

Uncertainty Analysis of a Dynamic Vapor Sorption–Fast Gas Chromatography–Flame Ionization Detection Method for the Rapid Analysis of Volatile Release from Glassy Matrices

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Uncertainty analysis was conducted with a dynamic vapor sorption–fast gas chromatography–flame ionization detection (DVS-fast GC-FID) method, developed to rapidly analyze the extent of volatile release that occurs from carbohydrate glasses due to humidification and temperature increases. Triplicate samples progressed through a two-step special automatic operation method in the DVS. Samples were exposed to relative humidities ranging from 40 to 90% (in 10% increments) at 15, 25, and 35 °C. Uncertainty analysis shows that the DVS-fast GC-FID method uncertainty is smaller than the natural sample uncertainty, indicating that the variability in a sample's physical properties has a dominant impact on the overall uncertainty of the volatile retention results obtained using the DVS-fast GC-FID method. Uncertainty analysis also indicates that the variance associated with the mass of benzaldehyde measured by the DVS-fast GC-FID is the largest contributor to the overall benzaldehyde retention variance when the cumulative mass of benzaldehyde measured is small.

KEYWORDS: DVS-fast GC-FID; uncertainty analysis; variation; volatile release; volatile retention

INTRODUCTION

Random errors of measurement can cause irreproducible results, which affect the precision and accuracy of the results obtained when using an analytical method (1). Day-to-day changes in the equipment and laboratory environmental changes can produce a bias in an individual run or variation among multiple runs. Variation in the matrices studied with the method can alter the operating range and linearity of the method. These, along with other potential sources of error, can be accounted for by estimating the uncertainty of the system.

EURACHEM (2) has defined uncertainty as “the dispersion of the values that could reasonably be attributed to the physical parameter being quantified by the measurement”. Van Zoonen and others (3) identified multiple possible sources of uncertainty such as sampling method, incomplete sample preparation, instrument resolution or discrimination threshold, inaccuracy of measuring equipment, and values of constants and other

parameters obtained from external sources. The four basic steps used to determine measurement uncertainty, as defined by the International Organization for Standardization (ISO), are identification, specification, quantification, and combination (4–6). Identification distinguishes all of the uncertainty parameters within the analytical method that can influence the resultant measurement. Specification requires the researcher to establish the mathematical model of the measurement process, which determines the analytical result. Quantification requires the researcher to determine the variance associated with each parameter. Combination includes calculating the overall uncertainty by combining the uncertainties of each parameter. The expanded uncertainty is the variance of the dependent *y* variable and can be estimated from the mathematical model illustrated in eq 1

$$\text{var}[y(x_1, x_2, \dots)] = (c_1^2 \times \text{var}[x_1] + \dots + c_i^2 \times \text{var}[x_i]) \quad (1)$$

where $\text{var}[y(x_1, x_2, \dots)]$ is the variance of *y* for the specified set of independent *x* variables; c_i is the sensitivity coefficient, which

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is estimated as $c_i = \partial y / \partial x_i$; and $\text{var}(x_i)$ is the calculated variance of the x_i parameter (1, 4–6).

Dynamic vapor sorption (DVS) (Surface Management Systems, London, U.K.) is a controlled-humidity system that can be incorporated into a rapid volatile analysis technique. DVS technology coupled with fast gas chromatography–flame ionization detection (DVS-fast GC-FID) allows the researcher to measure the true extent of volatile release due to the fact that the volatiles released from the sample travel from the humidified environment of the DVS directly into the sampling trap via a sampling line. Volatile release measurements can be made frequently throughout the humidification period, with the time-limiting factor being the amount of time required by the GC-FID to analyze the volatiles obtained during the sampling period. In addition, the DVS is a temperature-controlled instrument and, thus, the researcher can select a specific temperature at which to run a study.

Bohn and others (7) previously reported on the development and validation of the DVS-fast GC-FID system. In that study, they found that DVS-fast GC-FID proved to be an accurate and precise method. They exposed artificial cherry Durarome samples to environments of 30–90% relative humidity (RH) and 15, 25, and 35 °C. 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. Exposure to relative humidities of $\leq 60\%$ produced results with standard deviations that were $< 1.4\%$. Exposure to relative humidities of $> 60\%$, however, produced results with standard deviations as much as 10.9%. By controlling the particle size distribution of the Durarome, though, the standard deviation of benzaldehyde retention results at 80% RH and 25 °C decreased from 4.12 to 2.13%, a reduction of almost 50%. In addition, Bohn and others (8) utilized the DVS-fast GC-FID method to evaluate the physicochemical changes that occur in amorphous glasses (in particular, artificial cherry Durarome) upon humidification.

In an effort to identify the source(s) that contributes to the variability of the DVS-fast GC-FID method, uncertainty analysis was performed on the benzaldehyde release data collected by Bohn and others (7). The objectives of this study were to identify, specify, and quantify the parameters in the DVS-fast GC-FID method that contribute to the variance of the calculated percent of benzaldehyde retained values; compare method uncertainty to the uncertainty that arises from natural variability (e.g., particle size, percent relative humidity, temperature); and identify the effects of environmental conditions (e.g., percent relative humidity, and temperature) on benzaldehyde retention variance.

MATERIALS AND METHODS

Materials. Artificial cherry Durarome (Firmenich, Plainsboro, NJ; catalog no. 861515 TD 05.90) was used as the model system. 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 (9), 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 $\sim 5\%$ of other propriety flavor compounds. Durarome was sifted using U.S. standard testing sieves (ASTME-11 specification), and particles > 0.0117 in. (300 μm) and < 0.0234 in. (600 μm) were used in the DVS-fast GC-FID experiments.

The initial moisture contents of the artificial cherry Durarome lots used for this study were determined by Karl Fischer titration. The Durarome was dissolved in a 1:1 solution of anhydrous formamide (Mallinckrodt; 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 Durarome was kept in moisture-impermeable containers and stored in an air-conditioned laboratory at $\sim 22.8 \pm 0.98$ °C and $45.7 \pm 6.48\%$ RH. 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 moisture contents of the Durarome lots used for these studies ranged from 4.0 ± 0.02 to $5.4 \pm 0.03\%$ (g of water/g of sample). The initial measured A_w values were 0.21 ± 0.002 at 15 °C, 0.29 ± 0.002 at 25 °C, and 0.36 ± 0.001 at 35 °C.

Methods. Initial benzaldehyde concentration variation was calculated from the concentration measurements determined for three samples. Each sample was 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 \times 0.20 mm i.d. \times 0.33 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. 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 variation in the mathematical model used to determine the percent of benzaldehyde retained was also determined. According to the mathematical model, the percent of benzaldehyde retained was calculated from the mass of benzaldehyde released. The conditions under which release occurred and was measured were as follows. Triplicate samples progressed through a two-step special automatic operation (SAO) method. The sample runs were randomized within a percent relative humidity/temperature set. The first step exposed each sample to a relative humidity of 30% (approximately equal to the average innate water activity 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. 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, which occurred at all of the relative humidities, had diminished. Experiments were conducted at 15, 25, and 35 °C. An airstream (set rate = 500 mL/min, actual = 486.1 mL/min) at a specified relative humidity continually flowed through the chamber containing the sample. The average flow rate 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.

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 that 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. The volume of air sampled by the vacuum was confirmed via a flow meter.

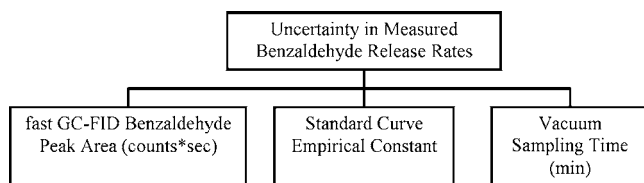


Figure 1. Uncertainty parameters associated with the benzaldehyde release rates for a single measurement of a single sample, as calculated from the peak areas determined by the DVS-fast GC-FID method.

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, Duisburg, 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 a sampling flow rate of 50 mL/min, 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 (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 total time necessary for sampling and analysis was ~20 min. Volatile detection was performed using a Hewlett-Packard 5890 series II gas chromatograph equipped with an EZ Flash accessory and a flame ionization detector. Fast GC-FID allowed for quick analysis of the volatiles and a short sampling interval (~20 min); however, it did not continuously analyze volatile release throughout the entire humidification interval. 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, and shoulders were not counted in the integration. The measurements obtained within a temperature/percent relative humidity set were averaged, and the variance of the mass of benzaldehyde released was determined as described below. The data collected were utilized to assess the uncertainty of the DVS-fast GC-FID method.

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 value obtained by the DVS was compared to deliquescence point literature value for each salt. The crystalline salts used for humidity calibration at 25 °C 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) (10). The Cahn microbalance used in the DVS system was calibrated with a known 1 g weight approximately once every 2 weeks.

RESULTS AND DISCUSSION

Identification. As noted above, the four basic steps of measurement uncertainty, as defined by ISO, are specification, identification, quantification, and combination (4). **Figure 1** is a flowchart that identifies the uncertainty parameters associated with the benzaldehyde release rates for a single measurement of a single sample, as calculated from the peak areas determined by the DVS-fast GC-FID method (6, 11). **Figure 2** identifies the uncertainty parameters associated with the average benzaldehyde release rate at a specific analysis time calculated from measurements of all samples within a percent relative humidity/temperature set and then corrected to the analysis time (6, 11).

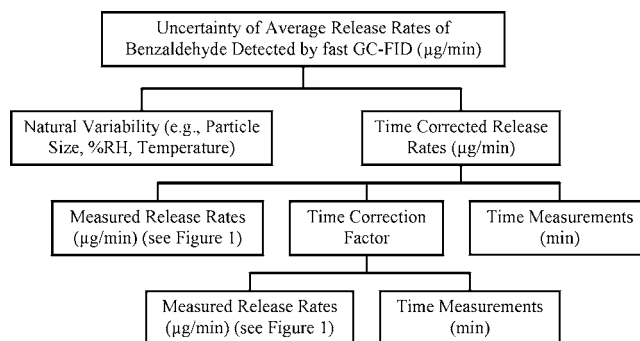


Figure 2. Uncertainty parameters associated with the average benzaldehyde release rate at a specific analysis time calculated from measurements of all samples within a percent relative humidity/temperature set and then corrected to the analysis time.

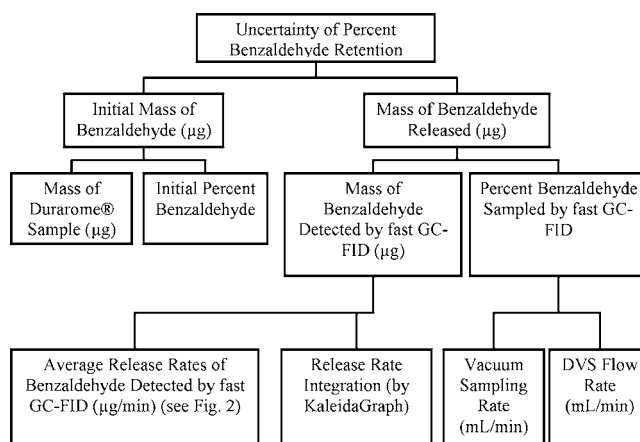


Figure 3. Uncertainty parameters associated with the benzaldehyde retention calculation.

Figure 3 identifies the uncertainty parameters associated with the benzaldehyde retention calculation (6, 11).

Specification and Quantification. For this study, specification and quantification will be discussed concurrently. Also, the benzaldehyde release results obtained at 80% RH and 35 °C are used to provide example calculations throughout the specification and quantification steps. Results at all of the percent relative humidity/temperature combinations can be found in Bohn (11). The results from the 80% RH/35 °C combination were selected because the percent benzaldehyde retention results at this percent relative humidity/temperature combination were the most variable among all of the percent relative humidity/temperature combinations run. Thus, the calculated uncertainty values determined using the release values at 80% RH and 35 °C illustrate the largest variances associated with the data collected by Bohn (11).

Uncertainty of Benzaldehyde Release Rates Calculated from the Peak Areas Determined by the DVS-Fast GC-FID Method. As is noted in **Figure 1**, the benzaldehyde peak area variance, standard curve empirical constant variance, and vacuum sampling time variance all contribute to the overall uncertainty of the benzaldehyde release rates calculated from the peak areas determined by the DVS-fast GC-FID method.

The benzaldehyde release rate was calculated using eq 2

$$m_B(t) = \frac{A}{S} \times \frac{1}{t_{\text{samp}}} \quad (2)$$

where $m_B(t)$ is the benzaldehyde release rate at time t (μg/min), A is the peak area detected by the fast GC-FID (counts·s), S is

Table 1. Analysis Time, Sampling Time, Initial Mass of Benzaldehyde, Benzaldehyde Peak Area, Benzaldehyde Released (As Measured by the Fast GC-FID), Benzaldehyde Release Rate (m_B), and Variance of the Release Rate of Sample A Exposed to 80% Relative Humidity and 35 °C^a

analysis time (min)	sampling time (min)	benzaldehyde peak area (counts·s)	benzaldehyde released (μg)	m_B ($\mu\text{g}/\text{min}$)	variance of m_B ($\mu\text{g}/\text{min}$) ²
36.0	7.0	6444	0.01	1.41E-03	1.30E-08
58.0	7.0	3148	0.00	6.91E-04	1.19E-08
79.9	6.9	1697780	2.61	3.78E-01	1.06E-04
101.9	7.0	2767700	4.25	6.08E-01	2.73E-04
124.0	7.1	2220810	3.41	4.81E-01	1.71E-04
146.0	7.0	1863820	2.86	4.09E-01	1.24E-04
168.0	7.0	1497980	2.30	3.29E-01	8.00E-05
190.0	7.0	1255060	1.93	2.76E-01	5.61E-05
212.0	7.0	1056670	1.62	2.32E-01	3.98E-05
234.1	7.1	930235	1.43	2.01E-01	3.00E-05
256.2	7.1	802916	1.23	1.74E-01	2.23E-05
278.3	7.1	779087	1.20	1.69E-01	2.10E-05
300.4	7.1	668166	1.03	1.45E-01	1.55E-05
322.4	7.0	590069	0.91	1.30E-01	1.24E-05
344.4	7.0	513498	0.79	1.13E-01	9.41E-06
366.4	7.0	456451	0.70	1.00E-01	7.44E-06
388.4	7.0	398806	0.61	8.76E-02	5.68E-06
410.4	7.0	350333	0.54	7.69E-02	4.39E-06
432.4	7.0	309699	0.48	6.80E-02	3.43E-06
454.5	7.1	268826	0.41	5.82E-02	2.51E-06
476.6	7.1	237006	0.36	5.13E-02	1.96E-06
498.7	7.1	206570	0.32	4.47E-02	1.49E-06
520.8	7.1	181272	0.28	3.92E-02	1.15E-06
542.9	7.1	161736	0.25	3.50E-02	9.17E-07
565.0	7.1	144890	0.22	3.14E-02	7.38E-07
587.0	7.0	129301	0.20	2.84E-02	6.07E-07
609.0	7.0	114459	0.18	2.51E-02	4.78E-07
631.1	7.1	102700	0.16	2.22E-02	3.76E-07
653.2	7.1	91248	0.14	1.98E-02	3.00E-07

^a Initial mass of benzaldehyde = 903 μg .

the standard curve empirical constant, and t_{samp} is vacuum sampling time.

Application of the mathematical model given in eq 1 to eq 2 gives eq 3, which was used to calculate the variances associated with the benzaldehyde release rates calculated from the benzaldehyde peaks area determined using the DVS-fast GC-FID method

$$\text{var}[m_B] = \left(\frac{1}{St_{\text{samp}}}\right)^2 \times \text{var}[A] + \left(\frac{-A}{S^2 t_{\text{samp}}}\right)^2 \times \text{var}[S] + \left(\frac{-A}{St_{\text{samp}}^2}\right) \times \text{var}[t_{\text{samp}}] \quad (3)$$

where the terms in parentheses are the “sensitivity coefficients” as described following eq 1.

For this study, the variance of A (peak area) was calculated from the peak area results obtained by altering the slope sensitivity integration parameter defined in the integration program. Changing the integration parameters for small peaks resulted in a significant change in the resultant peak area, when compared to larger peaks. Thus, the variance obtained from altering the integration parameters of small peaks was the largest variance in peak area that will result. The variance of A was equal to $\sim 2.40 \times 10^5$ (counts·s)². From the manufacturer’s specifications for the precision of the clock, the t_{samp} variance was equal to 2.16 (s)².

Equation 4 shows the calculation used to determine the standard curve empirical constant (S)

$$S = A/b \quad (4)$$

where b is the mass of benzaldehyde injected into the GC (μg) and A is the resultant peak area (counts·s) for that injection. The variance of S equaled the square of the standard error associated with the standard curve slope. This value was calculated by performing an ANOVA ($\alpha = 0.05$) on the benzaldehyde peak area results obtained from replicate standard benzaldehyde injections. The calculated variance of S equaled 3.08×10^8 . **Table 1** provides an example of the analysis time (min), sampling time (min), initial mass of benzaldehyde (μg), benzaldehyde peak area (counts·s), benzaldehyde released (as measured by the fast GC-FID) (μg), benzaldehyde release rate ($\mu\text{g}/\text{min}$), and variance of the release rate ($\mu\text{g}/\text{min}$) results obtained for sample A, run at 80% RH and 35 °C.

Uncertainty of Time-Corrected Benzaldehyde Release Rates. Due to the fact that benzaldehyde release analysis times varied from sample to sample within each set, average release rates had to be corrected for the analysis time variation in order to perform uncertainty analysis. The release rates determined for each sample were corrected to the reported analysis time (\hat{t}) by a gradient. This gradient was determined using eq 5

$$m_B(\hat{t}) = m_B(t) + \frac{\partial m_B}{\partial t}(\hat{t} - t) \quad (5)$$

where $m_B(\hat{t})$ is the sample’s benzaldehyde release rate corrected to the reported analysis time, $m_B(t)$ is the sample’s benzaldehyde release rate at time t , $\partial m_B/\partial t$ is the temporal gradient of the sample’s benzaldehyde release rate, \hat{t} is the reported analysis time, and t is the sample’s analysis time. The term $\partial m_B/\partial t$ was estimated using backward, central, and forward difference finite-difference calculations, to determine the change in m_B for some small change in t . Mathematical representations of the backward, central, and forward difference equations are shown in eqs 6, 7, and 8, respectively:

backward difference

$$\frac{\partial m_B}{\partial t_b} = \frac{m_B(t_j) - m_B(t_{j-1})}{t_j - t_{j-1}} \quad (6)$$

central difference

$$\frac{\partial m_B}{\partial t_c} = \frac{m_B(t_{j+1}) - m_B(t_{j-1})}{t_{j+1} - t_{j-1}} \quad (7)$$

forward difference

$$\frac{\partial m_B}{\partial t_f} = \frac{m_B(t_{j+1}) - m_B(t_j)}{t_{j+1} - t_j} \quad (8)$$

Subscripts j , $j-1$, and $j+1$ indicate that the values used in the equations are those at the analysis time being evaluated, the analysis time preceding the evaluated analysis time, and the analysis time after the evaluated analysis time, respectively.

For each sample, each of these gradients was multiplied by the difference between the reported analysis time and the sample analysis time, and the resulting values were added to the original sample release rate (eq 5), giving the corrected release rate for that sample. The average of the three corrected release rates was the value used in the subsequent calculations.

The variance of the gradients associated with adjusting the sample benzaldehyde release rates according to the differences in analysis times was determined by calculating the variance of the three estimates obtained using eqs 6–8. Variance of the backward difference, central difference, and forward difference

calculations was determined using eqs 9, 10, and 11, respectively:

backward

$$\text{var} \left[\frac{\partial m_B}{\partial t_b} \right] = \frac{1}{\Delta \hat{t}_b^2} \times (\text{var}[m_B(\hat{t}_j)] + \text{var}[m_B(\hat{t}_{j-1})]) + \left(\frac{\Delta m_{Bb}}{\Delta t_b^2} \right)^2 \times \text{var}[\Delta t_b] \quad (9)$$

where $\Delta t_b = t_j - t_{j-1}$ and $\Delta m_{Bb} = m_B(t) - m_B(t-1)$

central

$$\text{var} \left[\frac{\partial m_B}{\partial t_c} \right] = \frac{1}{\Delta \hat{t}_c^2} \times (\text{var}[m_B(\hat{t}_{j+1})] + \text{var}[m_B(\hat{t}_{j-1})]) + \left(\frac{\Delta m_{Bc}}{\Delta t_c^2} \right)^2 \times \text{var}[\Delta t_c] \quad (10)$$

where $\Delta t_c = t_{j+1} - t_{j-1}$ and $\Delta m_{Bc} = m_B(t+1) - m_B(t-1)$

forward

$$\text{var} \left[\frac{\partial m_B}{\partial t_f} \right] = \frac{1}{\Delta \hat{t}_f^2} \times (\text{var}[m_B(\hat{t}_j)] + \text{var}[m_B(\hat{t}_{j+1})]) + \left(\frac{\Delta m_{Bf}}{\Delta t_f^2} \right)^2 \times \text{var}[\Delta t_f] \quad (11)$$

where $\Delta t_f = t_{j+1} - t_j$ and $\Delta m_{Bf} = m_B(t+1) - m_B(t)$

The variances obtained from eqs 9–11 were used to determine the variance of the benzaldehyde release rate after the gradients were applied (average of the values obtained in eqs 6–8). This variance was calculated for all three samples. Equation 12 was used to determine the variance of the corrected benzaldehyde release rate:

$$\text{var}[m_B(\hat{t})] = \text{var}[m_B(t)] + \left[\frac{\left(\frac{\partial m_B}{\partial t_b} + \frac{\partial m_B}{\partial t_c} + \frac{\partial m_B}{\partial t_f} \right)^2}{3} \right] \times \text{var}(\hat{t} - t) + \left(\frac{\hat{t} - t}{3} \right)^2 \times \left(\text{var} \left[\frac{\partial m_B}{\partial t_b} \right] + \text{var} \left[\frac{\partial m_B}{\partial t_c} \right] + \text{var} \left[\frac{\partial m_B}{\partial t_f} \right] \right) \quad (12)$$

Table 2 shows an example of the analysis time (min), benzaldehyde release rate variance ($\mu\text{g}/\text{min}$), variance of the backward gradient, variance of the central gradient, variance of the forward gradient, and variance of the average release rate ($\mu\text{g}/\text{min}$) after the time adjustment results obtained for sample A, which was run at 80% RH and 35 °C.

The variance of the average corrected benzaldehyde release rate that can be attributed to the DVS-fast GC-FID method was calculated using eq 13

$$\text{var}[m_{B,\text{av}}(\hat{t})] = \left(\frac{1}{3} \right)^2 \times (\text{var}[m_B(\hat{t})_A] + \text{var}[m_B(\hat{t})_B] + \text{var}[m_B(\hat{t})_C]) \quad (13)$$

where $\text{var}[m_B(\hat{t})_A]$, $\text{var}[m_B(\hat{t})_B]$, and $\text{var}[m_B(\hat{t})_C]$ are the variances of the benzaldehyde release rate corrected for the analysis time difference for samples A, B, and C, respectively, each run at 80% RH and 35 °C.

Table 2. Analysis Time, Benzaldehyde Release Rate Variance, Variance of the Backward Gradient, Variance of the Central Gradient, Variance of the Forward Gradient, and Variance of the Average Release Rate after the Time Adjustment of Sample A Exposed to 80% Relative Humidity and 35 °C

analysis time (min)	variance of $m_B(\hat{t})$ ($\mu\text{g}/\text{min}$) ²	variance of $\partial m_B/\partial t$ backward ($\mu\text{g}/\text{min}$)	variance of $\partial m_B/\partial t$ central ($\mu\text{g}/\text{min}$)	variance of $\partial m_B/\partial t$ forward ($\mu\text{g}/\text{min}$)	variance of $m_B(\hat{t})$ ($\mu\text{g}/\text{min}$) ² after time adjustment
58.0	1.19E-08	5.36E-11	5.68E-08	2.28E-07	4.20E-08
79.9	1.06E-04	2.28E-07	1.46E-07	8.10E-07	1.80E-04
101.9	2.73E-04	8.10E-07	1.48E-07	9.48E-07	4.77E-04
124.0	1.71E-04	9.48E-07	2.12E-07	6.28E-07	3.04E-04
146.0	1.24E-04	6.28E-07	1.34E-07	4.35E-07	2.21E-04
168.0	8.00E-05	4.35E-07	9.63E-08	2.92E-07	1.43E-04
190.0	5.61E-05	2.92E-07	6.41E-08	2.05E-07	1.01E-04
212.0	3.98E-05	2.05E-07	4.59E-08	1.48E-07	7.14E-05
234.1	3.00E-05	1.48E-07	3.30E-08	1.11E-07	5.38E-05
256.2	2.23E-05	1.11E-07	2.71E-08	9.21E-08	4.01E-05
278.3	2.10E-05	9.21E-08	2.01E-08	7.80E-08	3.78E-05
300.4	1.55E-05	7.80E-08	1.79E-08	5.96E-08	2.81E-05
322.4	1.24E-05	5.96E-08	1.33E-08	4.66E-08	2.26E-05
344.4	9.41E-06	4.66E-08	1.06E-08	3.61E-08	1.73E-05
366.4	7.44E-06	3.61E-08	8.07E-09	2.80E-08	1.37E-05
388.4	5.68E-06	2.80E-08	6.31E-09	2.14E-08	1.05E-05
410.4	4.39E-06	2.14E-08	4.87E-09	1.68E-08	8.13E-06
432.4	3.43E-06	1.68E-08	3.68E-09	1.26E-08	6.40E-06
454.5	2.51E-06	1.26E-08	2.86E-09	9.52E-09	4.73E-06
476.6	1.96E-06	9.52E-09	2.13E-09	7.34E-09	3.69E-06
498.7	1.49E-06	7.34E-09	9.33E-10	2.03E-09	2.79E-06
520.8	1.15E-06	2.03E-09	7.23E-10	4.40E-09	1.98E-06
542.9	9.17E-07	4.40E-09	1.01E-09	3.53E-09	1.59E-06
565.0	7.38E-07	3.53E-09	8.14E-10	2.88E-09	1.28E-06
587.0	6.07E-07	2.88E-09	6.50E-10	2.31E-09	1.05E-06
609.0	4.78E-07	2.31E-09	5.25E-10	1.83E-09	8.23E-07
631.1	3.76E-07	1.83E-09	4.14E-10	1.44E-09	6.46E-07

Uncertainty in the Calculation of Average Benzaldehyde Release Rates Due to Natural Variability. The variance results described in the previous section solely explain the uncertainty of the DVS-fast GC-FID method and do not explain any uncertainty due to any other factors, such as the natural variability (e.g., particle size, percent relative humidity, temperature) shown in **Figure 2**. Equation 14 was used to estimate the variance of the average corrected benzaldehyde release rate that can be attributed to other factors (e.g., Durarome particle size variability)

$$\text{var}[m_{B,\text{av}}(\hat{t})]_{\text{other}} = \frac{\left(\sum (m_B(\hat{t}) - m_{B,\text{av}}(\hat{t}))^2 \right)}{n-1} - \text{var}[m_{B,\text{av}}(\hat{t})]_{\text{method}} \quad (14)$$

where n is the number of samples within a percent relative humidity/temperature combination.

Table 3 compares the variance of the average corrected benzaldehyde release rate that can be attributed to the DVS-fast GC-FID method (eq 13) and the average corrected benzaldehyde release rate that can be attributed to other factors (eq 14). The variance that is associated with the DVS-fast GC-FID method is as much as 2 orders of magnitude smaller than the variance associated with natural variability, indicating that the variance associated with calculating benzaldehyde release rates is primarily attributable to natural variability.

Relative humidity and temperature variation also can contribute to the overall variance of the percent benzaldehyde retention results. The variance of the percent retention results due to the variation at a specific relative humidity was estimated using a central difference calculation that determined the

Table 3. Comparison of the Sample and the Method Variances Associated with the Average Release Rates Corrected for Analysis Time Differences at 80% Relative Humidity and 35 °C

av analysis time (min)	sample A		sample B		sample C		av		
	$m_B(\hat{t})_A$ ($\mu\text{g}/\text{min}$)	variance of $m_B(\hat{t})_A$ ($\mu\text{g}/\text{min}$) ²	$m_B(\hat{t})_B$ ($\mu\text{g}/\text{min}$)	variance of $m_B(\hat{t})_B$ ($\mu\text{g}/\text{min}$) ²	$m_B(\hat{t})_C$ ($\mu\text{g}/\text{min}$)	variance of $m_B(\hat{t})_C$ ($\mu\text{g}/\text{min}$) ²	$m_B(\hat{t})_{av}$ ($\mu\text{g}/\text{min}$)	variance of $m_B(\hat{t})_{av}$ ($\mu\text{g}/\text{min}$), method	variance of $m_B(\hat{t})_{av}$ ($\mu\text{g}/\text{min}$), total variability
57.3	-5.13E-03	4.20E-08	2.21E-03	1.79E-08	4.46E-03	2.99E-08	5.16E-04	9.97E-09	2.51E-05
78.9	3.65E-01	1.80E-04	4.21E-01	2.27E-04	2.92E-01	1.07E-04	3.59E-01	5.71E-05	4.21E-03
100.5	6.05E-01	4.77E-04	6.64E-01	5.70E-04	4.09E-01	2.16E-04	5.59E-01	1.40E-04	1.78E-02
122.1	4.89E-01	3.04E-04	5.36E-01	3.75E-04	3.13E-01	1.30E-04	4.46E-01	8.99E-05	1.37E-02
143.8	4.17E-01	2.21E-04	4.09E-01	2.19E-04	2.60E-01	8.97E-05	3.62E-01	5.88E-05	7.83E-03
165.4	3.36E-01	1.43E-04	3.17E-01	1.32E-04	2.14E-01	6.09E-05	2.89E-01	3.73E-05	4.31E-03
187.0	2.81E-01	1.01E-04	2.50E-01	8.16E-05	1.96E-01	5.10E-05	2.42E-01	2.59E-05	1.87E-03
208.7	2.37E-01	7.14E-05	2.05E-01	5.49E-05	1.70E-01	3.82E-05	2.04E-01	1.83E-05	1.13E-03
230.4	2.05E-01	5.38E-05	1.83E-01	4.40E-05	1.53E-01	3.11E-05	1.81E-01	1.43E-05	6.73E-04
252.0	1.77E-01	4.01E-05	1.66E-01	3.59E-05	1.45E-01	2.76E-05	1.62E-01	1.15E-05	2.67E-04
273.7	1.72E-01	3.78E-05	1.49E-01	2.92E-05	1.31E-01	2.29E-05	1.51E-01	1.00E-05	4.05E-04
295.4	1.48E-01	2.81E-05	1.38E-01	2.52E-05	1.16E-01	1.80E-05	1.34E-01	7.92E-06	2.70E-04
317.0	1.33E-01	2.26E-05	1.24E-01	2.03E-05	1.03E-01	1.43E-05	1.20E-01	6.36E-06	2.31E-04
338.6	1.16E-01	1.73E-05	1.08E-01	1.53E-05	9.41E-02	1.19E-05	1.06E-01	4.94E-06	1.25E-04
360.2	1.03E-01	1.37E-05	9.51E-02	1.20E-05	8.48E-02	9.66E-06	9.44E-02	3.92E-06	8.75E-05
381.9	9.07E-02	1.05E-05	8.31E-02	9.16E-06	7.69E-02	7.99E-06	8.36E-02	3.07E-06	4.72E-05
403.5	7.96E-02	8.13E-06	7.15E-02	6.79E-06	7.08E-02	6.77E-06	7.40E-02	2.41E-06	2.39E-05
425.1	7.06E-02	6.40E-06	6.37E-02	5.40E-06	6.53E-02	5.78E-06	6.66E-02	1.95E-06	1.30E-05
446.8	6.07E-02	4.73E-06	5.63E-02	4.22E-06	5.79E-02	4.57E-06	5.83E-02	1.50E-06	5.07E-06
468.5	5.35E-02	3.69E-06	4.88E-02	3.19E-06	5.45E-02	4.04E-06	5.23E-02	1.21E-06	9.15E-06
490.2	4.68E-02	2.79E-06	4.30E-02	2.47E-06	4.93E-02	3.30E-06	4.64E-02	9.52E-07	1.01E-05
526.2	3.82E-02	1.98E-06	3.37E-02	1.46E-06	4.29E-02	2.39E-06	3.83E-02	6.48E-07	2.11E-05
547.9	3.43E-02	1.59E-06	3.09E-02	1.24E-06	3.93E-02	2.01E-06	3.48E-02	5.38E-07	1.80E-05
569.5	3.08E-02	1.28E-06	2.72E-02	9.63E-07	3.69E-02	1.77E-06	3.16E-02	4.46E-07	2.40E-05
591.1	2.78E-02	1.05E-06	2.47E-02	7.94E-07	3.43E-02	1.54E-06	2.90E-02	3.76E-07	2.42E-05
612.8	2.46E-02	8.23E-07	2.12E-02	5.89E-07	3.08E-02	1.24E-06	2.56E-02	2.95E-07	2.37E-05
634.4	2.19E-02	6.46E-07	1.96E-02	5.05E-07	2.82E-02	1.04E-06	2.32E-02	2.44E-07	1.98E-05

gradient of the percent benzaldehyde retention with respect to relative humidity (eq 15)

$$\text{var} [\% \text{ retention}]_{\% \text{RH}} = \left(\frac{\% \text{ ret}_{(\% \text{RH}+10)} - \% \text{ ret}_{(\% \text{RH}-10)}}{\% \text{ RH}_{(\% \text{RH}+10)} - \% \text{ RH}_{(\% \text{RH}-10)}} \right)^2 \times \text{var}[\% \text{ RH}] \quad (15)$$

where % ret_(%RH+10) is the percent benzaldehyde retention value at the percent relative humidity 10% above the percent relative humidity that is being evaluated, % ret_(%RH-10) is the percent benzaldehyde retention value at the percent relative humidity 10% below the percent relative humidity that is being evaluated, % RH_(%RH+10) is the percent relative humidity 10% above the percent relative humidity that is being evaluated, and % RH_(%RH-10) is the percent relative humidity 10% below the percent relative humidity that is being evaluated. Thus, the denominator is equal to 20% RH.

The variance of the percent retention results due to the variation at a temperature was estimated using a central difference calculation that determined the gradient of the percent benzaldehyde retention with respect to temperature (eq 16)

$$\text{var} [\% \text{ retention}]_{^\circ \text{C}} = \left(\frac{\% \text{ ret}_{(^\circ \text{C}+10)} - \% \text{ ret}_{(^\circ \text{C}-10)}}{^\circ \text{C}_{(^\circ \text{C}+10)} - ^\circ \text{C}_{(^\circ \text{C}-10)}} \right)^2 \times \text{var}[^\circ \text{C}] \quad (16)$$

where % ret_(°C+10) is the percent benzaldehyde retention value at the temperature 10 °C above the temperature that is being evaluated, % ret_(°C-10) is the percent benzaldehyde retention value at the temperature 10 °C below the temperature that is being evaluated, °C_(°C+10) is the temperature 10 °C above the temperature that is being evaluated, and °C_(°C-10) is the temperature 10 °C below the temperature that is being evaluated. Thus, the denominator is equal to 20 °C.

The results obtained using eqs 15 and 16 indicate that the percent relative humidity and temperature variance make only

a small contribution to the average time corrected release rate variance, indicating that the inherent variability of the Durarome is the largest contributor to the average time corrected release rate variance.

Uncertainty in the Integration Calculation Used To Determine the Cumulative Benzaldehyde Measured by the Fast GC-FID. To calculate M_B , the cumulative mass of benzaldehyde detected and measured by the fast GC-FID, the average release rates ($\mu\text{g}/\text{min}$) corrected for the analysis time difference (which were calculated by averaging the results of eqs 6–8) were plotted against reported fast GC-FID analysis times. The area under the curve was determined at each reported fast GC-FID analysis time using the “Integrate Curve” macro in KaleidaGraph 3.6 (Synergy Software, Reading, PA). The macro calculates the mass of benzaldehyde released as the incremental area under the curve using eq 17

$$M_B(\hat{t}_j) = \left(\frac{m_{B,av}(\hat{t}_j) + m_{B,av}(\hat{t}_{j-1})}{2} \right) \times (\hat{t}_j - \hat{t}_{j-1}) + M_B(\hat{t}_{j-1}) \quad (17)$$

where $m_{B,av}(\hat{t}_j)$ and $m_{B,av}(\hat{t}_{j-1})$ are consecutive release rate measurements ($\mu\text{g}/\text{min}$) and t_j and t_{j-1} are consecutive reported analysis times (min). The integrated value equals the cumulative mass of benzaldehyde released, as measured by the fast GC-FID, between the two fast GC-FID analysis times.

The variance of the cumulative mass of benzaldehyde measured by the fast GC-FID was determined using eq 18

$$\text{var}[M_B(\hat{t}_b)] = \left(\frac{m_{B,av}(\hat{t}_j) + m_{B,av}(\hat{t}_{j-1})}{2} \right)^2 \times \text{var}[\Delta \hat{t}_b] + \left(\frac{\Delta \hat{t}_b}{2} \right)^2 \times (\text{var}[m_{B,av}(\hat{t}_j)] + \text{var}[m_{B,av}(\hat{t}_{j-1})]) + \text{var}[M_B(\hat{t}_{j-1})] \quad (18)$$

where $\Delta \hat{t}_b = \hat{t}_j - \hat{t}_{j-1}$ and $m_{B,av}(\hat{t})$ is the average benzaldehyde

Table 4. Total Variance of the Calculated Percent Benzaldehyde Retention and the Percentage Each Parameter Contributed It for the "As Is" Sample at 80% Relative Humidity and 35 °C

reported analysis time (min)	% retention	total variance in % retention calculation	% of total variance due to Durarome mass variance	% of total variance due to initial % benzaldehyde variance	% of total variance due to vacuum sampling rate variance	% of total variance due to mass of benzaldehyde released (measured by GC-FID) variance	% of total variance due to DVS flow rate variance
35.7	99.99	2.27E-05	1.43E-13	1.71	0.61	97.58	0.10
57.3	99.98	2.25E-03	9.54E-15	0.11	0.04	99.84	0.01
78.9	96.61	4.64E-01	1.16E-12	13.92	4.97	80.30	0.82
100.5	88.00	3.45E+00	1.96E-12	23.40	8.35	66.88	1.37
122.1	78.59	8.73E+00	2.46E-12	29.49	10.53	58.25	1.73
143.8	70.98	1.37E+01	2.89E-12	34.55	12.33	51.09	2.03
165.4	64.88	1.79E+01	3.24E-12	38.76	13.83	45.13	2.28
187.0	59.91	2.14E+01	3.53E-12	42.21	15.07	40.24	2.48
208.7	55.71	2.45E+01	3.76E-12	45.03	16.07	36.26	2.64
230.4	52.10	2.73E+01	3.95E-12	47.25	16.87	33.11	2.77
252.0	48.88	2.99E+01	4.10E-12	49.10	17.52	30.49	2.88
273.7	45.94	3.24E+01	4.23E-12	50.65	18.08	28.30	2.97
295.4	43.26	3.48E+01	4.34E-12	51.92	18.53	26.51	3.05
317.0	40.87	3.71E+01	4.43E-12	52.96	18.90	25.02	3.11
338.6	38.75	3.91E+01	4.50E-12	53.84	19.22	23.79	3.16
360.2	36.88	4.10E+01	4.56E-12	54.57	19.48	22.74	3.20
381.9	35.20	4.27E+01	4.61E-12	55.20	19.70	21.86	3.24
403.5	33.73	4.43E+01	4.66E-12	55.73	19.89	21.11	3.27
425.1	32.41	4.57E+01	4.70E-12	56.18	20.05	20.47	3.30
446.8	31.23	4.69E+01	4.73E-12	56.57	20.19	19.92	3.32
468.5	30.19	4.81E+01	4.76E-12	56.91	20.31	19.44	3.34
490.2	29.26	4.91E+01	4.78E-12	57.19	20.41	19.03	3.36
526.2	27.94	5.06E+01	4.81E-12	57.58	20.55	18.48	3.38
547.9	27.25	5.14E+01	4.83E-12	57.78	20.62	18.20	3.39
569.5	26.63	5.21E+01	4.84E-12	57.96	20.69	17.96	3.40
591.1	26.06	5.28E+01	4.86E-12	58.11	20.74	17.74	3.41
612.8	25.55	5.34E+01	4.87E-12	58.25	20.79	17.54	3.42
634.4	25.10	5.40E+01	4.88E-12	58.37	20.83	17.37	3.43

Table 5. Total Variance of the Calculated Percent Benzaldehyde Retention and the Percentage Each Parameter Contributed It for the "As Is" Sample at 80% Relative Humidity and 25 °C

reported analysis time (min)	% retention	total variance in % retention calculation	% of total variance due to Durarome mass variance	% of total variance due to initial % benzaldehyde variance	% of total variance due to vacuum sampling rate variance	% of total variance due to mass of benzaldehyde released (measured by GC-FID) variance	% of total variance due to DVS flow rate variance
35.4	100.00	8.42E-07	3.98E-13	5.57	1.99	92.12	0.33
57.0	99.99	2.43E-05	9.68E-14	1.35	0.48	98.08	0.08
78.3	97.29	1.07E-01	2.76E-12	38.68	13.81	45.24	2.27
99.7	90.68	9.65E-01	3.61E-12	50.45	18.01	28.58	2.96
121.1	83.76	2.67E+00	3.95E-12	55.34	19.75	21.65	3.25
142.5	77.98	4.57E+00	4.25E-12	59.45	21.22	15.84	3.49
164.0	72.83	6.69E+00	4.42E-12	61.91	22.10	12.36	3.63
185.4	68.26	8.92E+00	4.53E-12	63.39	22.62	10.27	3.72
206.8	64.02	1.12E+01	4.63E-12	64.76	23.12	8.32	3.80
228.2	60.23	1.35E+01	4.69E-12	65.68	23.44	7.03	3.86
249.7	56.81	1.58E+01	4.74E-12	66.33	23.68	6.10	3.89
271.1	53.72	1.80E+01	4.77E-12	66.76	23.83	5.49	3.92
292.5	50.87	2.02E+01	4.79E-12	67.06	23.94	5.07	3.94
313.9	48.17	2.24E+01	4.81E-12	67.33	24.03	4.69	3.95
335.3	45.67	2.45E+01	4.83E-12	67.54	24.11	4.39	3.96
356.7	43.31	2.66E+01	4.84E-12	67.71	24.17	4.15	3.97
378.1	41.08	2.87E+01	4.85E-12	67.86	24.22	3.94	3.98
399.5	39.00	3.07E+01	4.86E-12	67.98	24.26	3.76	3.99
420.9	37.02	3.27E+01	4.87E-12	68.09	24.30	3.62	4.00
442.3	35.13	3.46E+01	4.87E-12	68.16	24.33	3.51	4.00
463.7	33.33	3.65E+01	4.88E-12	68.22	24.35	3.42	4.00
485.1	31.61	3.84E+01	4.88E-12	68.29	24.37	3.33	4.01
506.5	29.99	4.02E+01	4.88E-12	68.35	24.39	3.24	4.01
527.9	28.46	4.20E+01	4.89E-12	68.40	24.41	3.17	4.01
549.3	27.00	4.37E+01	4.89E-12	68.45	24.43	3.10	4.02
570.7	25.61	4.53E+01	4.90E-12	68.50	24.45	3.02	4.02
592.2	24.30	4.69E+01	4.90E-12	68.55	24.47	2.96	4.02
613.5	23.04	4.84E+01	4.90E-12	68.59	24.48	2.90	4.03
634.9	21.83	4.99E+01	4.90E-12	68.64	24.50	2.84	4.03

Table 6. Total Variance of the Calculated Percent Benzaldehyde Retention and the Percentage Each Parameter Contributed It for the Homogenous, Small-Particle Size Sample at 80% Relative Humidity and 25 °C

reported analysis time (min)	% retention	total variance in % retention calculation	% of total variance due to Durarome mass variance	% of total variance due to initial % benzaldehyde variance	% of total variance due to vacuum sampling rate variance	% of total variance due to mass of benzaldehyde released (measured by GC-FID) variance	% of total variance due to DVS flow rate variance
35.4	99.91	6.62E-04	1.47E-14	1.06	0.38	98.50	0.06
56.8	99.75	1.56E-03	4.27E-14	3.08	1.10	95.65	0.18
78.1	99.65	1.83E-03	7.21E-14	5.19	1.85	92.65	0.30
99.5	97.56	1.66E-02	3.93E-13	28.31	10.10	59.93	1.66
120.9	92.58	1.18E-01	5.11E-13	36.74	13.11	47.99	2.16
142.3	87.80	2.67E-01	6.11E-13	43.94	15.68	37.80	2.58
163.7	84.52	3.76E-01	6.98E-13	50.20	17.92	28.93	2.95
185.1	81.94	4.81E-01	7.43E-13	53.44	19.07	24.36	3.14
206.5	79.62	5.94E-01	7.65E-13	55.05	19.65	22.08	3.23
227.9	77.33	7.13E-01	7.89E-13	56.73	20.25	19.69	3.33
249.2	75.11	8.34E-01	8.14E-13	58.53	20.89	17.14	3.44
270.6	72.98	9.60E-01	8.33E-13	59.90	21.38	15.21	3.52
292.0	70.94	1.09E+00	8.48E-13	61.01	21.77	13.64	3.58
313.4	68.93	1.23E+00	8.61E-13	61.96	22.12	12.28	3.64
334.7	67.01	1.37E+00	8.71E-13	62.63	22.35	11.34	3.68
356.0	65.23	1.51E+00	8.79E-13	63.20	22.56	10.54	3.71
377.4	63.47	1.65E+00	8.86E-13	63.72	22.74	9.80	3.74
398.9	61.64	1.81E+00	8.92E-13	64.15	22.90	9.19	3.77
420.2	59.87	1.96E+00	8.98E-13	64.58	23.05	8.58	3.79
441.6	58.00	2.14E+00	9.02E-13	64.89	23.16	8.15	3.81
463.0	56.12	2.33E+00	9.05E-13	65.10	23.24	7.84	3.82
484.3	54.39	2.51E+00	9.08E-13	65.35	23.32	7.49	3.84
505.6	52.59	2.70E+00	9.10E-13	65.49	23.38	7.28	3.84
527.0	50.75	2.91E+00	9.12E-13	65.64	23.43	7.08	3.85
548.3	48.99	3.11E+00	9.16E-13	65.90	23.52	6.71	3.87
569.7	47.33	3.30E+00	9.20E-13	66.17	23.62	6.33	3.88
591.0	45.74	3.49E+00	9.23E-13	66.38	23.69	6.03	3.90
612.3	44.11	3.70E+00	9.25E-13	66.51	23.74	5.85	3.90
633.6	42.51	3.91E+00	9.25E-13	66.56	23.76	5.77	3.91

release rate corrected for the analysis time difference due to sample uncertainty or any unknown uncertainty parameters. $\text{var}[m_{B,av}(\hat{t})]$ was calculated as the variance observed from the three time-corrected benzaldehyde release rates (eq 13).

Uncertainty in the Percent of Expelled Humidified Air Sampled by the Vacuum Sampling Line. The variances of R_{DVS} , the DVS air flow rate, and R_{VS} , the vacuum sampling rate, were both determined by recording eight flow rate measurements using a mini-Buck calibrator flow meter (AP Buck, Inc., Orlando, FL). The average, standard deviation, and variance of the measured values were calculated.

Combination. *Uncertainty Associated with the Mathematical Model Used To Determine the Percent of Benzaldehyde Retained.* To determine the uncertainty associated with the mathematical model used to determine benzaldehyde retention, the variances of (1) the initial mass of the Durarome samples in a percent relative humidity/temperature set, (2) the percent benzaldehyde originally contained in the Durarome samples, (3) the mass of benzaldehyde detected by the fast GC-FID, (4) the flow rate out of the DVS system, and (5) and the vacuum sampling rate were all specified mathematically and quantified. The mathematical model developed to determine the percent of benzaldehyde retained by the Durarome matrix after \hat{t} minutes at a specific percent relative humidity/temperature combination is given in eq 19

$$\% \text{ retention} = \frac{\left[D \times B - M_B \times \frac{R_{DVS}}{R_{VS}} \right]}{D \times B} \times 100\% \quad (19)$$

where D is the initial mass of the Durarome sample prior to

humidification (μg), B is the percent of the initial Durarome mass that is benzaldehyde (as a decimal), M_B is the mass of benzaldehyde released between time = 0 and time \hat{t} as measured by the fast GC-FID (μg), R_{DVS} is the flow rate out of the DVS system (mL/min), R_{VS} is the vacuum sampling rate into the fast GC-FID (mL/min), and 100% is a constant that translates the Durarome retained from a dimensionless fraction to the commonly used expression of retention as a percent of the original benzaldehyde present in the Durarome. Simplifying, eq 19 is reduced to eq 20

$$\% \text{ retention} = 100\% \frac{-100\% \times M_B \times R_{DVS}}{R_{VS} \times D \times B} \quad (20)$$

where the variables are the same as those defined previously.

The overall variance of the mathematical model used to calculate percent benzaldehyde retention was calculated using eq 21

$$\begin{aligned} \text{var}[\% \text{ retention}] = & \left(-\frac{100 \times R_{DVS}}{D \times B \times R_{VS}} \right)^2 \times \text{var}[M_B] + \\ & \left(-\frac{100 \times M_B}{D \times B \times R_{VS}} \right)^2 \times \text{var}[R_{DVS}] + \left(\frac{100 \times M_B \times R_{DVS}}{D^2 \times B \times R_{VS}} \right)^2 \times \\ & \text{var}[D] + \left(\frac{100 \times M_B \times R_{DVS}}{D \times B^2 \times R_{VS}} \right)^2 \times \text{var}[B] + \\ & \left(\frac{100 \times M_B \times R_{DVS}}{D \times B \times R_{VS}^2} \right)^2 \times \text{var}[R_{VS}] \quad (21) \end{aligned}$$

where $\text{var}[D]$ is the variance of the analytical balance, equal to

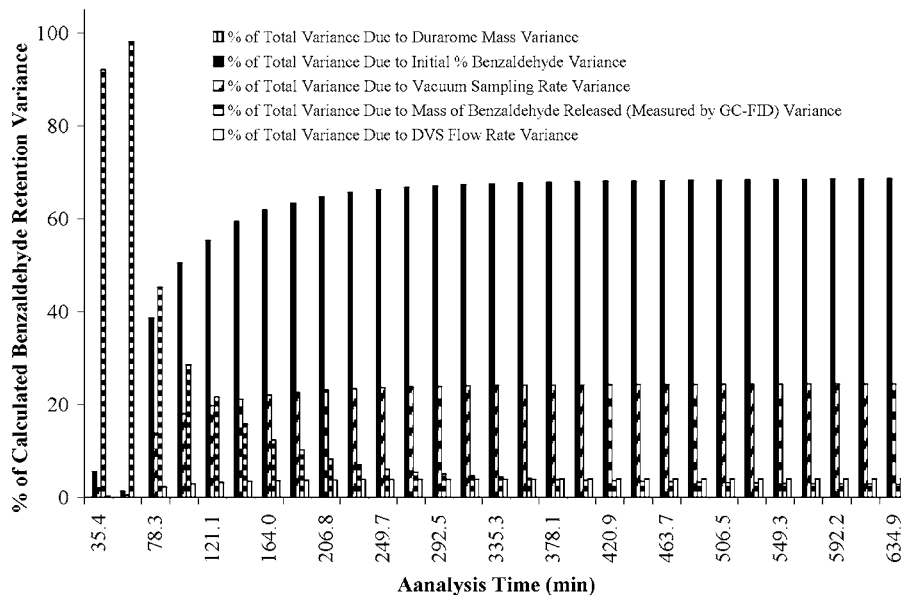


Figure 4. Graphical representation of the percentage each parameter contributed to the variance of the calculated percent benzaldehyde retention for the “as is” sample at 80% RH and 25 °C.

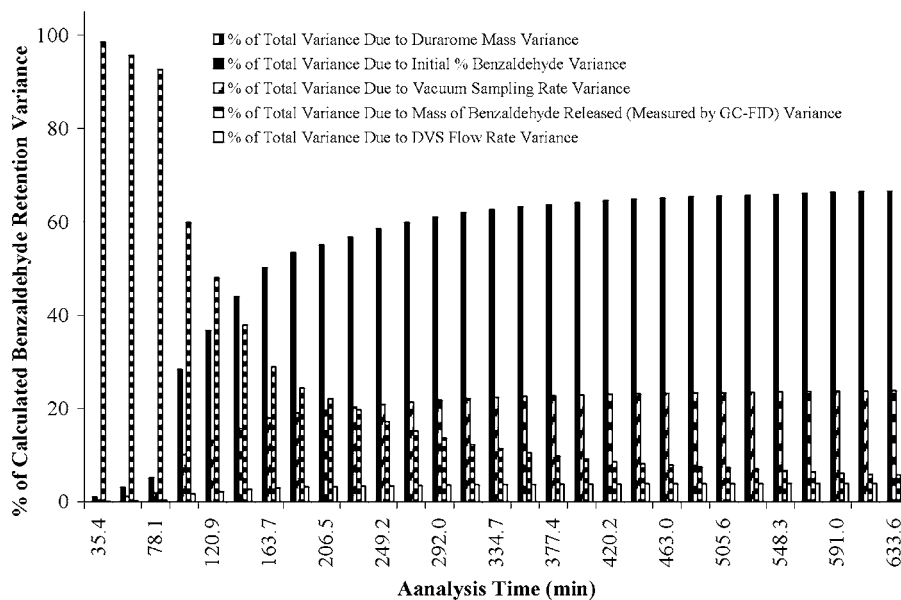


Figure 5. Graphical representation of the percentage each parameter contributed to the variance of the calculated percent benzaldehyde retention for homogeneous, small-particle size sample at 80% RH and 25 °C.

$8.86 \times 10^{-8} \mu\text{g}^2$, which was determined empirically, and $\text{var}[B]$ is the variance of the benzaldehyde content, equal to $2.48 \times 10^{-5} \mu\text{g}$ of benzaldehyde²/ μg of Durarome².

Table 4 shows an example of the results obtained for the variance of the calculated percent benzaldehyde retention at 80% RH and 35 °C. Taking the square root of the variance gives the standard deviation of the percent benzaldehyde retention values based on the results of the uncertainty analysis.

Artificial cherry Durarome particles were further ground and sifted to produce particle size homogeneity among the samples evaluated. Although the particle size of samples evaluated in sections above was limited to particles >0.0117 in. ($300 \mu\text{m}$) and <0.0234 in. ($600 \mu\text{m}$) in size, the surface area of each particle did vary. Differences in surface area cause variability in the rate at which moisture from the humidified air adsorbs onto the particle and enables the escape of the volatile

compounds. By grinding and further sifting the particles, particle surface area became more uniform and moisture adsorption rates were more consistent among the evaluated samples. **Table 5** shows the results obtained for the variance of the calculated percent benzaldehyde retention for the “as is” samples at 80% RH and 25 °C. **Table 6** shows the variance results for the samples also at 80% RH and 25 °C with the homogeneous particle size. Comparing the values in **Table 5** to the values in **Table 6** illustrates that the variance of the percent benzaldehyde retention decreases by ~ 1 order of magnitude when the particle size was more homogeneous.

To determine the percentage each parameter contributed to the variance of the calculated percent benzaldehyde retention, the variance resulting from each parameter was divided by the total variance. For example, the percentage of the overall percent benzaldehyde retention that is attributed to the variance

in the measured mass of benzaldehyde is (eq 22)

% of the overall uncertainty due to

M_B is the mass of benzaldehyde released =

$$100\% \times \frac{\left(-\frac{100 \times R_{DVS}}{D \times B \times R_{VS}}\right)^2 \times \text{var}(M_B)}{\text{var}(\% \text{ retention})} \quad (22)$$

Similar calculations were performed for all of the parameters in eqs 19 and 20. The percentages that each parameter contributed to the overall variance at 80% and 25 °C are also shown in **Tables 4** and **5**. The results shown in **Tables 4** and **5** are also graphically presented in **Figures 4** and **5**, respectively.

Tables 4 and **5** and **Figures 4** and **5** show that when the measured cumulative mass of benzaldehyde released is small, the variance associated with this value (natural and method uncertainty) is the largest contributor to the variance of the percent benzaldehyde retention. As the cumulative mass of benzaldehyde released increases, the largest contributor to the variance of the percent benzaldehyde retention switches to the initial percent of benzaldehyde in the Durarome sample. This can be attributed to two reasons. One, the cumulative mass of benzaldehyde released increases with time and, therefore, the number of observations from which the cumulative mass was calculated also increases. Because the variance of the cumulative mass decreases as the number of observations increases, the error associated with the mass of benzaldehyde measured becomes smaller. Two, as more benzaldehyde was released, the error associated with the initial percent of benzaldehyde in the Durarome had a greater influence on the percent benzaldehyde retention value.

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