentrations in packages of ripe tomatoes by using CO_2 scrubbers. However, they could not match storage life in flow through system. None of the mathematical models developed for MAP systems to date has comprehensively considered all the interactive factors which affect the performance of MA packages of fresh produce (72).

Humidity Factor in Produce Packaging

Most polymeric films utilized in MAP have low water vapor transmission rates relative to transpiration rates of fresh produce. This difference in rates leads to nearly saturated conditions within packages (22, 27, 55). The high in-package relative humidity (IPRH) can favor microbial spoilage and/or cause condensation which limit the usefulness of MAP for extending the shelf life of produce. A variety of approaches have been taken to overcome these problems.

Aseptic processing and packaging of fresh tomatoes has been discussed (48). Possible drawbacks of this approach might include the high investment and operation costs. Ionizing radiation has a potential in controlling decay of fruits in storage (61). However, when applied to packaged produce, may lead to an intensified monomer migration. The workers safety problem and consumption reluctance should also be considered. Modified atmospheres containing above 10% CO2 and below 1% 0_2 have significantly suppressed fungal growth in some occasions (16). However, the opposite has also been observed (11). Generally, high levels of CO_2 should only be used with commodities which can tolerate such levels. Carbon monoxide has been utilized in an attempt to inhibit yeast and mold growth on packaged fruits and vegetables. It has been shown that atmospheres with 5-10% CO and less than 5% O_2 are effective in controlling fungal growth, however, careful use of such atmospheres is a must since CO is very toxic to humans (16). Packages of fresh strawberries and nectarines have also been flushed with one or a

combination of preservative gases in an attempt to inhibit bacterial growth with some success (42). Ethanol vapor has been utilized in sealed food packs to inhibit bacterial growth and prolonging shelf life (18). Sorbates have been used successfully to control benzimidazoleresistant Penicillium on citrus fruits (51).

Fungicides have been in use to control mold development on fresh produce since the 1950's (17, 32). However, their use has not been satisfactory since; 1) they are most of the time partially effective, if at all; 2) in some cases they have caused problems of their own (19, 49); 3) there are health concerns; and 4) they do not control bacterial development which can also be associated with high humidity (49).

Another alternative for control of condensation and microbial decay would be to reduce RH within the package. Effects of relative humidity on decay and postharvest life of fresh fruits and vegetables have been discussed (23, 68). High RH may either increase or decrease decay depending on the produce. This contradictory physiological response to high RH can be attributed in part to the fact that commodities have different transpiration coefficients (40) and that fresh produce items have different water potentials (12). Humidity approaching or reaching 100% can be detrimental to onions, potatoes, sweet potatoes, citrus, tomatoes, and soft fruits such as plums (27). In the case of tomatoes in particular, it is reported that decay in storage is directly related to humidity levels and that infection and rotting are increased markedly by storage at high RH (23, 64).

Variability among pathogens with respect to their water activity requirements has also a bearing on decay development on the produce (66). Obviously, growth of a pathogen in contact with the surface of a

fruit or vegetable (i.e., host) will take place only if its intrinsic water potential is lower than those of the produce items or the environment surrounding both pathogen and the host. Therefore, limiting the availability of water in the environment through regulation of humidity can retard or prevent the growth of microorganisms and, thereby the development of decay. The recommended levels of RH for storage of fresh produce represent a balance between desiccation of the commodity by low humidity on the one hand and increased decay by high humidity on the other (29).

Perforation of the packages has been used to reduce IPRH (25, 36). However, unless the perforation size can be very carefully controlled, they eliminate the formation of a desirable modified atmosphere within the package. Calcium chloride has been employed to reduce IPRH and control microbial decay and/or condensation problem (15, 55). Use of $CaCl_2$ for the control of mold development in fresh produce packages has been incorporated into a patent recently (7). However, $CaCl_2$ is a desiccant which establishes an equilibrium RH of 31 to 40% when kept in confined spaces at temperatures between 5 and $25^{\circ}C$ (70). This is far below the recommended RH levels for storage of fresh produce.

Development of a secure method for the control of humidity in produce packages using sorbents requires a good understanding of the mechanisms involved in the sorption of moisture. Hereunder, a brief review of the interactions between water and sorbent materials will be presented.

Physical Adsorption: General Considerations

Adsorption processes have been the subjects of interest for several decades (1, 9, 13, 21, 39, 44, 52, 58). The term adsorption refers to a

process involving attachment of gases, liquids, or dissolved substances to the surfaces of solids. The adsorbents do not go through a physical phase change. Absorption connotes penetration of a substance into the body of another followed by a change in the physical state of the absorbents (9, 70). Although the term sorption can be used to embrace adsorption and absorption the designation adsorption is frequently employed to denote uptake in general (21).

Surface of an actual solid

Solids have a fixed shape and volume since their individual units are firmly bound together such that there is little freedom of translational motion (38). The surface of solids are often extremely uneven. Various kinds of imperfections, including cleavage steps and dislocations are formed in the surface of a solid as a result of variability in preparation processes.

The details of preparation of a solid considerably affect the crystal habit and with it the proportion of different crystal faces (planes) exposed. Thus solids may end up with two or more crystal faces exposed. Crystal planes have different surface free energies (1). With this in mind, variation in crystal habit and the presence of imperfections invariably produce energetically heterogeneous surfaces. Therefore, the state of the surface of a solid is best considered in terms of distribution of site energies, each of the minima being regarded as an adsorption site (21).

Origin of the Sorption Forces

The average number of atoms or molecular neighbors at the surface of solids is only half as great as underneath it. Therefore, there is an unbalance of forces at the surface, and a marked attraction of the

surface toward atoms and molecules in its environment. A greater attraction among surface atoms results in the establishment of stronger bonds and closer distance between them compared with atoms underneath the surface. The surface tension which emerges in this process, is the energy of cohesion per unit area and peculiar to each compound. The attraction forces at the surface of a solid (or liquid) are merely the extensions of the forces of cohesion within the body of the material (44).

The unbalanced attraction forces at the surface of a material (sorbent) can be neutralized by the attachment (sorption) of atoms or molecules of another species (sorbate). Sorption is brought about by the forces acting between the individual sorbate molecules and the atom or ion composing the solid. These interacting forces, also referred to as the heat of adsorption (13), are similar to the van der Waals forces which produce condensation in liquids and their magnitude is usually less than 4 kcalories per mole (1). These forces include dispersion (i.e. attractive, together with short-range repulsive) and electrostatic forces (if the solid and/or the sorbate are polar in nature). These attraction forces arise from the rapid fluctuations in electron density within each atom, which induces an electrical moment in a near neighbor and thus leads to attraction between the two atoms (21).

The sorption of water reduces surface tension of the compound and continues until the surface free energy of the compound reaches a minimum (44). That is, during sorption by dry chemicals, water molecules neutralize some unfilled forces of attraction of the compound during condensation and concomitant release of energy (heat of liquefaction). In this process, some of the cohesion bonds in the solid

break apart, opening way for penetration of water molecules into the solid. For instance, in the case of dry sugar, at high humidities, the overall net water-sugar interaction reaches a level enough to cause sugar-sugar dissociation. At this point, water begins to penetrate into the crystal and dissolves sugar molecules which causes new surfaces to be exposed for further interaction (39).

When ionic sorbents are present the electric potential at the surface of the sorbent induces specific orientations in water molecules which carry permanent moments and leads to a very strong interaction between water and the polar groups of the sorbent (58).

Type III Isotherms

Sorption is most generally described in terms of isotherms which show the relationship between the pressure of the sorbate gas and the amount of gas sorbed at a constant temperature. The contour of a complete isotherm, from zero pressure to saturation, depends upon a number of factors including the nature of both the sorbent and the sorbate, the pore structure and the specific surface $(m^2.g)$ of the sorbent (38, 44, 52). Isotherms in physical adsorption have been grouped into five major Types (9). This classification is sometimes referred to as the BET classification. A stepped isotherm designated as Type VI has also been of theoretical interest (21).

Type III isotherm is much less common than other types in BET classification (9, 21). A few compounds have been shown to exhibit Type III sorption isotherm behavior including sucrose and some proteins (33), xylitol (3,), and NaCl (37). This type of isotherm characterizes weak interaction between a gas and a nonporous or macroporous solid (21) which possesses a homogeneous surface (58). It occurs only when the forces of monomolecular adsorption are small (44). Its occurrence also requires that the heat of adsorption of the first layer (i.e. sorbentsorbate interaction force) be in the same order of magnitude as (13, 58) or smaller than (9, 52) the heat of liquefaction (i.e. sorbate-sorbate attraction).

In the systems giving rise to Type III isotherms, the uptake of water is small at low pressures due to the weakness of water-solid attraction forces. However, once the monolayer sorption is completed, the water uptake behavior changes drastically due to hydrogen bonding among water molecules. As vapor pressure increases beyond this point, a considerable increase in the water content of the sorbent takes place as a result of the attachment of water chains of indefinite length to the first layer. This change takes place once a critical vapor pressure is reached. These mechanisms together give a parabolic shape to the isotherm (i.e. convex to the pressure axis), suggesting a humistatic potential to be associated with such sorbents.

The reduction of number of water molecules as a result of adsorption in a finite environment depresses vapor pressure which can be measured in terms of RH. In a produce package made of a good water vapor barrier, the extent of this depression is principally determined by the rates of two interacting processes of produce transpiration and water sorption by the compound. When these rates reach a lasting steady state for a period of time, the RH within the package remains stable for that period.

The ability to create a stable RH in optimized produce packages within the recommended levels would be valuable for improving the success of MAP systems. So far, a method capable of achieving this

desired feature has not been available. In the following study a new concept for regulation of RH within packages of fresh produce is presented utilizing the unique water ad/absorption properties of compounds exhibiting the Type III sorption isotherm.

The purpose of this study was to demonstrate that RH can be controlled in packages by compounds possessing Type III sorption isotherm behavior and to test effectiveness when combined with MAP systems.

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CHAPTER 1

MODIFIED HUMIDITY PACKAGING A NEW CONCEPT FOR EXTENDING THE SHELF LIFE OF FRESH PRODUCE

INTRODUCTION

Polymeric films have been used to prolong the storage life of fresh produce by reducing the rate of water loss and by providing modified (2,4,13,19,26,29,30). Modified atmosphere conditions atmosphere packaging (MAP) can be used as a supplement (13) or even a substitute for refrigeration during transport and retail (8) handling of horticultural products. Polymeric films utilized for MAP invariably have low water vapor transmission rates relative to transpiration rates of fresh produce which invariably leads to nearly saturated conditions within packages (6,15,16,27). Condensation and/or microbial decay are often associated with high in-package relative humidity (IPRH) and limit the practical application of MAP for prolonging storage life of fresh produce.

Fungicides have been used in an attempt to control mold development in produce packages (5,20). However, in most cases, they have been only partially effective if at all and, in some cases, have caused problems of their own (14,26). Fungicides incorporated directly into films also have not been fully effective (7). Furthermore, fungicides do not control bacterial development which can also be associated with high humidity (26).

Another alternative to reduce microbial spoilage and/or condensation problems would be to reduce IPRH. The minimum water activity requirements have been defined for a large number of microorganisms (11,28,31). For example, most of the major pathogens affecting
postharvest life of tomato fruit need an environment with an a_w of more than 0.80 for their growth (Table 1). Thus, one can logically expect that reduction of humidity to levels below the critical water activity of microorganisms should be an effective way to limit their activity. The optimum RH for storage of fresh produce has not been well established. The generally recommended levels of 85 to 95% (18) represent a compromise to prevent excessive weight loss while providing some control of microbial spoilage.

Past attempts to lower IPRH have been limited. Perforation of bags has been utilized as a means of reducing IPRH (17,21) although it should be noted that even a small number of perforations preclude the possibility of modified atmosphere conditions within the package. Desiccants such as calcium chloride have been used to lower IPRH (3,12,27) although few direct measurements have been made to determine the extent of RH reduction. Scott et al. (27) measured 67-72% RH in polyethylene packages sealed with tape containing apples with 10 g calcium chloride per fruit at 0° C. A Szulmayer probe was used to measure RH (unpublished specifications). Ben-Yehoshua et al. (6), using a hair hygrometer, measured an increase in RH from 80 to 88% (temperature not specified) over a week in bell pepper packages containing 5 g of calcium chloride per fruit. It is well established that the equilibrium RH (ERH) over saturated solutions of calcium chloride is within the range of 31 to 40% at temperatures between 5 and $25^{\circ}C$ (32). This is far below the recommended levels for storage of fresh produce.

The ability to create a stable RH within sealed packages which might reduce decay problems without causing shriveling would be valuable

for improving the success of MAP systems. Currently, no reliable method for controlled reduction of RH within fresh produce packages has been reported. A new concept for regulation of IPRH is presented in this chapter which utilizes the unique properties of water absorption by several compounds exhibiting type III sorption isotherm characteristics.

The shelf life of moisture sensitive foodstuffs has long been studied using the concept of sorption isotherm (24). The moisture content of any material approaches an equilibrium level after exposure to a given RH by gaining (ad/ab-sorption of) or losing (desorption of) water from or to the environment. The plot of equilibrium moisture content of a given compound versus ERH at constant temperature is referred to as a sorption isotherm curve. The shape of the curve depends on the nature, pore structure and specific surface of the adsorbent. Isotherms involving physical adsorption have been grouped into five classes by Brunauer (9), commonly referred to as the BET classification Compounds such as sucrose which exhibit Type III sorption system. isotherm behavior according to BET classification possess a unique character (Figure 1). Dry sucrose absorbs relatively little moisture until the RH approaches 70%. As the RH is increased from 70-80%, sucrose absorbs increasingly greater amounts of water vapor at At higher RHs, sucrose absorbs more than its own dry equilibrium. weight in water (Figure 1).

It is interesting that Figure 1 predicts that near 80% RH, additional water vapor added to the system would be absorbed by the sucrose and, if equilibrium is reestablished quickly enough, should not markedly increase the RH. This is actually similar to the concept of RH

control by saturated salt solutions which has long been used for experimental purposes.

The primary objective of this study was to demonstrate the feasibility of using predried crystals of compounds possessing Type III sorption isotherm behavior for control of RH surrounding seal-packaged produce.

MATERIALS AND METHODS

(Lycopersicon esculentum cv. Tropic or Duke) were Tomatoes harvested mature green from the Plant Science greenhouses at Michigan State University or purchased locally red ripe. The fruits were held in PE bags at 20[°]C for a minimum of 24 hours before the start of experiments to reach temperature equilibrium. Cylindrical chambers of a total volume of ca. 670 cm³ (8.3 cm height, 10.16 cm internal diameter, I.D.) were constructed from 6.4 mm clear polyacrylic materials (Figure 2). Two holes of 6.4 mm I. D. were made in the cylinder wall for probe access and headspace gas sampling. All chemicals were dried at 75°C for 48 hours before use; NaCl and KCl were analytical reagents (Mallinckrodt Chemical Works), CaCl₂ was anhydrous, either granular 8 mesh (J. T. Baker Chemical Co.) as in the 21-day long experiment or desiccant grade (Mallinckrodt Chemical Works) as in the 48-day long experiment, D-Sorbitol was anhydrous (Sigma Chemical Co.), and Xylitol was crystalline with a mean crystal size of 0.57 mm (Xyrofin LTD. Switzerland).

To initiate an experiment, tomatoes were placed in the chambers with 0 to 25 g of the desired compound depending on the experiment. The chemical of interest was spread evenly in a 100x15 mm Petri dish base around a 60x15 mm dish at the center (covering an area of ca. 50 cm^2). A fruit was placed in the smaller dish without contacting the chemical in each chamber. A piece of 0.051 mm thick low density polyethylene (LDF-301, Dow Chemical) film was held in place at the top of the chamber by two rubber gaskets for exchange of oxygen and carbon dioxide. The permeability 20⁰C 838 213 film's at was and cc.mm.m⁻².day⁻¹.atm⁻¹ for oxygen and carbon dioxide 20[°]C. at respectively (25). Water vapor transmission rate of the film was 0.81

 $g.m^{-2}.day^{-1}$ (a permeability coefficient of 20,000 cc(STP).cm.m⁻².day⁻¹) as measured at 20°C and 50% RH. A combined temperature and humidity probe (General Eastern, Model 850 with an accuracy of ± 2 % RH at 25°C within the range of 15 to 99%) was inserted above the fruit after closing each chamber. The probe was precalibrated by the manufacturer and had a sensitivity of 0.1% RH, repeatability of 0.5%, and accuracies of ± 2 % within 15-99% RH at 25°C and ± 0.5 °C within 5° to 50°C according to specifications. The performance of the probe was checked against known humidities before each experiment.

Temperature and humidity values were collected at regular intervals with a datalogger (Omnidata International, Model No. 516B-32). A simple program was written for data acquisition by the datalogger (Appendix). The actual data taken directly from the datalogger were used for construction of Figures without change. All experiments were conducted at 20° C and repeated at least 3 times with similar results unless otherwise noted.

Head space of the simulated packages was sampled at least two times for determination of oxygen and carbon dioxide content, using 1 cc plastic syringes. The gas analyzing system consisted of an Ametek Oxygen Analyzer (Model S-3A) and an ADC Infra-red Gas Analyzer (Type 225 MK3) connected in series and a strip chart recorder (Linear Instruments Corp., Model 1200). Nitrogen was used as the carrier gas at 200 ml per minute.

Several 3-day-long preliminary simulated packaging studies were performed to identify compounds capable of producing a stable RH using ca. 0.5 g of each chemical with a single red tomato or a 100-ml beaker of deionized water. Among the selected compounds, sodium chloride,

sorbitol and xylitol were previously known to exhibit Type III sorption isotherms (1,22,23). Potassium chloride and calcium chloride were found to exhibit the same behavior in the preliminary studies. An additional reason for choosing calcium chloride was the fact that it has been used to lower the humidity in produce packages (12,27). The selected compounds were used in further studies of chemical quantity to fruit ratio to explore the effect of mass on IPRH.

RESULTS AND DISCUSSION

In preliminary studies, several compounds showed potential for control of IPRH (data not shown). The selected compounds kept stable RH's when used in packaging experiments for extended times. For instance, with 10 grams of sorbitol, the IPRH was stable (ca. 80%) for the 21 days of the experiment (Figure 3). In this and most all other experiments, the IPRH in control packages without any chemical was at 99-100%.comparison, the IPRH over 10 g CaCl₂ with one tomato fruit was in the range of 30-35%.

Xylitol, KCl, NaCl, and sorbitol held IPRH at 78-79, 84-85, 73-76 and 72-74%, respectively for 48 days (Figure 4). The RH over NaCl and KCl were very similar to ERH values over their saturated solutions which are 75 and 85%, respectively (32). The IPRH over xylitol, however, was approximately 6% lower than the published ERH over a saturated solution (1).

The simulated packages used in the above experiments had not been optimized with respect to O_2 and CO_2 concentration requirements as reported for postharvest storage of tomatoes (8). Without exception, the concentration of O_2 within the packages was above the recommended levels (Table 2). Carbon dioxide concentration remained slightly above the recommended levels in 50% of the cases throughout the experiments. However, no obvious injuries were found on the fruit as a result of these relatively high CO_2 levels. Ripening of the fruit took place 2 to 3 weeks after initiation of the experiment and could have been partially responsible for the discrepancies.

The amount of each compound used affected the respective IPRH. In the case of sorbitol, very little reduction of IPRH took place when 0.01

or 0.1 g per fruit was used (Figure 5). One g sorbitol reduced IPRH to 80% initially but apparently became saturated with time since IPRH slowly increased over 3 days to approximately 90%. Five and 10 g both produced similar IPRH's near 79%. Twenty five g produced a slightly lower IPRH value initially but equilibrated about 2% lower than 5 and 10 g on the 3rd day.

Xylitol showed a similar pattern as for sorbitol (Figure 6). In this case 1 g produced a relatively stable IPRH over 3 days. The IPRH values corresponding to 5, 10 and 25 g xylitol were generally similar and about 84%.

One, 5, 10 and 25 g of KCl produced RH's within the range of 88 to 91% RH (Figure 7). With less than 1 g, no stable RH was obtained.

Little decrease was observed among IPRH's produced when 0.5 to 25 g of NaCl were used over a 3 day period (Figure 8). All of the stated levels held stable RH's within ca. 74 to 77%. No stable IPRH was obtained when 0.1 g NaCl was used.

In experiments with $CaCl_2$, 5,10 and 25 g produced largely similar results around 20 to 30% RH (Figure 9). When 1 g of $CaCl_2$ was used, RH stabilized at ca. 35% for nearly one day and then increased as saturation followed. A similar pattern was observed with 0.5 g of $CaCl_2$ although the duration of stable RH lasted only for ca. one third of a day.

Relative humidity in control packages reached nearly 100 per cent within 1 or 2 hours after sealing the package and remained at that level for the duration of the experiment. The RH of the internal atmosphere of nearly all fruits and vegetables is at least 99 per cent (18). Based on water vapor transmission rates of films and transpiration rates of produce items, it can be shown that RH in sealed packages should theoretically be more than 99 per cent (10,31). However, not all measured values by different researchers agree (Table 3). Our measured values varied from 96 to 100 per cent when different probes of the same make and model were used. However, most of the times it was 99 to 100 per cent. The discrepancies among our values and those measured by others probably reflect equipment limitations which make accurate measurement of RH greater than 95% unreliable.

The differences observed between the corresponding IPRH values in the various experiments (e.g., up to about 9% for sorbitol and 23% for $CaCl_2$) might have been due to a variety of factors including limited accuracy of humidity probes (± 2 % by specifications), intercultivar differences in the transpiration rates of tomatoes, and the details of preparation of the chemicals. Also, the transpiration rates of some tomatoes might have been different than those of others. For instance tomatoes used in the 21-day long experiment had an average weight of 95 g as opposed to 83 g in the 48-day long experiment and larger fruits might have transpired relatively more water into the package system.

Tomatoes packaged with CaCl₂ lost 9.3 and 15.5 per cent of their fresh weights over 21 and 48 days of storage, respectively. These fruits underwent severe shriveling in both experiments. No shriveling was observed in fruits in either experiments as long as they had a weight loss less than 7% (data not shown). The majority of water lost by fruits was measured as weight gain by the absorbents (data not shown).

The humidity control system described above provides a method of producing predetermined humidities within fresh produce packages in the RH range currently recommended. It was found that in-package RH can be

controlled to a specific level by the use of chemicals exhibiting sorption isotherm behavior of Type III, according to BET classification. Herein, this concept has been demonstrated using two sugar alcohols and two salts which are all among non-hazardous chemicals. Production of a particular RH in packages containing one tomato fruit was a function of the type of the chemical insert. Depending on the desired shelf life, a certain amount of the selected chemical has to be used in order to keep IPRH stable. Ten grams of all chemicals tested was found to create a stable humidity in packages containing one mature green tomato for more than 48 days and hence provide a means for control of microbial spoilage without refrigeration. Varietal differences and possibly the stage of maturity of produce may have a bearing on IPRH. Accuracy and precision of humidity transmitters may account for some discrepancies observed in the measured IPRH values. Accuracy of the units was found to conform to the specifications when tested against an electric psychrometer (± 2 % RH at 25°C, 20 to 85% RH).

Study of the kinetics of water loss by fresh produce versus water sorption by package components will pave the way for better understanding of humidity control mechanism in produce packages and for modeling of the system.

Table 1. Approximate minimum levels of water activity (a_w) which permit growth at temperatures near optimal of selected tomato fruit pathogens during postharvest storage (from Troller and Christian, 1978).

Pathogen	aw	
Bacteria		
<u>Bacillus</u> sp.	0.90-0.95	
<u>Clostridium</u> sp.	0.94-0.97	
Molds		
<u>Alternaria citri</u>	0.84	
Aspergillus niger	0.77	
Botrytis cinerea	0.93	
Penicillium expansum	0.83	
Rhizopus sp.	0.93	



Figure 1. Equilibrium moisture content of sucrose versus water activity (i.e., Water Sorption Isotherm) at 23°C (adapted from 21).



Figure 2. Chamber (simulated package) constructed from clear polyacrylic materials for controlled humidity storage studies of tomatoes.



Figure 3. In-package RH's for 21 days at 20^oC with one mature green tomato (cv. Tropic) only (control) or with 10 grams of sorbitol or .calcium chloride. Experiments were conducted in simulated packages shown in Figure 2.



Figure 4. In-package RH's for 48 days at 20° C with one mature green tomato (cv. Duke) only (control) or with 10 grams of sorbitol, xylitol, sodium chloride, potassium chloride or calcium chloride. Experiments were conducted in simulated packages shown in Figure 2.

Table 2. Oxygen and carbon dioxide concentrations in simulated packages of single mature green tomatoes containing water absorbents. The experiments were conducted at 20 °C for 21 and 48 days. Fruits used in these experiments were of the Tropic and Duke cultivars, respectively.

			Per	cent		
Absorbent	co2	°2	^{CO} 2	°2	co2	02
21-day experiment						
	7th	day	20t1	n day		
none (control)	7.1	6.3	7.8	5.8		
sorbitol	6.3	15.1	6.4	16.7		
CaCl ₂	2.7	18.6	2.3	20.0		

48-day experiment

	6th	day	30t1	h day	_47tl	h day ^z
none (control)	5.8	13.0	9.4	9.0	7.5	9.4
sorbitol	2.3	20.2	3.1	18.3	1.8	18.8
xylitol	5.4	14.8	7.1	13.5	5.1	14.7
NaC1	4.5	16.7	5.1	16.0	3.4	17.2
KC1	7.6	8.6	9.8	7.2	7.2	10.8
CaCl ₂	5.0	15.3	7.0	13.7	4.7	16.0

^ZStorage temperature dropped to 17.5°C and then rose to 33°C during the last 24 hours due to technical problems.



Figure 5. In-package RH as a function of the amount of sorbitol added with a single red tomato fruit. Experiment was conducted at 20° C for 3 days. Experiments were conducted in simulated packages shown in Figure 2.

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Figure 6. In-package RH as a function of the amount of xylitol added with a single red tomato fruit. Experiment was conducted at 20° C for 3 days. Experiments were conducted in simulated packages shown in Figure 2.



Figure 7. In-package RH as a function of the amount of KCl added with a single red tomato fruit. Experiment was conducted at 20° C for 3 days. Experiments were conducted in simulated packages shown in Figure 2.



Figure 8. In-package RH as a function of the amount of NaCl added with a single red tomato fruit. Experiment was conducted at 20° C for 3 days. Experiments were conducted in simulated packages shown in Figure 2.



Figure 9. In-package RH as a function of the amount of CaCl₂ added with a single red tomato fruit. Experiment was conducted at 20° C for 3 days. Experiments were conducted in simulated packages shown in Figure 2.

Produce	KH	Measurement Temperature	conditions Device	Film type	Ref.
		°C			
Apples	96-98	0	Szulmayer	1.5-Mil PE	35
Bell Peppers	67	0 & 17	Hair Hygrometer	HDPE ^z	9
Cucumbers & Lima Beans	98-100	10 & 20-27	Elec. Hygrometer	Cellophane & Pliofilm ^z	20
Oranges	100	4 & 21	Honeywell W809	PE ^z	17
Tomatoes ^y	69-1 00	20	Gen Eastern 850	2-Mil LDPE	

Table 3. Relative humidity measured in various fresh produce packages.

^zThickness not reported.

^yPresent study.

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CHAPTER 2

A METHOD FOR MEASURING TRANSPIRATION RATES OF SMALL FRUITS AND VEGETABLES

INTRODUCTION

The loss of moisture due to transpiration reduces the salable weight and ultimately the quality of fresh produce during postharvest storage and handling. In addition, the increased water vapor in the storage environment can affect refrigeration requirements. Thus, there has been an interest in measurement and characterization of transpiration rates of horticultural products (1 - 7).

A review of the literature indicated that there were very few detailed studies on transpiration and that published values were often conflicting. One of the problems has been a lack of reliable methodology for characterization of transpiration rates. Several different approaches have been presented (5). Yet, the most common method is to simply follow the loss of weight (which is equated with loss of moisture) versus time. It would be preferable to control both temperature and humidity and hence the vapor pressure deficit (VPD) during these experiments, but this is not always the case.

Van den Burg and Lentz (7) monitored transpiration rates by weighing a variety of produce items at 24-hour intervals on a 1 mg accuracy balance, while they were held in a constant temperature room. RH was controlled to approximately 82% by heating air saturated over ice. An obvious problem with this method is that it is time consuming and does not take into account possible structural or other changes of the produce during the course of the experiment.

A modification of this method was presented by Fochens and Meffert (3) in which an entire balance was enclosed within a chamber where humidity could be controlled. In this case, the chamber was more than 1 cu. meter and the balance was of low accuracy. Thus, there was still a limited ability to measure the effects of humidity or temperature over relatively short time intervals.

To study the effect of humidity (VPD) on transpiration, Sastry and Buffington (6) bubbled air through saturated salt solutions and then through chambers of unspecified size containing tomatoes. The fruit was weighed before and after a 24-hour treatment to measure transpiration. Thus, this method is still relatively slow and requires that various humidities be tested on different individual fruits. In addition, our experience has been that flow systems employing salt solutions require a great deal of care and at high flow rates (45 1 min⁻¹ as stated in Sastry and Buffington, 6) there can be various problems including pressure buildup and carry-over of the salts.

This chapter presents a simple modification of a weight loss method which can be used for measuring the effects of VPD and temperature on transpiration. Among the attractive features of the method is that the produce weight loss can be monitored at short time intervals on a high accuracy analytical balance. In addition, the method permits the study of the effect of a wide range of RHs on transpiration of an individual fruit.

MATERIALS AND METHODS

Unless otherwise stated, tomato fruits (<u>Lycopersicon esculentum</u>, cv. Duke) were harvested from the Plant Science greenhouses at Michigan State University. Strawberries used were purchased from local supermarkets. All fruits were held at 20°C for 24 hours in non-sealed polyethylene bags before experiments started.

The transpiration of produce was measured by monitoring weight loss for a given duration on a Mettler AE163 dual range balance with a minimum accuracy of 0.1 mg using the system shown in Figure 1a.

A small chamber was constructed from a clear, round polyethylene food container. The wider end of the chamber (I.D. 10.7 cm) fitted over the balance pan (O.D. 8 cm) within the weighing compartment. The pan was accessible simply by removing the cap from the top of the chamber.

A ring manifold was constructed from 6.4 mm copper tubing with final dimensions of 10.5 cm (0.D.) and 9.2 cm (I.D.) to fit around weighing pan within the chamber (Figure 1b). Air outlets (1.8 mm holes), spaced 2 cm apart, directed air from the manifold into the chamber.

The RH in the chamber was controlled using a water vapor generator (ADC, Type WG600). This instrument can produce a wide range of known humidities in air from essentially dryness to approximately 90% in a flow stream at approximately 400 ml.min⁻¹ by making use of the water of crystallization of ferrous sulfate. The resultant humidity depends on the flow proportions and the salt temperature. At thermal equilibrium, the humidity generated is approximately $\pm 0.3^{\circ}$ C dew point by specifications and can be changed to a new level within minutes. To achieve humidities higher than 90%, the air flow was bubbled through one

or more 2-liter mason jars containing deionized water. During the course of experimentation, RH was considered to be stable when it changed less than 0.2% per minute. This assured an RH within ± 0.5 % of the intended level during a 5-minute test.

The RH and temperature were monitored in the chamber with a small probe (Model 850, General Eastern). The probe was precalibrated by the manufacturer and had a sensitivity of 0.1% RH, repeatability of 0.5%, and accuracies of ± 2 % within 15-99% RH at 25°C and ± 0.5 °C within 5° to 50°C according to specifications. The performance of the probe was checked against known humidities before each experiment. For the purpose of consistency, the probe was always placed approximately 2 cm from upper edge of the produce item under investigation, although there was no observed effect of position of the probe placement on RH measured (data not shown).

Weight loss data were collected at 30 sec. intervals unless otherwise noted and transferred to a microcomputer (Leading Edge Model No. DC-2011) through a Mettler Option 012 Data Interface and RS232C port, using standard acquisition software. A simple computer program was developed which allowed the user to define the time interval and duration for data collection (Appendix).

The RH and temperature data were collected at 1-minute intervals and transferred initially to a datalogger (Model 516-16, Omnidata International, Inc.) and later to a personal microcomputer for further analysis. All experiments were repeated a minimum of 3 times.

The weight loss of 8 tomato fruits (purchased locally) was monitored at 45 ± 5 RH and $20\pm1^{\circ}$ C over a 35-day period by weighing. Weight loss pattern of a single tomato was investigated with the method

presented here at 51% RH and 20°C for 24 hours at 10-minute intervals. Two 30-minute experiments were also performed using the same fruit at the same temperature with slightly different RHs just before and after the 24-hour experiment.

In order to determine the optimum (shortest) run length for monitoring the fruit weight loss, linear regression was performed on the 5-, 10-, 15-, 20-, 25-, and 30-minute parts of data obtained in single experiments.

Effect of weighing frequency (interval) on the calculated rates of weight loss was studied at low and high RHs at 20° C for periods of at least 10 minutes. The weighing intervals were 10, 20, 30, and 60 seconds at 88% and 15, 30, 45, and 60 seconds at 47% RH.

Effect of bidirectionally transient humidity on weight loss pattern was investigated using a single fruit (strawberry or tomato) at 20° C. The fruit weight, temperature and RH data were monitored at 1-minute intervals for several hours during which RH in the chamber was changed back and forth between 52% and 85% (strawberries) or 47% and 84% (tomatoes).

Effects of relatively small increases in RH (levels of 28, 52, 72, and 80%) on the weight loss pattern were also studied using single tomato fruits and 20-minute duration between the changes.

To demonstrate the results of experiments using transient humidity, the weight loss data were multiplied by a factor to obtain values of comparable magnitude with the respective RHs. Then the moving mean of 5 to 7 such values was plotted along with corresponding RH versus time.

Determination of fruit transpiration rate at a given RH was initiated by adjusting vapor pressure of the air stream. After 10 minutes, or as soon as the change in RH reached a maximum of 0.2% per minute, data collection was initiated and continued for a minimum of 5 minutes. The rate of weight loss was calculated using standard regression technique. The surface area of tomatoes was calculated using the fruit weight and the equation developed by Sastry and Buffington (1983). Average temperature and RH values were used to calculate VPD for each experiment.

Permeability of fruit was calculated using the following relationship (2):

$$P = J/(A \cdot \Delta C)$$

where,

- $P = Permeability, cm.hr^{-1}.kPa^{-1}$
- $J = Flux, cm^3.hr^{-1}$
- A Surface area, cm^2
- ΔC = Concentration gradient, i.e., vapor pressure deficit, kPa.

RESULTS AND DISCUSSION

Weight loss patterns of locally purchased tomatoes studied by conventional weighing method followed a slightly decreasing trend over an extended period of 19 days in a controlled temperature room at 20° C and 45 ± 5 RH (Figure 2). However, when the results were subjected to a linear regression analysis, r² values for all fruit were higher than 0.99 (Table 1). The pattern of weight loss remained unchanged for as long as 35 days provided the fruit did not lose its integrity during the experiment. Transpiration rates of the fruit did not relate to the weight or surface area (r²=0.18) and varied from 1.32 x 10⁻⁴ to 1.97 x 10^{-4} ml cm⁻² s⁻¹ (cv=17.2%). Larger variability (\pm 50%) has been observed by others (7) in transpiration of individual potatoes and onions of a given size and variety.

A similar pattern was observed for the fruit weight loss over periods of 24 hours using the present system (Figure 3). The average rate of weight loss of a single fruit was 1.32×10^{-3} and 1.30×10^{-3} g.min⁻¹ during 30-minute experiments performed at the same temperature with slightly different RHs just before and after the 24-hour experiment, respectively. Transpiration rates of individual fruits of the same variety weighing 137 and 123 grams measured at the same temperature but at 51 and 40% RHs were found to be largely different and were 1.76×10^{-4} and 8.22×10^{-5} mg cm⁻² s⁻¹. The corresponding permeabilities were 7.39 $\times 10^{-1}$ and 2.82 $\times 10^{-1}$ cm.hr⁻¹.kPa⁻¹, respectively. However, transpiration rates of the same individual fruit were found to be very close at 8.22×10^{-5} and 7.96 $\times 10^{-5}$ mg cm⁻² s⁻¹

kPa⁻¹) under the same conditions but 5 and 7 days after harvest, respectively. This corresponds to a 3% drop.

Calculated rates of weight loss for a single tomato fruit from successively longer run lengths (i.e., multiples of 5 minutes) extracted from a 30-minute run were very similar (Table 2). The rates had a coefficient of variation of 0.3%. All of the regression coefficients (r^2) were higher than 0.99.

Weight loss rates of a single fruit at 47% RH (20° C) at all data collection intervals down to 15 seconds were very similar (Figure 4a). Coefficient of variation among the rates was calculated to be 2.6% while all respective r^2 values were higher than 0.99 (Table 3). Under conditions of low transpiration rates, however, short intervals on the order of 10 seconds were not suitable since the sensitivity of the balance was not sufficient for the interval (Figure 4b). For example, at 88% RH and 20° C when a 10-second interval was used, the rate of water loss was less than could be measured by the balance. The coefficient of variation in calculated slopes in high humidity runs was 3.4% (Table 4). It should be noted, however, that in all cases, the regression coefficient (r^2) was 0.99 or higher and probability was less than all tabulated levels.

No evidence suggests that there is a real difference in the effect of either the run length or the time interval on the calculated rates of weight loss. On this basis, and to save time for data collection, the duration of experiment (run length) was chosen to be 5 minutes. In order to obtain a reasonable number of data points (about 10) in each experiment, an interval of 30 seconds was chosen.

According to the output from the RH probes, the transition from 52% to 85% RH in the weighing chamber took about 60 minutes before a stable RH was obtained. It took 25 minutes to reach a change of less than 0.2% RH per minute during transition from 52 to 85% RH and about 100 minutes in the reverse direction (40 minutes to a change of less than 0.2% RH per minute) (Figure 5). However, the rate of weight loss from individual strawberry fruit re-equilibrated in approximately 10 minutes, as calculated by change in weight over one-minute time intervals. In fact, there was a significant drop in the rate of weight loss measured in the first minute after the RH in the flow stream was altered. Similar results were obtained with tomatoes (Figure 6). However, the time to reach equilibrium required for tomato was slightly shorter than the time required in the strawberry experiment. Note that chamber volume (760 cu. cm) was approximately two times the rate of flow per minute (ca. 400 ml/min). This should provide one air exchange in about 2 minutes or even less when fruit volume is taken into account. That is, a minimum of five air exchanges would have taken place before a weight loss determination experiment started.

These data would suggest that the humidity probes did not rapidly equilibrate with the RH in the chamber. The data also suggests that strawberry weight loss is largely linear using one-minute intervals.

Less time was generally required for equilibration during shorter RH shifts to higher levels. The RH probes needed about 10 minutes to equilibrate while the rate of weight loss from individual tomato fruit equilibrated in only about 6 minutes (Figure 7). This data implies that equilibration is faster when shorter upward RH shifts are employed.
Weight loss at different humidities always followed linear patterns with highly significant regression coefficients (Figure 8). Lower humidities generally yielded higher regression coefficients, as previously discussed (Table 5). The plots of the corresponding transpiration rates in terms of g kg⁻¹ day⁻¹ and mg cm⁻² hr⁻¹ versus RH and VPD are shown in Figures 9 and 10, respectively. Both plots are largely linear with regression coefficients greater than 0.99. The permeability coefficient of the fruit used for these experiments changed from 4.12 x 10⁻¹ to 4.42 x 10⁻¹ cm.hr⁻¹.kPa⁻¹ as RH increased from 23 to 86%.

In a preliminary experiment using small sample size, 3 individual cherry tomato fruit showed different relationships between VPD and transpiration rate (Figure 11). In this experiment, the water permeability of fruit tripled as the temperature increased from 10° to 25° C (Table 6). This suggests that temperature could affect the relationship between VPD and transpiration rate. However, variability among individual fruit was encountered in another experiment. That is, the relationship between VPD and transpiration rate for 3 regular size tomato fruit at nearly equal temperatures was different (Figure 12). These fruit were found to be more than 2 times different in water permeability (Table 6). Therefore, the effect of temperature on the relationship between VPD and transpiration rate of tomato fruit is not certain but merits further study.

A common aspect of plots of transpiration rates versus RH or VPD was that they always extrapolated to a positive transpiration rate at an apparent VPD of zero (RH-100%). One possible cause for this residual transpiration is the heat generated as a result of respiration.

Weight loss pattern of tomatoes determined by this method is similar to that obtained in the more time-consuming conventional studies. The rapidity of the method makes possible collection of a . considerable volume of useful data in a relatively short time. The method takes advantage of improved accuracy in weighing (0.1 mg over 0-160 g, and 0.01 mg over 0-30 g) and new technology for control of RH in an air flow system. The method has a high precision and works within wide ranges of humidity values (ca. 0-90% RH) and temperature (10° -45°C). With this method it is possible to study the response of a single fruit to both steady and relatively fast changing conditions. The method is highly flexible in controlling the conditions as well as in setting the duration and interval of monitoring the weight loss. The method is also potentially useful in study of water sorption by a large number of materials.

Short upward RH shifts (e.g., 10% RH increments) are recommended for faster equilibration. Intervals of 30 seconds or more are recommended when low transpiration rates are involved. A minimum of 10minute waiting time is advisable between the changing of RH and the monitoring of produce weight change. Some modifications in design of the system would be required if the study of transpiration of larger produce items is desired.



Figure 1a. A system designed for monitoring the change in weight of small fruits and vegetables at various humidities. The components are a microcomputer, a datalogger, a vapor generator, a humidity and temperature transmitter, and a high accuracy balance equipped vith humidity control system.



Figure 1b. A close-up of the weighing chamber of the balance equipped with humidity control system.



Figure 2. Weight loss of red tomatoes at $45\pm5\%$ RH and 20° C as determined by conventional weighing over a period of 19 days. The data was generated from 5 individual fruit with a range of initial fresh weights. Line shown are best fit equations obtained by linear regression analysis at 0.05 level (See table 1).

Table 1. Best fit line parameters for the weight loss data of five red tomato fruit obtained by linear regression analysis at 0.05 level. All weight loss data were collected at 45 ± 5 RH and 20° C by conventional weighing over a period of 19 days. Fruit weight is reported to the nearest gram (See Figure 2).

Fruit g	Intercept g	Slope mg.min ⁻¹	r ²
140	139.7306	-1.2561	0.999
135	134.3508	-1.0106	0.998
128	127.1727	-0.9543	0.999
125	124.4173	-1.4005	0.998
112	111.8583	-1.1723	0.999



Figure 3. Weight loss of a single red 137-gram tomato fruit (cv. Duke) at 49% RH and 20° C. Data were collected at 10-minute intervals over a 24 hour period.

Table 2. Effect of run length on rates of water	loss (calculated
from weight loss) of a single red 137-gram tom	nato fruit (cv.
Duke). All weight loss data were collected a 20° C using a 30-second interval. r^2 and calculated by linear regression analysis at 0.0	at 52.5% RH and F values were D5 level.

Run length minutes	Rate of loss ml H ₂ O.hr ⁻¹	r ²	F Value
5	119.92	0.99951	18358
10	120.64	0.99982	105537
15	120.56	0.99994	483304
20	120.72	0.99996	974961
25	120.88	0.99997	1633284
30	120.96	0.99998	2949941



Figure 4a. Weight loss of a 139-gram red tomato fruit (cv. Duke) at 47% RH and 20° C measured at 15-, 30-, 45-, and 60-second intervals over 10-minute periods. All data were collected from a single fruit in less than 1 hour. Best fit line data are shown in Table 3.

Table 3. Effect of interval length on rates of water loss (calculated from weight loss) of a single red 139-gram tomato fruit (cv. Duke). All weight loss data were collected at 47% RH and 20°C using a 30-second interval. The entire run length in all cases was 10 minutes. r^2 and F values were calculated by linear regression analysis at 0.05 level (See Figure 4a).

Interval seconds	Rates of loss ml H ₂ O.hr ⁻¹	r ²	F Value
15	93.07	0.9998	174965
30	90.50	0.9999	169983
45	88.10	0.9999	127896
60	88.18	1.0000	



Figure 4b. Weight loss of a red 122-gram tomato fruit (cv. Duke) at 88% RH and 20° C measured at 10-, 20-, 30-, and 60-second intervals over 10-minute periods. All data were collected from a single fruit in less than 1 hour. Best fit line data are shown in Table 4.

Table 4. Effect of interval length on rates of weight loss of water loss (calculated from weight loss) of a single red 122gram tomato fruit (cv. Duke). All weight loss data were collected at 88% RH and 20° C using a 30-second interval. The entire run length in all cases was 10 minutes. r^2 and F values were calculated by linear regression analysis at 0.05 level (See Figure 4b).

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Interval seconds	Rates of loss ml H ₂ 0.hr ⁻¹	r ²	F Value
10	16.27	0.9978	26759
20	15.63	0.9965	8257
30	15.95	0.9944	3374
60	16.91	0.9975	3591



Figure 5. Effect of bidirectional change in humidity on the rate of weight loss of a single strawberry fruit determined at 20° C using 1-minute intervals. RH was initially 52% and was changed to 85% after one hour. The humidity was changed back to 52% two hours later. Rate of weight loss was calculated by subtraction of successive weights without averaging.



Figure 6. Effect of bidirectional change in humidity on the rate of weight loss of a single red 139-gram tomato fruit (cv. Duke). Data were collected at 20° C using 1-minute intervals. RH was initially 47% and was changed to 84% after 45 minutes. The humidity was changed back to 47% three hours later. Rate of weight loss was calculated by subtraction of successive weights and plotted as the average of five successive values.



Figure 7. Effect of short upward jumps in humidity on the rate of weight loss of a single red 130-gram tomato fruit (cv. Duke). The experiment was conducted at 20° C using 28%, 52%, and 72% RH and 1-minute intervals. Rate of weight loss was calculated by subtraction of successive weights and plotted as the average of seven successive values.



Figure 8. Weight loss of a single red 144-gram tomato fruit (cv. Duke) at a series of different humidities at 20° C. In all cases data were collected at 30-second intervals for a period of 5 minutes. The recorded weight data in each experiment were subtracted from the initial weight such that all lines could be plotted from a single intercept on the same graph. The respective best fit lines data are shown in table 5.

Table 5. Best fit line parameters for the weight loss data of a single red 144-gram tomato fruit (cv. Duke) obtained by linear regression analysis at 0.05 level. All weight loss data were collected at selected humidity levels and 20° C using a 30-second interval. The entire run length in all cases was 5 minutes. All measurements were made within a 2 hour period. The recorded weight data in all experiments were subtracted from the initial weight such that all lines can be plotted from a single intercept (0.000 gram) on the same graph (See Figure 8).

RH %	Slope mg.min ⁻¹	r ²
23	-1.2563	0.999
47	-0,8800	0.991
67	-0.6001	0.995
75	-0.4218	0.992
86	-0.2581	0.974



Figure 9. Transpiration rates of a single red 144-gram tomato fruit (cv. Duke) versus RH at 20° C. Each datapoint was calculated from regression analysis of weight loss at 30-second intervals over 5-minute duration. The data covers an RH range of 23 to 86% with a best fit line equation y = 16.1209 - 0.1548X ($r^2=0.996$).



Figure 10. Transpiration rates of a single red 144-gram tomato fruit (cv. Duke) versus vapor pressure deficit. Each datapoint was calculated from regression analysis of weight loss at 30second intervals over 5-minute duration. The data were obtained at 20° C and covers a range of 0.3 to 1.8 kPa with a best fit line equation y = 0.6304 + 0.8255X (r²=0.996).



Figure 11. Transpiration rates of 3 single cherry tomato fruit versus vapor pressure deficit. Each datapoint was calculated from regression analysis of weight loss at 30-second intervals over 5-minute duration. Each fruit was run only at one temperature (10, 17, or 25° C). The respective best fit line and permeability data are shown in Table 6.

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Fruit g	л,°с	Permeability cm.hr ⁻¹ .kPa ⁻¹	Slope mg.cm ^{-2.s-1} .kPa ⁻¹	Intercept mg.cm ⁻² .s ⁻¹	r ²
Cherry tomato fruit					
27 25	25 17	0.916 0 450	13.480 7 914	5.246 0.787	.989
18	10	0.313	7.308	-0.322	.862
Regular tomato fruit					
159	21	0.547	9.135	1.755	166.
144	21	0.439	8.255	0.630	.996
111	20	0.969	11.118	5.596	.993



Figure 12. Transpiration rates of 3 single tomato fruit (cv. Duke) versus vapor pressure deficit. Each datapoint was calculated from regression analysis of weight loss at 30-second intervals over 5-minute duration. The experiment with 111-gram fruit was run at 20° C. The other two fruit were run at 21° C. Fruit weight is reported to the nearest gram. The respective best fit line and permeability data are shown in Table 6.

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CHAPTER 3

.

MODIFIED HUMIDITY PACKAGING:

A KINETIC ANALYSIS

INTRODUCTION

Modified atmosphere packaging can prolong storage life of many horticultural commodities (2,5,10,11,13-15). Deily and Rizvi (6) developed analytical formulae for simulating transient and equilibrium state gas concentrations of produce packaged in polymeric films which could be solved for optimization of packaging parameters. However, they could not create the optimum package since the proper film was not commercially available. Boylan-Pett (3) demonstrated that desired oxygen levels can be achieved in package. However, the author could not attain the same storage life in packages that had been found in flow systems at the same oxygen concentrations due, in part, to high inpackage humidity. In fact, high humidity in the package has been found to be a recurring problem in modified atmosphere packaging or controlled atmosphere storage of many produce (1,6-8, 11, 14).

In Chapter 1, a technique was demonstrated for control of package humidity using compounds such as sorbitol, xylitol and sodium chloride which possess type III sorption isotherm behavior. However, in-package relative humidity (IPRH) was found to be a function of the ratio of quantity of compound to fruit. This was probably due to the fact that RH is at equilibrium in sorption isotherm cases, whereas in a produce package the steady state RH depends on the relationship of the relative rates of transpiration and water absorption of the system components.

The ability to develop a data base which could permit prediction of amount of chemical to add per weight of fruit to achieve predetermined

IPRH would be desirable. For this purpose, it would be necessary to measure the absolute rates of transpiration and absorption at different humidities. In Chapter 2, a method was presented which allows relatively rapid and accurate measurement of this data.

In this Chapter, an approach will be presented for kinetic analysis and development of prediction information for controlled humidity packaging as applied to tomato fruit. The information can be directly utilized for application of controlled humidity packaging systems.

MATERIALS AND METHODS

Tomatoes (Lycopersicon esculantom, cv. Duke) were harvested red ripe from the Plant Science greenhouses at Michigan State University and held in plastic bags at 20° C for a minimum of 24 hours before the start of each experiment to reach temperature equilibrium. All chemicals were predried at 75°C for 48 hours prior to use. The rates of transpiration and absorption were measured using the method described in Chapter 2.

To initiate an experiment, a single fruit or the desired amount of a chemical (weighed in a 100 ml polystyrene boat) was placed on the balance pan. Once the intended humidity reestablished (about 10 minutes), the change in weight of the sample was monitored for a total of 6 minutes at 30-second intervals. The rate of weight loss was calculated from the data using linear regression analysis.

In order to study the rates of water absorption per unit weight, a 0.5 g sample of one of several chemicals was exposed to a humidity within the range of ca. 15 to 85%. For determination of rates of water absorption at higher vapor pressures (beyond the vapor pressure corresponding to 85% RH at 20° C), 0.5 g samples of each chemical were exposed to humid air flows from 0.45 to 8.0 liter per minute. In these experiments, humidification was achieved by bubbling pressurized air through aerators in 5 two-liter bottles of deionized water connected in series. Air bubbles travelled a total water head of 100 cm before reaching the chamber through a flow meter.

The chemical mass effect on the rate of water absorption was determined by exposing 0 to 10 g samples of each compound to 85% RH. The duration of each experiment for determination of a transpiration or

water absorption rate was 16 to 20 minutes at each humidity. All experiments were conducted at 20° C and replicated 3 times.

RESULTS AND DISCUSSION

Water absorption rate pattern of sorbitol was very similar in shape to a typical Type III sorption isotherm as shown in Chapter 1 (Figure 1). The rate of water absorption of sorbitol was less than 50 mg.hr⁻¹.g⁻¹ at humidities less than 75%. As the relative humidity increased from near 80 to 90%, the rate of absorption underwent a shift and increased by almost 8 fold which infers a capacity to absorb up to almost 40% its weight of water per hour. It was not feasible to attain humidities higher than 90% using the present system, partially because the compound absorbed the water so quickly. The rate of absorption was nearly 0.4 g H₂0.hr⁻¹ per gram of the compound at 90% and 20°C, which amounts to nearly 500 cc H₂0 vapor per hour.

Similar patterns were exhibited by xylitol , NaCl and KCl. Xylitol absorbed less than 10 mg.g⁻¹.hr⁻¹ at 75% RH and lower (Figure 2). As RH increased from 80 to 90%, the rate of water absorption by xylitol increased from ca. 10 to 200 mg.g⁻¹.hr⁻¹. This corresponds to a 20-fold increase in water absorption which equalled 20 to 25% of its weight per hour. NaCl showed almost the identical rate and pattern of water absorption as xylitol (Figure 3). KCl had much lower rates of water absorption or only 8% of its weight per hour (Figure 4). For KCl, the RH at which there was a shift in the rate of water absorption was around 85%.

The pattern of water absorption rate of $CaCl_2$ was different from those of other chemicals (Figure 5). Water absorption was detectable at the lowest humidity tested (11% RH). The rate of absorption was essentially constant between 25 to 45% RH and equalled almost 60 mg.g⁻¹.hr⁻¹. The rate of absorption increased substantially as RH

increased over 50%. At RH's around 80%, the rate of absorption reached a maximum of 0.7 $g.g^{-1}.hr^{-1}$ which amounts to 65% of its weight of water absorbed per hour. The absorption rate of CaCl₂ surpassed those of all other compounds and would be expected to increase even more if RH could have been increased over 85%.

The total water absorption rate of sorbitol increased with an increase in mass of the chemical during constant exposure to 85% RH (Figure 6a). However, this increase in rate of absorption did not follow a linear pattern with weight of sorbitol added. The unit absorption rate showed a relative decrease from ca. 177.4 to 6.5 mg $H_20.g^{-1}.hr^{-1}$ for 0.06 and 10.1 g of sorbitol, respectively (Figure 6b).

The total water absorption rates of xylitol followed a pattern similar to that of sorbitol (Figure 7a). A relative decrease of 31.8 to 3.6 mg H_2O . g⁻¹ hr⁻¹ occurred in the unit absorption rate when 0.5 and 10 g of xylitol were used, respectively (Figure 7b).

A nonlinear relationship was also observed between the mass and the corresponding total water absorption rates for NaCl (Figure 8a). The unit absorption rate showed a relative decrease of 23.5 to 2.5 mg H_2O . g^{-1} .hr⁻¹ when 0.5 and 10.1 g of NaCl were used (Figure 8b).

KCl had relatively slow total water absorption rates at 85% RH, compared to other chemicals tested (Figure 9a). The unit water absorption rates of KCl followed a nonlinear pattern when more compound was added (Figure 9b). The unit rate of water absorption dropped from 11.3 to 1 mg.g⁻¹.hr⁻¹ as the amount of KCl added was increased from 0.5 to 10 grams.

CaCl₂ absorbed more water than all other compounds at all weight levels, although the pattern of total water absorption rate versus chemical mass was not different than the other four chemicals tested (Figure 10a). The unit absorption rate underwent a relative decrease from 977.4 to 23 mg $H_2O.g^{-1}.hr^{-1}$ when .05 and 10.1 grams of the chemical were used, respectively (Figure 10b).

The rate of of water absorption by all of the compounds tested kept increasing as 0.5-gram samples of each were exposed to higher humidities. The relationship between the rate of absorption of water and the RH closely resembled a Type III sorption isotherm curve for the tested chemicals. In the case of $CaCl_2$ the pattern was more similar to a stepped isotherm curve. All of the tested compounds were able to quickly absorb water while exhibiting a hyperbolic pattern similar to the Type III sorption isotherm. Such a desirable characteristic makes their use possible as humidity buffers.

Though capable of buffering humidity right around 30% as shown in Chapter 2, $CaCl_2$ behaves differently than the Type III isotherm compounds: 1) it absorbs water even at low humidities and 2) its absorption rates are drastically higher than those of others. This is due to the fact that $CaCl_2$ has a much higher heat of absorption. $CaCl_2$ bonds water energetically and, therefore, may drive water forcibly out of the produce and cause shriveling. In fact $CaCl_2$ is classified as one of the efficient drying agents (16).

The water absorption rate was found to vary with chemical structure of the compound. In general, the magnitude of the absorption rate was inversely related to that of the RH produced in presence of each compound in a closed package environment (Chapter 1). The difference in crystal and chemical structures of the compounds could account in part for the observed differences in the respective water absorption rates

and IPRH's. The crystals of sorbitol and xylitol are of needle and monoclinic shape, respectively, whereas NaCl and KCl are cubic crystals (15). NaCl has some advantages as a better humidity buffer since it absorbs more rapidly than KCl and it is nonfermentable and less costly than the sugar alcohols. KCl had the lowest water absorption rates among the chemicals tested, which might have been expected since it was associated with the highest IPRH in tomato packages (Chapter 1). Variations in processing and preparation of a chemical may also affect its pore structure and surface extent and thereby, the water absorption properties. For example, "the porous granular calcium chloride ...is a more rapid and more efficient desiccating agent than the fused salt... At 25°C, the vapor pressure of the fused salt is 0.35 mm and of the granular 0.14-0.25 mm" (4).

The water absorption rates of all the compounds increased in a nonlinear fashion as larger amounts of each were exposed to the same humidity (Figures 6a-10a). Logically, a linear trend is expected. The data obviously is bound to the limitation of the system. The water absorption rates on a unit basis decreases progressively in a hyperbolic fashion with increasing weight of the compounds (Figures 6b-10b). This is due to the fact that relatively fewer absorption sites were rendered available as larger mass of each chemical were placed in the same size containers for experimentation. It is obvious that dispersion pattern and contiguous area between compounds and water vapor are of cardinal importance in the absorption process and thus merit further studies.

A typical interaction between water absorption rates of chemicals and transpiration rates by produce can be seen in Figure 11. Here, the rates of water absorption by one gram of each sorbitol and CaCl₂ have been coplotted with the rates of transpiration by a 125-gram red ripe tomato versus RH. The points of intersection predict that the IPRH produced in a package containing a single tomato would be ca. 70% or 25% if 1 g of sorbitol or $CaCl_2$ were added to the same tomato package, respectively. The data compares reasonably well with those obtained in a previous study (see Chapter 1). This modeling technique provides a feasible means for prediction of humidity in modified humidity packages as well as a sound basis for developing a data base which can provide information as to the right proportions of package components, once the desired shelf life and IPRH are known.



Figure 1. Water absorption rates of 0.5-gram-samples of dried sorbitol versus relative humidity at 20° C. Each point represents a single run using 30-second intervals over five minutes at given RH.



Figure 2. Water absorption rates of 0.5-gram-samples of dried xylitol versus relative humidity at 20° C. Each point represents a single run using 30-second intervals over five minutes at given RH.



Figure 3. Water absorption rates of 0.5-gram-samples of dried NaCl versus relative humidity at 20° C. Each point represents a single run using 30-second intervals over five minutes at given RH.


Figure 4. Water absorption rates of 0.5-gram-samples of dried KCl versus relative humidity at 20° C. Each point represents a single run using 30-second intervals over five minutes at given RH.



Figure 5. Water absorption rates of 0.5-gram-samples of dried CaCl₂ versus relative humidity at 20° C. Each point represents a single run using 30-second intervals over five minutes at given RH.



Figure 6. Effect of 0.06 to 10.1 grams of sorbitol on (a) the total rate of water absorption and (b) the unit absorption rate (i.e., expressed as rate of absorption per mass of sorbitol added). Each point represents a single run using 30-second intervals over five minutes at 85% RH and 20° C.



Figure 7. Effect of 0.52 to 10.0 grams of xylitol on (a) the total rate of water absorption and (b) the unit absorption rate (i.e., expressed as rate of absorption per mass of xylitol added). Each point represents a single run using 30-second intervals over five minutes at 85% RH and 20° C.



Figure 8. Effect of 0.5 to 10.1 grams of NaCl on (a) the total rate of water absorption and (b) the unit absorption rate (i.e., expressed as rate of absorption per mass of NaCl added). Each point represents a single run using 30-second intervals over five minutes at 85% RH and 20° C.



Figure 9. Effect of 0.5 to 10.0 grams of KCl on (a) the total rate of water absorption and (b) the unit absorption rate (i.e., expressed as rate of absorption per mass of KCl added). Each point represents a single run using 30-second intervals over five minutes at 85% RH and 20° C.



Figure 10. Effect of 0.05 to 10.8 grams of $CaCl_2$ on (a) the total rate of water absorption and (b) the unit absorption rate (i.e., expressed as rate of absorption per mass of $CaCl_2$ added). Each point represents a single run using 30-second intervals over five minutes at 85% RH and 20°C.



Figure 11. Simultaneous plot of the transpiration rate of a 125-gram tomato fruit (cv. Duke) and the water absorption rates by one gram of sorbitol or $CaCl_2$ placed in a package at $20^{\circ}C$.

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SUMMARY AND RECOMMENDATIONS

SUMMARY AND RECOMMENDATIONS

The present work has demonstrated the feasibility of controlling humidity within fresh produce packages to recommended levels taking novel advantage of compounds exhibiting Type III sorption isotherm behavior. A relatively small amount of chemical is required in order to keep IPRH stable for extended periods with tomatoes. For example, ten grams of each tested compound kept the RH stable within a package containing a mature green tomato (<u>Lycopersicon esculentum</u> cv. Duke) for an extended period of 48 days. However, there is a lower limit of how much compound is needed and experiments were developed to investigate the relationship.

The study of moisture relations of fresh produce has been limited in the past by lack of good techniques. In Chapter 2, a method for studying the transpiration of small fruits and vegetables was presented. The method is rapid, accurate, precise, flexible, and works within wide ranges of humidity and temperature. The method is also potentially useful in study of water sorption by a large number of materials. The weight loss pattern of tomatoes determined by this method was slightly nonlinear and similar to that obtained in time consuming conventional studies.

Using this method, a series of kinetic studies were conducted which showed, except for $CaCl_2$, that the relationship between the rate of water absorption and the RH closely resembled a Type III sorption isotherm curve for the tested chemicals. Such a desirable characteristic makes their use possible as humidity buffers. $CaCl_2$, known as a desiccant, exhibited a water absorption rate pattern similar

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to a stepped isotherm curve with much higher water absorption rates than other tested chemicals, which increased the rate of shriveling.

The method indicated that the rates of absorption by chemicals could be very rapid in the range of ratio weights studied. The water absorption rates of all the chemicals increased in a nonlinear fashion as larger mass of each was exposed to the same humidity. The physical limitation in uniform dispersion of larger amounts of the chemicals probably plays an important role in setting this nonlinearity.

An extension of the research presented in Chapter 3 could provide information to be used for predicting successful package combinations as to the weights of both produce and absorbent. The introduction of modified humidity packaging opens ground for research on a variety of subjects such as the following:

- A comprehensive list of humistats can be put together by characterization of compounds (preferably nonfermentable), including natural and synthetic polymers.

- Transpiration rates of many horticultural commodities can be measured over wide ranges of humidities and temperatures using the method presented in Chapter 2. It is also possible to study the response of many small single fruits or vegetables to both steady and relatively fast changing conditions. This method provides a valuable tool for the study of the rate of growth or desiccation of a variety of plant materials.

- Water sorption rates of a large number of materials can be measured at various humidities and temperatures. Effects of processing and preparation techniques of a material as well as that of its dispersion pattern in the system on its water sorption rates can also be investigated.

- The humidity adjusting agents can be added to the otherwise optimized packages of produce as a means of controlling condensation and/or microbial development. Presentation of the compound will be extremely important in a package system. The absorbing compounds may be placed in food grade spun bonded polyethylene packets which permit movement of vapor but not liquid water. These packets are reusable and thus economical. This presentation technique has worked in produce packaging trials which might be of interest in the packaging of mushrooms, bell peppers and citrus fruits. The humidity controlling packets can be used in other experimentation where control of humidity is important and use of saturated salt solutions is impractical. Such applications include tissue culture and seed technology. APPENDIX

Datalogger program used for temperature and humidity data acquisition in Section I.

AUTOLOG PROGRAM

9. \$N7.2\$RH8 %* \$

VR SUBROUTINE

1.	53	AON			1.	75	PSH	
2.	11	DLY	5		2.	75	PSH	
3.	31	OPN	TMP	RH	3.	26	CON	25.0810
4.	66	TIM			4.	81	MLT	
5.	76	POP			5.	26	CON	-25.2314
6.	77	STF			6.	79	ADD	
7.	61	ICP			7.	13	DCM	2
8.	23	SCN	250	1,2,3,4,5,6,7,8,9	8.	20	CDS	16 16
9.	15	RCL	0		9.	12	WID	16
10.	32	65B	VT		10.	37	VUA	
11.	15	RCL	1		11.	11	DLY	10
12.	32	gsb	VR		12.	77	STF	
13.	15	RCL	2		13.	61	ICP	
14.	32	65B	VR		14.	0	END	
15.	15	RCL	3					
16.	32	gs B	VR		VT	SUBROU	TINE	
17.	15	RCL	4					
18.	32	gsb	VR		1.	75	PSH	
19.	15	RCL	5		2.	75	psh	
20.	32 :	gsb	VR		3.	26	CON	12.5464
21.	15	RCL	6		4.	81	MLT	
22.	32	GSB	VR		5.	26	CON	-12.8233
23.	15	RCL	7		6.	79	ADD	
24.	32	65 b	VR		7.	13	DCM	2
25.	15	RCL	8		8.	20	CDS	16 16
26.	32	ĢSB	VR		9.	12	WID	16
27.	54	AFF			10.	37	VUA	
28.	35	ZZZ			11.	11	DLY	10
29.	0	END			12.	77	STF	
					13.	61	ICP	
					14.	0	END	
FORMAT, TMPRH								
1.	TNOT		.	•				
2.	IN7.2							
3.	#N7.24	FKH1	77	*				
-	*N7.24		74					
3.	¥N7.24	KH3	77	*				
3.	4N7.21		77	*				
e .	#N/.21		74	T				
7.	#N7.24		74	T				
8.	#N7.21	INH7	77	¥				

BASIC computer program used for weight loss data acquisition in Section II.

```
90 CLEAR . . 20000
100 ON ERROR GOTO 850
110 GOSUS 500
115 LOCATE 5.1
120 INPUT "Enter interval in seconds to measure ";NUM
130 ON TIMER(NUM) BOSUE 400
140 INPUT "Enter length of time in minutes to record each sample "; TIMLEN
150 TOTIN-TIMLEN-60: LOOP-TOTIN/NUM
150 LINE INPUT "Enter Drive and Filename (i.e. A:Test)? ";DSKFILS
170 GOSUB 800
180 OPEN DEXFILE FOR OUTPUT AS #3
190 OPEN COMFILS AS #1
200 OPEN "SCRN: " FOR OUTPUT AS #2
210 PAUSE-FALSE
220 I-1
230 TIMER ON
240 AS-INKEYS: IF AS-" THEN 260
250 IF ASC(AS)-MENU THEN SOO ELSE PRINT #2, AS
260 IF LOC(1)-0 THEN 240
270 IF LOC(1)>62 THEN PAUSE-TRUE: PRINT #1, XOFFS;
250 AS-INPUIS(LOC(1),#1)
250 PRINT #2,AS;: IF LOC(1)>0 THEN 270
300 IF PRUSE THEN PRUSE-FALSE: PRINT #1, XONS;
310 GOTO 240
400 REM ********* INPUT FILE ROUTINE *****************
410 PRINT #1,55;CRS;LFS;
420 LINE INPUT #1,85
430 DT-VAL(HIDS(85,4,10))
440 PRINT #3, DT: PRINT #2, DT
450 I-I+1 : IF I>-LOOP THEN 700
460 GOTO 230
SOO TIMER OFF:LOCATE 15.1: PRINT STRINGS(30, " "):LOCATE 15.10
SIO LINE INPUT"(C)antinue or (E)xit? ":TXRXS
S20 IF (TXRXS-"C") AND (TXRXS-"E") THEN S10
S30 IF TXRXS-"C" THEN 710
S40 IF TXRXS-"C" THEN 230
700 TIMER OFF
710 CLOSE : CLS: LOCATE 25, 10: PRINT ". File saved ."
720 INPUT "Hore weighings"
730 IF CHKS<> "N" THEN 160
                              ": CHKS
740 CLOSE: KEY ON
750 END
800 OPEN DSKFILS FOR INPUT AS #3
810 INPUT "That fileness is already in use!!! OVERWRITETT(Y/N) "; CHKFILS
SEO IF CHKFILS - "Y" THEN CLOSE #3: RETURN
830 CLOSE #3
840 GOTO 160
850 IF ERR-53 AND ERL-800 THEN PRINT "Opening new file ...": RESUME 180
860 PRINT "ERROR CODE - "; ERR
870 PRINT "ERROR LINE - "; ERL
660 STOP
SOO SCREEN 0,0
910 KEY OFF: CLS: CLOSE
SEO DEFINT I-K
330 CONFILS="CON1:1200, E,7,1,055": 55-"S": CRS-CHRS(13): LFS-CHRS(10)
SHO FALSE-O: TRUE- NOT FALSE
SSO MENU-S ' WHEN CRTL-E IS HIT, MENU IS DISPLAYED
SO XOFFS-CHRS(19): XONS-CHRS(17)
570 LOCATE 25,1:PRINT STRINGS(60, * *)
580 LOCATE 25,1:PRINT "Balance Reader Program, Press CRTL-E to abort file save";
330 RETURN
```

Datalogger program used for temperature and humidity data acquisition in Section II.

AUTOLOG PROGRAM

.

VR SUBROUTINE

1.	53	AON		1.	75	PSH		
2.	11	DLY	5	2.	75	PSH		
3.	31	OPN	FILE	3.	26	CON	25.	0810
4.	66	TIM		4.	81	MLT		
5.	76	POP		5.	26	CON	-25.3	2314
6.	77	STF		6.	79	ADD		
7.	61	ICP		7.	13	DCM	2	
8.	23	SCN	250 1,2	8.	20	CDS	16	16
9.	15	RCL	0	9.	12	WID	16	
10.	32	GSB	VR	10.	37	VUA		
11.	15	RCL	1	11.	11	DLY	10	
12.	32	GSB	VT	12.	77	STF		
13.	54	AFF		13.	61	ICP		
14.	35	ZZZ		14.	0	END		
15.	0	END						

FORMAT, FILE

1.	*N6*TIME*	*
2.	*N7.2*RH* >	K
3.	\$N7.2*TMP*	*

VT SUBROUTINE

1.	75	PSH		
2.	75	PSH		
3.	26	CON	12.	5464
4.	81	MLT		
5.	26	CON	-12.	8233
6.	79	ADD		
7.	13	DCM	2	
8.	20	CDS	16	16
9.	12	WID	16	
10.	37	VUA		
11.	11	DLY	10	
12.	77	STF		
13.	61	ICP		
14.	0	END		

