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Development and Validation of a Dynamic Vapor Sorption−Fast Gas Chromatography−Flame Ionization Detection Method for Rapid Analysis of Volatile Release from Glassy Matrices

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Historically, saturated salt solutions in desiccators have been used to investigate the effects of increasing relative humidity and temperature on the volatile retention efficiency of amorphous glasses. Obtaining data using desiccators is a static process that gives the researcher discrete data points with which to draw conclusions. Dynamic vapor sorption (DVS; SMS, London, U.K.) is a humidification system that creates specific relative humidity and temperature environments within a chamber that contains the material being investigated. This study had two specific aims: (1) to develop a DVS-fast GC-FID method that dynamically evaluates the effects of humidification and temperature increases on volatile release from amorphous carbohydrate glasses and (2) to evaluate the validity of the DVS-fast GC-FID method. Artificial cherry Durarome (Firmenich, Plainsboro, NJ) was used as the model system. The DVS-fast GC-FID method proved to be an innovative, accurate, and precise technique that can be used to conduct humidification/temperature−volatile release studies.

KEYWORDS: DVS-fast GC-FID; amorphous glass; volatile retention; volatile release

INTRODUCTION

Loss of volatile compounds from foods is known to greatly deteriorate a food's flavor quality (*1*−*4*). Conditions that expose a food to high relative humidities and/or high temperatures during processing, storage, or distribution greatly increase the potential for volatile loss. Many studies have investigated the effect of increasing relative humidity and temperature on volatile release using saturated salt solutions in desiccators. However, obtaining data using desiccators is a static process that provides the researcher discrete data points with which to draw conclusions about how humidification and resultant moisture sorption affect a food system's stability. Essentially, certain limitations that are inherent to saturated salt solutions in desiccators make it difficult to obtain an accurate profile of volatile release from glassy carbohydrate entrapping systems. Levoguer and Williams (*5*) identified four main issues with employing desiccators to conduct relative humidity studies: (1) the lengthy period of time it takes the product to achieve equilibrium; (2) the difficulty of obtaining conclusive, accurate measurements due to the protocol of continuously removing the sample from the desiccator and exposing it to an environment that often possesses a different relative humidity (and possibly temperature); (3) the requirement of using large sample sizes (typically >1 g) to obtain a measurement; and (4) the time-consuming, cumbersome efforts of the researcher to obtain weight measurements during the period that it takes for the product to equilibrate within the desiccator.

In 1997, Surface Management Systems (London, U.K.) developed a fully automated humidification system, called dynamic vapor sorption (DVS), that can expose a food or other biopolymer system to relative humidity and/or temperature changes according to the specifications determined by the researcher. DVS is a temperature-controlled incubator that contains two chambers, the reference chamber and the sample chamber, within which the specified relative humidity is produced. The changes in relative humidity in each chamber occur by mixing a specific ratio of saturated vapor (100% relative humidity generated by passing the air through a vapor humidifier), controlled by mass flow controller one, and dry

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air, controlled by mass flow controller two (*5*). Temperature and relative humidity probes are present to monitor the conditions in each chamber. Within each respective chamber, a reference pan and a sample pan hang from a wire that is attached to a Cahn microbalance. The Cahn microbalance is capable of measuring relatively small changes in sample mass, as small as 10^{-6} g (*5*), thus allowing the researcher to minimize the initial sample mass and, therefore, the length of time required for the sample to reach equilibrium. The Cahn microbalance is highly sensitive to the changes in moisture that occur throughout the incubator; therefore, a dry purge gas passes over the balance to avoid potential complications with baseline stability.

Preliminary results have shown that DVS systems can be incorporated into rapid analysis techniques that evaluate the effects of humidification and temperature on volatile retention in amorphous carbohydrates (*6*−*10*). DVS technology coupled with fast gas chromatography−flame ionization detection (DVS-fast GC-FID) is a rapid analysis method that would enable the researcher to obtain frequent, real-time volatile release data resulting from a constant relative humidity and temperature environment without making invasive, condition-altering retention measurements.

Dronen and Reineccius (*11*) and Reineccius (*12*) also conducted preliminary studies on volatile release from amorphous carbohydrate glasses using a rapid analysis technique that coupled a vapor generator instrument (VGI) (Surface Management Systems, London, U.K.) with atmospheric pressure chemical ionization mass spectrometry (APCI-MS). In their study, various volatile compounds, entrapped in different amorphous glasses via spray-drying, were exposed to relative humidities ranging from 30 to 80% at 40 °C. Each sample was taken through a 13-step humidity ramp program. The 13 steps comprised 7 ramps to each of the 6 relative humidities and 6 6-min dwell periods at each relative humidity. Volatile release measurements were determined approximately every 45 s, and the total run time was ∼60 min. Two of the key advantages of the VGI-APCI-MS rapid analysis technique that were identified in their study were shorter analysis times and nearly continuous volatile analysis measurements.

The first objective of this study was to develop a method to study the effects of humidification and temperature on benzaldehyde release from an amorphous sucrose-based entrapping matrix that utilizes DVS for humidification and fast gas chromatography−flame ionization detection for volatile release determination. The second objective of this study was to validate the scientific soundness of the DVS-fast GC-FID method for studying the effects of humidification and temperature on benzaldehyde release from artificial cherry Durarome.

MATERIALS AND METHODS

Artificial cherry Durarome (Firmenich, Plainsboro, NJ; catalog no. 861515 TD 05.90) was used as the model system. In general, Duraromes are commercially available encapsulated flavor delivery systems, which can be incorporated into a variety of food products, such as confectionary and ready-to-eat cereal products. Duraromes are prepared by first incorporating flavor compounds into a sucrose−maltodextrin melt in approximately a 1:9 ratio of volatiles to carbohydrates. An emulsifier (<0.02%) is also often added to the blend. The blended melt is then extruded and dropped into a 2-propanol bath, which rapidly cools the extrudate, setting up the amorphous glass. The 2-propanol bath also eliminates any volatiles remaining on the surface of the entrapping system. According to the manufacturer (*13*), the finished Durarome used in this study contains at least 5% (w/w) benzaldehyde, the volatile compound primarily responsible for cherry aroma and flavor, and in addition contains ∼5% of other propriety flavor compounds. Durarome samples were sifted using USA Standard Testing sieves (ASTME-11 specification) and particles >0.0117 in. (300 μm) and <0.0234 in. (600 μm) in all of the experiments.

The initial moisture content of the two artificial cherry Durarome lots used for this study was determined by Karl Fischer titration. The Durarome was dissolved in a 1:1 solution of anhydrous formamide (Mallinckrodtt; catalog no. 3797-4*NY) and anhydrous methanol (Fisher; catalog no. A935-5) and titrated with Karl Fischer titrant (GFS Chemicals; catalog no. 99605). The titration was considered to be complete when the free iodine in the titrant was no longer reduced to iodide (which occurs in the absence of water) and the free iodine produces a large current that is detected by the Karl Fischer moisture meter (Mitsubishi, Norwood, NJ). The initial moisture contents of the Durarome lots used for these studies ranged from 4.0 ± 0.02 to 5.4 ± 0.03% (grams of water per gram of sample). The initial water activity of the Durarome was determined at 15, 25, and 35 °C using an Aqua Lab series 3 TE water activity meter (Decagon Devices, Philadelphia, PA) in triplicate. The initial A_w was 0.21 ± 0.002 at 15 °C, 0.29 ± 0.002 at 25 °C, and 0.36 ± 0.001 at 35 °C. The Durarome was kept in moisture-impermeable containers and stored in an air-conditioned laboratory at approximately 22.8 ± 0.98 °C and 45.7 ± 6.48% relative humidity.

The initial benzaldehyde concentration of the "as is" Durarome was determined for the two sample lots using ether extraction. Triplicate Durarome samples from each lot were diluted with 20 mL of deodorized deionized water and 10 mL of ether. One hundred microliters of internal standard solution, composed of 100 μL of 2,5-dimethylbenzaldehyde in 10 mL of methanol, was added to the water/ether solution. Prior to extraction, the solution was gently agitated and vented for ∼1 min. Approximately 1 g of NaCl was added to the solution to break the emulsion formed during agitation. The top layer was pipetted off after 1 min of rest. Two microliters of sample was injected into the Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector (FID). The column used was an HP-5MS capillary column (5 m × 0.20 mm i.d. × 0.33 μm film, Hewlett-Packard). The injection temperature was set at 250 °C. The oven was held at 40 °C for 5 min, ramped to 225 °C at 8 °C/min, and held at 225 °C for 5 min. The FID temperature was 300 °C. The total amount of benzaldehyde in the initial sample was determined using an internal standard calibration, with 2,5-dimethylbenzaldehyde added as the internal standard. The mass of benzaldehyde was calculated using an internal standard calibration, with 2,5-dimethylbenzaldehyde (Sigma-Aldrich, St. Louis, MO) being the internal standard used. The average percents benzaldehyde of the two lots used were 6.7 ± 0.50 and 9.6 ± 0.46%, which is somewhat greater than expected on the basis of the "at least 5% benzaldehyde" reported by Firmenich (*13*).

Methods. *DVS-Fast GC-FID Method.* **Figure 1** is a schematic diagram illustrating its internal components. Over the duration of the experiment, the humidified air containing the volatile compounds expelled from the back of the DVS is conveyed to the fast-GC-FID for volatile quantification via the copper tubing sampling line.

All artificial cherry Durarome samples were humidified using the DVS 2000 system (Surface Measurement Systems Ltd.). A new sample was used for each relative humidity and temperature. The sample was placed directly on a DVS 19 mm quartz video pan. This pan provided enough area for the particles to be evenly distributed about the pan, which enabled exposure of the humid air to most of the surface area of the sample.

The DVS humidification system was calibrated by performing a step method experiment with different crystalline salts approximately once a month. The target percent relative humidity (RH) value obtained by the DVS was compared to the deliquescence point literature value for each salt. The crystalline salts used for humidity calibration were lithium chloride (11.05% RH), magnesium chloride (33.00% RH), magnesium nitrate (52.86% RH), sodium chloride (75.28% RH), and potassium chloride (84.26% RH) (*14*). All calibrations were conducted at 25 °C. The Cahn microbalance was calibrated with a known 1 g weight approximately once every two weeks.

Samples progressed through a two-step special automatic operation (SAO) method. The first step exposed each sample to a relative humidity of 30% (approximately equal to the average innate water activity

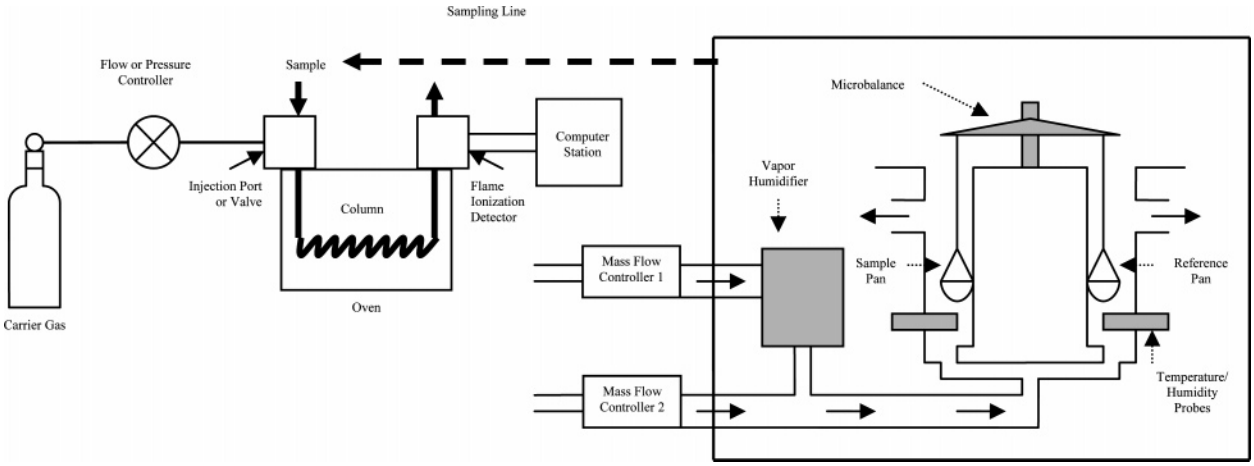

Figure 1. Schematic diagram of DVS-fast GC system. The components on the left comprise the fast-GC FID system. The components on the right comprise the DVS system.

multiplied by 100%) for 60 min. This step allowed the sample to internally equilibrate prior to humidification. It also removed any residual surface volatiles. The second step exposed the samples to a relative humidity of 40, 50, 60, 70, 80, or 90% for 360 min. Triplicate samples were exposed to all relative humidities at 15, 25, and 35 °C. The starting relative humidity was 40% because it was the interval of 10% RH immediately greater than the Durarome's innate water activity. Three hundred and sixty minutes was chosen as the maximum amount of time because by that time, the characteristic burst of volatile release that occurred at all of the relative humidities had diminished. An air stream (set rate = 500 mL/min, actual rate = 486 mL/min) at a specified relative humidity continually flowed through the chamber containing the sample. The average flow rate of this air stream was measured by a mini-Buck calibrator flow meter (AP Buck, Inc., Orlando, FL). This flow rate allowed sufficient dynamic humidification of the sample without forcing an overloading volume into the vacuum sampling line.

Volatile detection was performed using a Hewlett-Packard 5890 series II gas chromatograph equipped with an EZ Flash accessory and flame ionization detector (FID). Fast GC-FID allowed for quick analysis of the volatiles and a short sampling interval; however, it did not continuously analyze volatile release throughout the continuous humidification interval. The total time necessary for sampling and analysis was ~20 min.

Deactivated silica beads (Restek, Bellefonte, PA; catalog no. 20791) and Tenax-TA 60/80 (Supelco, Bellefonte, PA; catalog no. 11982) composed the absorbent trap. Tenax-TA is a polymer of 2,6-diphenyl-*p*-phenylene oxide. The benefits of this trap are that it is essentially impurity free and it inhibits the compound from prematurely bleeding from the trap. Approximately 60 mL of the 486 mL of humidified air expelled from the DVS per minute was trapped for ~6 min. The volume of air sampled by the vacuum was confirmed via a flow meter. This sampling method and rate provided enough sample to the GC without overloading the column.

Once the sampling step was complete, the trap was heated and flushed with helium carrier gas to desorb the volatiles. The carrier gas−volatile complex was then cryofocused in a cooled injector system (CIS-3, Gerstel GmBh & Co., KG, Mülheim an der Ruhr, Germany) and thermally desorbed into an HP-5MS capillary column (5 m × 0.20 mm i.d. × 0.33 μm film, Hewlett-Packard). An HP-5MS capillary column is a nonpolar, general use column that is composed of (5%-phenyl)-methylpolysiloxane. Cryofocusing cools the sample to below the temperature at which the compounds being analyzed will volatilize, producing clean peaks with little to no tail. The CIS ran in splitless mode with an equilibration time of 0.25 min, a splitless time of 1.10 min, an initial temperature of 0 °C, an initial hold time of 0.1 min, a ramp rate of 12 °C/s, a final temperature of 280 °C, and a final hold time of 2 min. The thermal desorption system (Gerstel) (TDS-G) ran in solvent vent mode with a 1 min purge, an initial temperature of 30 °C, a final temperature of 210 °C, a ramp rate of 60 °C/min, a sampling valve temperature of 250 °C, and a transfer line temperature of 280 °C. The transfer line temperature of 280 °C also purged any lingering volatile compounds from the system. The integration parameters were set as follows: slope sensitivity = 281.58, peak width = 0.693 s, peak area reject = 138.16 counts × s, height reject = 16.612 counts; shoulders were not counted in the integration.

DVS-fast GC-FID Method Validation. *Comparison of Release and Retention Data.* Benzaldehyde release measurements determined by the DVS-fast GC-FID method were compared to benzaldehyde retention measurements determined by the ether extraction method (described under Materials) after humidification. For the benzaldehyde release measurements, the Durarome sample was placed directly on the DVS 19 mm quartz video pan. Triplicate samples progressed through a two-step special automatic operation (SAO) method at 25 °C. The first step exposed the sample to a relative humidity of 30% (approximately equal to the average innate water activity multiplied by 100%) for 60 min. The second step exposed the samples to a relative humidity of 60 or 70% for 360 min. The sample pan was removed from the DVS upon completion of the second SAO step and placed in the water/ether/internal standard solution (described under Materials). The total amount of volatile retained was quantified using the ether extraction method described under Materials; however, the instrument used was a Hewlett-Packard 5890 series II gas chromatograph equipped with a FID. The column used was a DB-5MS capillary column (15 m × 0.53 mm i.d. × 1.0 μm film, Hewlett-Packard). Injection temperature was set at 250 °C. The oven was held at 40 °C for 5 min, ramped to 225 °C at 8 °C/min, and held at 225 °C for 5 min. The FID temperature was 300 °C. A comparison was made between the mass of benzaldehyde retained (calculated on the basis of the release data measured by the DVS-fast GC-FID method) and the mass of benzaldehyde retained (determined by ether extraction). Each extraction was evaluated in triplicate. The mean retention value obtained from the extraction technique was compared to the retention value obtained from the DVS-fast GC-FID method.

Comparison of Release and Retention Data—Extended Time Experiment. At 80% RH, the amount of volatile released was compared to the amount of benzaldehyde originally contained in the Durarome. Durarome samples were placed in the DVS and taken through a two-step SAO method at 25 °C. The first step exposed the sample to 30% RH for 60 min. The second step exposed the samples to 80% RH until peaks >10000 were no longer detected. A peak of 10000 equals ~0.024 μg of benzaldehyde, which is slightly greater than the smallest mass of benzaldehyde confirmed for detection when the standard curve was developed. The mass of benzaldehyde released was then compared to the total amount of benzaldehyde in the sample prior to humidification.

Variability of Benzaldehyde Release/Retention Measurements within a Sample Set. The variability of benzaldehyde release/retention measurements for each Durarome sample in a percent relative humidity/temperature set was also evaluated. Triplicate samples progressed through a two-step SAO method. The samples were randomized within a percent relative humidity/temperature set. The first step exposed each

sample to a relative humidity of 30% for 60 min. The second step exposed the samples to a relative humidity of 40, 50, 60, 70, 80, or 90% for 600 min. All relative humidities were evaluated at three different temperatures (15, 25, and 35 °C). The percent of benzaldehyde retained by the artificial cherry Durarome throughout the humidification period was calculated from the benzaldehyde release data.

Variability in Homogeneous, Small-Particle Size Samples. To determine the amount of variability that was due to the DVS-fast GC-FID method (rather than from sample variability), the Durarome's particle size was decreased and further standardized. Artificial cherry Durarome was crushed with a mortar and pestle and once again sifted using USA Standard Testing Sieves (ASTME-11 specification). Particles of <0.0117 in. (300 μm) were selected. Triplicate samples progressed through a two-step SAO method at 25 °C. The first step exposed each sample to a relative humidity of 30% for 80 min. The second step exposed the samples to a relative humidity of 80% for 600 min.

RESULTS AND DISCUSSION

DVS can be easily coupled with fast GC-FID for evaluating the effects of humidification and temperature changes on volatile retention by amorphous carbohydrate-entrapping matrices. In addition, the DVS-fast GC-FID method is an innovative, suitable, accurate, and precise technique with which to conduct studies of this nature. Application of the DVS-fast GC-FID method, in conjunction with DVS-DSC, to investigate how humidification induces physicochemical changes in amorphous glassy matrices resulting in the release of entrapped volatiles is reported by Bohn and others (*15*).

Optimal volatile release/retention results were obtained when samples progressed through a two-step SAO method, in which the first step exposed each sample to a relative humidity equal to the innate water activity for 60 min and the second step exposed the samples to the desired relative humidity for 360 min. Setting the sampling rate to 60.5 mL/min/486.1 mL/min for ~6 min provided enough sample to the GC without overloading the column. Using the DVS-fast GC-FID method, volatile release data points were collected approximately every 20 min; thus, only 10 h was required to collect 28−30 data points at each percent relative humidity/temperature set. DVS-fast GC-FID quickly analyzed the volatiles released into the humidified air and provided a semicontinuous view of the effects of humidification and temperature changes on volatile release/retention.

Comparison of Release and Retention Data. Table 1 shows the comparison between the mass of benzaldehyde retained according to the DVS-fast GC-FID method and the ether extraction method and the percent difference in their values. The mass of benzaldehyde retained by the Durarome matrix after 360 min at 60 or 70% RH was calculated using the following protocol. The peak area recorded by the FID was divided by the standard curve empirical constant to obtain the mass of the benzaldehyde released and measured during a sampling interval. This value was then divided by the sampling time interval to obtain the release rate throughout the sampling interval. Release rates (micrograms per minute) were plotted against fast GC-FID analysis times using KaleidaGraph 3.6 (Synergy Software, Reading, PA). The area under the curve was determined at each fast GC-FID analysis time using the integrated curve macro in KaleidaGraph 3.6. The macro calculates the incremental area under the curve using

$$\text{area} = \left(\frac{y_2 + y_1}{2} - y_{\text{ref}}\right)(x_2 - x_1) \qquad (1)$$

where y_1 and y_2 are consecutive release rate measurements (μg/

Table 1. Comparison of the Mass of Benzaldehyde Retained According to the DVS-Fast GC-FID Method to the Mass of Benzaldehyde Retained According to the Ether Extraction Method after 360 min at 60 or 70% Relative Humidity[a]

sample	initial mass of benzaldehyde (μg)	mass of benzaldehyde released according to DVS-fast GC-FID (μg)	mass of benzaldehyde retained according to DVS-fast GC-FID (μg)	av mass of benzaldehyde retained according to ether extraction (μg)	SD of mass of benzaldehyde retained according to ether extraction (μg)	% of benzaldehyde retained according to DVS-fast GC-FID	av % of benzaldehyde retained according to ether extraction	av % diff in % retention
60% RH A	894.4	117.6	776.9	796.3	27.6	86.9	89.0	2.51
60% RH B	908.9	50.5	858.4	840.9	19.1	94.4	92.5	−2.04
60% RH C	1337.7	57.0	1280.6	1357.9	11.1	95.7	101.5	6.03
70% RH A	977.4	322.8	654.6	680.4	15.8	67.0	69.6	3.94
70% RH B	830.7	229.9	600.8	595.7	35.8	72.3	71.7	−0.84
70% RH C	1232.9	128.9	1104.0	1113.9	23.7	89.5	90.4	0.90
av absolute % diff								2.7
SD								1.99

[a] Abbreviations: av, average; SD, standard deviation; RH, relative humidity; diff, difference.

Table 2. Comparison of the Initial Mass of Benzaldehyde in the Durarome Sample to the Mass of Benzaldehyde Released As Measured by the DVS-Fast GC-FID Method and the Percent Difference between the Masses at 80% Relative Humidity and 25 °C until Volatile Release No Longer Occurred[a]

sample	time exposed to 80% RH (min)	initial mass of benzaldehyde (μg)	mass of benzaldehyde released as measured by DVS-fast GC-FID (μg)	% diff between masses
80% RH A	9073.3	2032.3	2027.7	0.22
80% RH B	7692.7	1262.2	1194.5	5.37
80% RH C	5081.9	1064.2	1043.1	1.99
av % diff				2.5
SD				2.62

[a] Abbreviations: av, average; SD, standard deviation; RH, relative humidity; diff, difference.

min), y_{ref} equals 0, and x_1 and x_2 are consecutive analysis times (min). The integrated value equals the mass of benzaldehyde released, as measured by the fast GC-FID, between the two fast GC-FID analysis times.

The mass of benzaldehyde retained in the Durarome sample was determined by ether extraction after the humidification period (360 min) was complete. The amount of benzaldehyde in the ether extraction was determined from an internal standard (2,5-dimethylbenzaldehyde) calibration.

The percent difference between the retention values calculated from the benzaldehyde release measurements obtained from the DVS-fast GC-FID method at 60 and 70% RH and 25 °C and the retention values obtained by the ether extraction technique ranged from −2.04 to 6.03%, with the smallest percent difference being −0.84% and the largest percent difference being 6.03%. The average of the absolute values of the percent differences between the retention determined by the DVS-fast GC-FID method and the retention determined by the ether extraction method was 2.7 ± 1.99%.

To determine whether the retention values obtained from the DVS-fast GC-FID method and ether extraction method were statistically different, the retention values obtained at 60 and 70% RH from the two methods were combined and then compared using a paired sample for means Student *t* test at $\alpha = 0.05$. The *p* value for this comparison was 0.24, confirming that the retention values obtained by each method were not significantly different. The statistical analysis performed indicates that the variability between samples (A, B, and C) run at either 60 or 70% RH is not due to the method, but rather the sample itself. Thus, the DVS-fast GC-FID method is an accurate method for obtaining volatile release/retention data from a glassy matrix.

Comparison of Release and Retention Data—Extended Time Experiment. Table 2 provides a comparison of the initial mass of benzaldehyde to the mass of benzaldehyde released according to the DVS-fast GC-FID method and the percent difference in the values. The average percent difference between the initial amount of benzaldehyde measured in the sample and the amount of benzaldehyde released was 2.5 ± 2.62%. The initial mass of benzaldehyde between samples varied due to the difference in the initial Durarome mass. The initial mass of benzaldehyde was compared to the mass of benzaldehyde released according to the DVS-fast GC-FID method using a two-sample Student *t* test assuming equal variances at $\alpha = 0.05$. The *p* value for the values was 0.92, indicating that the initial mass of benzaldehyde was not statistically different from the mass of benzaldehyde released according to the DVS-fast GC-FID method.

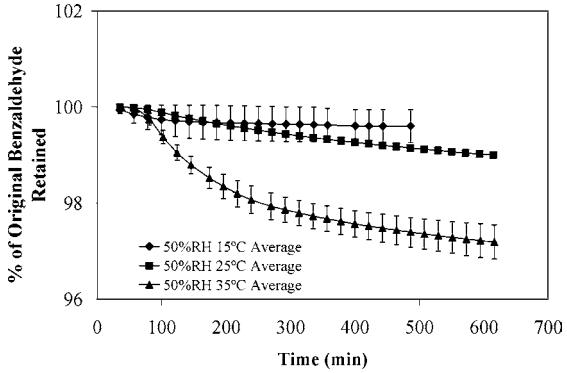

Figure 2. Average percent of benzaldehyde retained by the Durarome matrix over time at 50% RH and 15, 25, and 35 °C. The length of the bars above and below each data point is equal to the data point's standard deviation. Bars flanking the 25 °C data points are included, although, due to their small magnitude, they are hidden by the data points themselves.

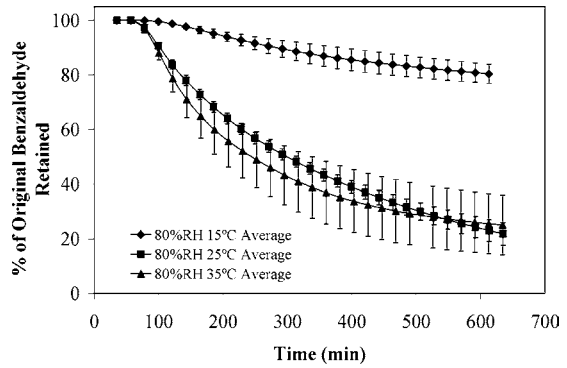

Figure 3. Average percent of benzaldehyde retained by the Durarome matrix over time at 80% RH and 15, 25, and 35 °C. The length of the bars above and below each data point is equal to the data point's standard deviation.

Variability of Benzaldehyde Release/Retention Measurements within a Sample Set. Figures 2 and **3** illustrate the percent of benzaldehyde retained by the Durarome matrix over time at 50 and 80% RH and 15, 25, and 35 °C, respectively. These two figures provide examples of volatile retention trends at the low-end relative humidities (40−60% RH) and the high-end relative humidities (70−90% RH). The specific results for the other percent relative humidity/temperature combinations are given in Bohn (*16*). The mass of benzaldehyde retained by the Durarome matrix was calculated using the benzaldehyde release values according to the protocol described previously. It should be noted that the sample exposed to 50% RH and 15 °C was run for the entire 600 min; however, a benzaldehyde peak was no longer detected by the fast GC-FID after ∼500 min (**Figure 2**). Perhaps after 500 min, the Durarome matrix had not adsorbed enough moisture to initiate benzaldehyde diffusion and release, thus, allowing only for the release of the surface benzaldehyde. Overall, the results of this study show that increases in relative humidity and/or temperature cause increases in benzaldehyde release and, thus, decreases in benzaldehyde retention by the Durarome matrix.

The length of the bars above and below each data point is equal to the data point's standard deviation. After a thorough, systematic investigation that looked for possible trends in the standard deviations as a function of temperature and relative humidy, a consistent trend was not observed across the three

temperatures and six relative humidities. A general trend was identified when comparing the lower relative humidities (40−60%) were compared to the higher relative humidities (70−90%). At 40, 50, and 60% RH, the standard deviations of the percent retention values in each percent relative humidity/temperature set were <1.4%. At these relative humidities, though, <7.0% of the benzaldehyde is released at all three temperatures, which limits the amount of variability that exists in these samples at these relative humidities. At 70, 80, and 90% RH, the standard deviation was as much as 10.9%; however, at these higher relative humidities, as much as 94% of the volatile was released. Volatile retention variability at these high relative humidities is postulated to be due to the difference in the particle size distribution between replications within a sample set (e.g., 80% RH at 25 °C, replications A−C). Although the lots were sifted and selected to obtain samples with uniform particle size, variation in particle size distribution (i.e., variation in sample surface area) still existed between sample replications within a sample set. This variation in the particle size distribution may greatly affect the rate of moisture sorption, which may cause a larger variation in volatile release between replications within a sample set at a specific analysis time. We postulate that a uniform rate of moisture sorption between replications within a sample set would allow benzaldehyde diffusion to occur at a more consistent rate, thus decreasing the benzaldehyde release and retention variability. A deeper exploration of the factors affecting the magnitude of the standard deviation was completed in Bohn and others (*17*), where uncertainty analysis of the DVS-fast GC-FID technique was conducted.

Figure 3 shows a crossing-over of the benzaldehyde retention curves between 25 and 35 °C curves after 500 min. This may be due to the Durarome matrix going through structural collapse at a more rapid rate at 35 °C than at 25 °C. Levi and Karel (*18*) proposed that when collapse occurs rapidly, the ability of the volatile to diffuse to the surface and expel from the matrix is slower due to a reduction in the matrix's free volume. As a result, the volatile releases from the collapsed amorphous matrix at a slower rate.

Variability in Homogeneous, Small-Particle Size Samples. Artificial cherry Durarome particles were further ground and sifted to produce a homogeneous, small-particle size sample [particle size of <0.0117 in. (300 μm) was used]. Grinding the Durarome sample decreased the benzaldehyde concentration from 9.6 ± 0.46 to 2.5 ± 0.04%. Although the particle size of the original samples evaluated was limited to particles >0.0117 in. (300 μm) and <0.0234 in. (600 μm), the distribution of particle size, and thus surface area, of each particle within a sample did vary. Differences in particle size distribution can cause variability in the rate at which particles adsorb humidified air, which, as a result, can cause volatile release variability. At a fixed relative humidity and temperature, the rate of moisture sorption is the main determinant of volatile release from amorphous carbohydrates.

Figure 4 shows the average percent of benzaldehyde retained by the Durarome matrix over time at 80% RH and 25 °C, as well as by the homogeneous, small-particle size samples over time at 80% RH and 25 °C. Benzaldehyde retention values were determined using the benzaldehyde release values measured by the DVS-fast GC-FID system. Once again, the length of the bars above and below each data point is equal to the data point's standard deviation. By grinding and further sifting the particles, particle size distribution became more uniform and moisture adsorption rates were more consistent among the evaluated samples. For example, the average standard deviation of the homogeneous particle size Durarome samples at 80% RH and 25 °C was 1.36% (range = 0.08−2.13%), whereas the average standard deviation of the sifted Durarome samples at 80% RH and 25 °C was 2.28% (range = 0.001−4.12%). Thus, it can be postulated that when exposed to the same conditions, Durarome samples with less particle size variability (i.e., more homogeneous) decrease the variability of the volatile retention results.

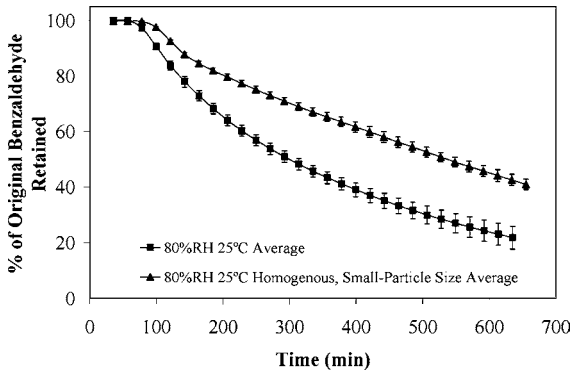

Figure 4. Average percent of benzaldehyde retained by the Durarome matrix over time at 80% RH and 25 °C. The average percent of benzaldehyde retained by the homogeneous, small-particle size samples over time at 80% RH and 25 °C is also shown. The length of the bars above and below each data point is equal to the data point's standard deviation.

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