

5. DISHWASHER EXPERIMENTS

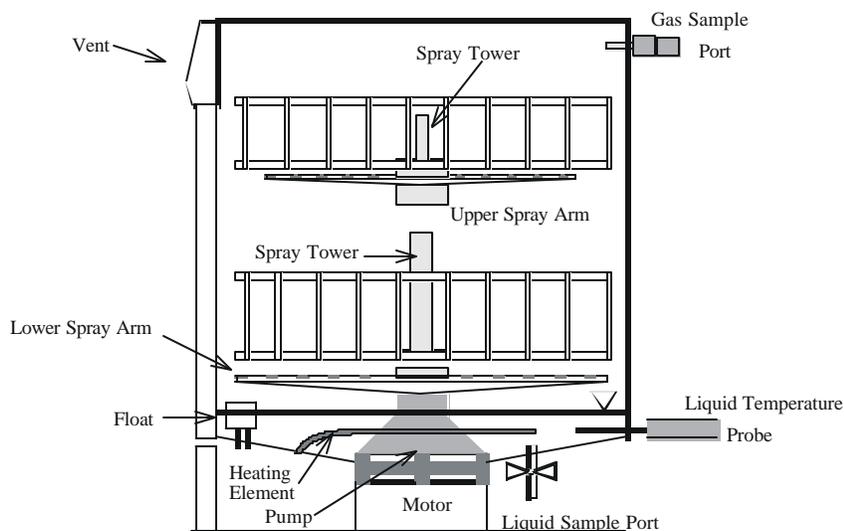
In dishwasher operation, chemicals originating in tap water can enter the machine and then be emitted to indoor air during one to five cycles (depending on wash cycle option selected). These cycles have similar operating characteristics. Thus, only a single cycle was studied experimentally. For this experimental cycle, a wide range of operating conditions was applied to adequately characterize the features associated with all of the cycles.

5.1. EXPERIMENTAL SYSTEM

A Kenmore™ dishwasher (Model No. 17651) was purchased and used for all experiments. The experimental system is illustrated in Figure 5-1. The experimental dishwasher had an interior volume of 188 L. It had five different types of wash/rinse cycle: Quick Rinse, China Light, Water Miser, Normal, and Pots and Pans. These cycle options differed only by the number of fills, that is, total volume of water used and length of operation.

The sequence of operation was as follows: the dishwasher was directly plumbed to a pressurized hot water line. At the start of each cycle, water entered the dishwasher from the hot water line at a flowrate of 4.1 L/minute. Twenty seconds after starting the fill, water from the basin pool was pumped to the rotary arm, which began spinning and spraying water throughout the dishwasher headspace. Water continued to enter the dishwasher from the hot water line for 99 seconds, such that a total of 6.8 L of water was present in the dishwasher. During the wash cycle, detergent was released from the holder as the dishwasher filled. At the end of each cycle, the water was pumped from the basin to a drain. Once all wash and rinse cycles were completed, there was an approximate 30-minute drying time.

The dishwasher was configured to allow for the required variable measurements to solve the dishwasher mass balance equations (Equations 2-23 and 2-24). A liquid sample port was installed at the bottom of the dishwasher. A 15 cm length of 0.635 cm OD Teflon™ tubing and a Teflon™ sample valve were connected to this port. The port inlet was observed to be submerged at all sampling times,



and the residence time of the sample tube was estimated to be approximately 2 seconds. Liquid samples were collected as described in Section 3.3.1.

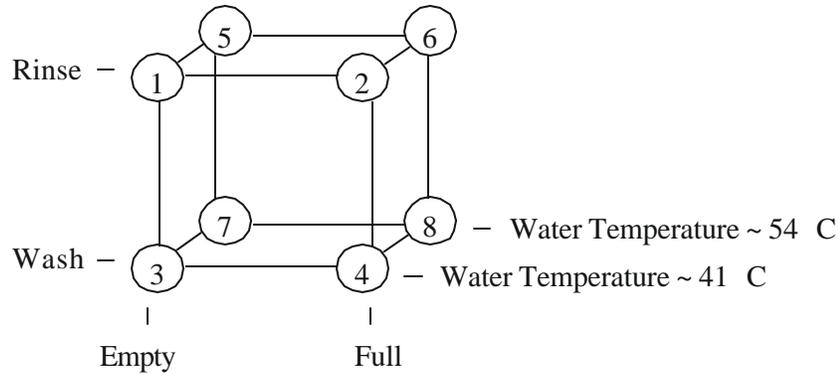
Figure 5-1. Dishwasher experimental system.

Gas samples were collected on sorbent tubes as described in Section 3.3.2. The sorbent tube was attached to a sample port located in the headspace of the dishwasher. A 2.5 cm OD Teflon™ tube was connected to the port on the inside of the dishwasher. Sample flowrates were in the range of 0.2 to 0.4 L/minute, as measured using a bubble flowmeter, and sampling times were approximately 30 seconds.

In addition to the liquid and gas sample ports, the dishwasher was configured to allow for liquid temperature monitoring. A thermocouple probe was submerged in the dishwasher pool and connected to a digital monitor to allow for constant temperature readings.

5.2. EXPERIMENTAL DESIGN

Dishwasher operating variables included water temperature, dish-loading pattern, and use of detergent (wash versus rinse portions). Experiments were designed to study the effects of these parameters on chemical volatilization rates using the $2 \times 2 \times 2$ factorial array shown in Figure 5-2. The numbers in Figure 5-2 correspond to the experiment number that was completed with the associated



operating conditions. For example, Experiment 1 had the operating conditions of a rinse cycle (no detergent present), empty machine (no dishes present),

Figure 5-2. Factorial experimental design for dishwasher experiments.

and a water temperature of 41°C. In order to fulfill the factorial requirements, eight experiments were completed. Additional experiments included replicates and quality assurance tests.

5.3. SOURCE-SPECIFIC METHODOLOGY

A standard protocol was developed for preparing the dishwasher for an experiment. The following tasks were completed prior to starting an experiment:

- The appropriate dishwasher settings (normal cycle, water heat on or off) were applied
- The dishwasher was started at the beginning cycle (prerinse cycle) and allowed to run to completion of the first cycle
- The tracer bags were agitated during the first cycle
- The fill of the wash cycle (2nd cycle) was timed
- For experiments using the water heat option, the dishwasher was allowed to run until the appropriate elevated temperature (~ 54°C) was reached
- The dishwasher was stopped after fill was complete (or appropriate water temperature was reached) and the door was opened
- An initial background liquid sample was collected from the dishwasher
- The chemical tracer cocktail was added to the dishwasher basin

- The liquid-phase temperature was recorded
- An initial gas-phase sample was collected and served as the initial gas-phase concentration
- Two liquid-phase samples were collected and averaged, and served as the initial liquid-phase concentration value.

5.3.1. Sample Schedule

Experiments were designed to last 10 minutes. Experiments using the water heat option tended to be shorter, depending on cycle time required to reach the appropriate temperature. For dishwasher experiments, it was expected that a rapid loss of chemical from the liquid phase would occur in the first minute of operation, followed by a relatively constant liquid-phase concentration. The liquid-phase sample schedule was designed to reflect this behavior such that samples were collected at experimental times of 0.25, 0.75, 1.5, 3.0, and 7.0 minutes. Two additional samples were collected at 10 minutes for applicable experiments. In total, 10 liquid-phase samples were collected for each dishwasher experiment.

Gas samples were collected for 30 seconds and scheduled such that a liquid sample was collected at the midpoint of the gas sampling time. At least four gas-phase samples were collected for each experiment.

5.3.2. Ventilation Rate

A grated exhaust vent was located on the top face of the dishwasher door from which gas naturally exited the dishwasher. This ventilation rate was estimated using an isobutylene tracer gas. Isobutylene has a Henry's law constant of $23 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ and will not dissolve appreciably into dishwasher water. Before starting the dishwasher, isobutylene was introduced at 100 ppm to the dishwasher headspace. The concentration inside the dishwasher was continuously monitored using a photo-ionization detector (PhotovacTM Microtip). An exponential line was fitted through data points on a plot of C_g vs. time, with the gas flowrate serving as the adjustable best-fit parameter.

5.3.3. Parameter Estimation

Experiments were completed using all five chemical tracers (acetone, ethyl acetate, toluene, ethylbenzene, and cyclohexane). In addition to peaks associated with the five tracers, the GC method used to analyze liquid-phase samples (see Section 3.4.1) indicated chemical peaks associated with compounds in the dishwasher detergent. A compound present in Cascade™ liquid dishwasher detergent eluted from the GC at the same retention time as ethyl acetate, thereby masking ethyl acetate's volatilization results. Correcting for this problem by altering the GC method resulted in a loss of definition for other tracer peaks. Thus, the original GC method was used to analyze dishwasher experimental samples, and ethyl acetate results were not reported for this source.

There were two distinct zones of chemical mass transfer for a dishwasher. Within the first 90 seconds of all experiments, a significant portion of the initial mass was volatilized to the dishwasher headspace. With the exception of cyclohexane, which completely volatilized, the dishwasher headspace behaved as if in dynamic equilibrium, a steady-state condition, for the remainder of the wash cycle (90 seconds to 10 minutes). This phenomenon made it difficult to estimate values of $K_L A$ that were representative of the entire cycle. Thus, values of $K_L A$ were determined for each chemical based on measurements collected within the first 45 seconds of an experiment. After this time the value of $K_L A$ became unimportant because the system had reached equilibrium conditions; that is, emissions could be determined via a simple equilibrium analysis without knowledge of specific mass transfer kinetics.

For cyclohexane, Equation 2-19 may be simplified to Equation 5-1 because C_g/H_c for this compound was negligible compared with C_1 for initial measured data:

$$\frac{dC_1}{dt} = -\frac{K_L A}{V_1} \cdot C_1 \quad (5-1)$$

where

- C_1 = Chemical concentration in water (M/L^3).
- t = Time (T).
- K_L = Overall mass transfer coefficient (L/T).

- A = Interfacial surface area between water and adjacent air (L^2).
V₁ = Liquid volume (L^3).

For all experiments, cyclohexane was completely stripped from the wash water within 90 seconds. By means of measured liquid-phase concentration values from 0 to 45 seconds, a best-fit exponential curve (forced through the measured initial liquid-phase concentration value) was used to estimate $K_L A$ for cyclohexane.

Acetone, toluene, and ethylbenzene were not completely transferred from the wash water because of equilibrium limitations. As with cyclohexane, the maximum volatilization rate for the other three chemicals occurred within the first 90 seconds. At this point, however, the system was near equilibrium such that little chemical mass transferred from the liquid phase to the headspace. As for cyclohexane, an exponential curve was fitted through the first three liquid-phase concentration data points, and the negative slope of this curve multiplied by the total liquid volume resulted in a $K_L A$ value. For some experiments, this method was less accurate for toluene, ethylbenzene, and especially acetone, because of the increased C_g/H_c value as the chemicals approached equilibrium within the headspace. In those cases, the reported value of $K_L A$ would be underestimated.

Using the dishwasher mass balance models (Equations 2-23 and 2-24) also proved difficult for determining values of $K_L A$ based on the initial 45 seconds of operation because of the nature of gas sampling. First, for several experiments an initial gas-phase sample was not collected, and thus the initial gas-phase concentration was assumed to be zero. This assumption maximized the concentration driving force term in Equation 2-19, thus leading to potential underestimation of $K_L A$. Also, gas-phase samples were collected for 30 seconds, over which time the average gas-phase concentration was predicted. During the rapid volatilization period of the first minute, gas-phase concentrations for each chemical increased at an exponential rate, such that the average measured value did not accurately characterize the headspace concentration during this time. Later in the experiment, when equilibrium conditions were reached, the gas samples better represented the actual conditions.

Thus, to be consistent, the method adopted to calculate values of $K_L A$ for acetone, toluene, and ethylbenzene was the same as that used for cyclohexane. Fortunately, the exact value of $K_L A$ for

these compounds is not critical because the system reached an equilibrium condition rapidly for all experiments. Knowing equilibrium will be reached, the amount of mass transferred from the liquid phase to the gas phase can be routinely determined given knowledge of the headspace ventilation rate and Henry's law constant for a chemical of interest.

5.4. DISHWASHER RESULTS

A total of 11 dishwasher mass transfer experiments and 18 ventilation experiments were completed to characterize the emission rate from a residential dishwasher. Each mass transfer and ventilation experiment was completed with the same wash cycle. Dishwasher cycles are similar in operation, such that experimental results based on a single cycle can be applied to all cycles in order to predict total chemical emissions during use. The ventilation rates, stripping efficiencies and mass transfer coefficients ($K_L A$, $k_1 A$, $k_g A$, and k_g/k_1) are presented in this chapter and are based on the experimental methodology presented in Sections 3.0 and 5.3. In addition, the effects of liquid temperature, detergent use, and dish loading pattern on each response are discussed.

The operating conditions for each mass transfer experiment are listed in Table 5-1.

5.4.1. Ventilation Rates

Ventilation rates as well as mass transfer coefficients were difficult to estimate during a single experiment. Therefore, ventilation rates were determined separately, following the

Table 5-1. Dishwasher experimental operating conditions

Experiment #	Liquid temp. (°C)	Liquid volume (L)	Headspace volume (L)	Ventilation rate (L/min)	Cycle portion type	Dish-loading pattern
1	43	7.4	181	5.7	Rinse	Empty
2	42	7.4	181	5.7	Rinse	Full
2 replicate	39	7.4	181	5.7	Rinse	Full
3	43	7.4	181	5.7	Wash	Empty
4	45	7.4	181	5.7	Wash	Full
4 replicate	38	7.4	181	5.7	Wash	Full
5	55	7.4	181	5.7	Rinse	Empty

6	55	7.4	181	5.7	Rinse	Full
7	54	7.4	181	5.7	Wash	Empty
8	55	7.4	181	5.7	Wash	Full
8 replicate	53	7.4	181	5.7	Wash	Full

methodology given in Section 5.3.2, for operating conditions similar to those used during mass transfer experiments. A total of 18 ventilation rate experiments were completed, including 11 replicate experiments. A summary of the ventilation experimental operating conditions and results is provided in Table 5-2.

As shown in Table 5-2, ventilation rates for all combinations of experimental conditions ranged from 4.6 to 7.2 L/minute. There was little deviation in ventilation rates between different water temperatures, using detergent or no detergent, and using dishes or no dishes. Thus, all experimental values were averaged to give an overall ventilation rate of 5.7 L/minute. This value was applied to all dishwasher mass transfer experimental analyses. The relatively low ventilation rate of the dishwasher allowed for low chemical emissions during operation and subsequent accumulation of chemicals in the dishwasher headspace.

A representative data plot for a ventilation experiment is shown in Figure 5-3. The experimental conditions for this plot were water heat on, detergent present, and full dishwasher (Ventilation Experiment 18). The slope for the exponential line was -0.0315 with an R^2 value of 0.99. Values of R^2 ranged from 0.95 to 1.0 for all ventilation plots. These high R^2 values indicated a relatively constant ventilation rate for the duration of the dishwasher cycle. For this experiment, the washing machine filled at 4.1 L/minute for 99 seconds, resulting in a total liquid volume of 6.8 L. Given a total volume of 188 L, the remaining headspace volume was 181 L. The corresponding ventilation rate for this experiment was 181 L multiplied by the negative of the slope, for a value of 5.7 L/minute.

In addition to the wash cycle, ventilation rates were determined for the entire time of operation (all cycles used). In general, values based on all of the cycles did not deviate significantly from the wash cycle results. Thus, the 5.7 L/minute average ventilation rate may be applied to any dishwasher cycle.

5.4.2. Chemical Stripping Efficiencies

Chemical stripping efficiencies (η) are reported in Table 5-3 for all tracer chemicals. Stripping efficiencies for dishwasher experiments were based on the initial and final liquid-phase

Table 5-2. Dishwasher ventilation rate experimental results

Experiment #	Water heat on?	Detergent present?	Dishes present?	Ventilation rate (L/minute)	Exponential fit R^2
1	No	No	No	6.3	0.95
2	No	No	No	5.0	0.98
3	No	No	No	5	0.98
4	No	No	No	5.9	0.98
5	No	No	No	7.2	0.99
6	No	No	No	4.7	0.98
7	No	No	No	5.6	0.99
8	No	No	No	5.5	0.98
9	No	No	No	5.3	0.99
10	Yes	No	No	6.5	0.95
11	Yes	No	No	5.2	0.98
12	Yes	No	No	4.6	0.99
13	No	Yes	No	5.5	0.99
14	No	No	Yes	6.4	0.98
15	Yes	No	Yes	5.5	0.99
16	No	Yes	Yes	6.2	0.98
17	Yes	Yes	Yes	7.2	1.0
18	Yes	Yes	Yes	5.7	0.99

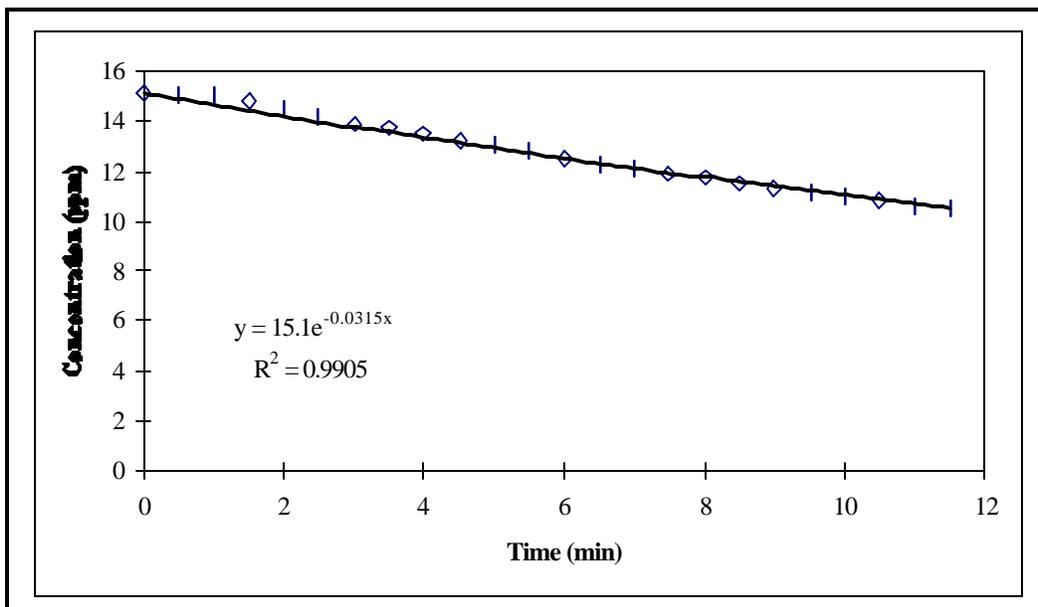


Figure 5-3. Isobutylene decay because of ventilation for Experiment 18.

Table 5-3. Chemical stripping efficiencies (h) for experimental dishwasher

Experiment #	Liquid temperature (°C)	Cycle type	Dish-loading pattern	Acetone h (%)	Toluene h (%)	Ethylbenzene h (%)	Cyclohexane h (%)
1	43	Rinse	Empty	50 ^a	97 ^a	97 ^a	100 ^a
2	42	Rinse	Full	34	96	97	100
2 replicate	39	Rinse	Full	45	97	98	100
3	43	Wash	Empty	37	96	97	100 ^a
4	45	Wash	Full	47	97	98	100
4 replicate	38	Wash	Full	42	96	97	100 ^a
5	55	Rinse	Empty	55 ^a	98	98	100
6	55	Rinse	Full	18	96	97	100 ^a
7	54	Wash	Empty	51	98	98	100
8	55	Wash	Full	37	97	97	100
8 replicate	53	Wash	Full	40 ^a	97 ^a	98 ^a	100 ^a

^aInitial liquid-phase concentration based on average of duplicate samples with a relative difference greater than 20%, but no more than 36%.

concentrations measured in the basin (Equation 2-2). The time for experiments using the water heat option was typically 3 minutes shorter than the time for experiments not using this option. Because the dishwasher headspace reached equilibrium within 2 minutes of operation, additional chemical volatilization from 7 to 10 minutes was assumed to be minimal. Thus, differences in experimental times were not accounted for in stripping efficiency results.

Stripping efficiencies for acetone ranged from 18% to 55%, with an overall average value of 41%. The highest value corresponded to the conditions of a rinse cycle, no dishes, and water temperature of 55°C.

For acetone, the stripping efficiencies were grouped to complete a factorial main effect analysis (see Section 3.7 for methodology). To illustrate this analysis, the calculation of the main effect of dish-loading pattern on stripping efficiency is presented below:

Corresponding experiments:		Difference in stripping efficiencies
1 – Average (2 and 2 rep)	=	11%
3 – Average (4 and 4 rep)	=	8.0 %
5 - 6	=	37 %
7 – Average (8 and 8 rep)	=	12%
Average	=	13 %

As shown in this example calculation, the main effect for dish-loading pattern was 13%. A positive value indicated that stripping efficiencies for acetone tended to increase with no dishes present. Acetone's stripping efficiencies were grouped according to dish-loading pattern and averaged giving values of 48% for an empty dishwasher and 37% for a full dishwasher, both values similar in magnitude to the overall average.

The second highest main effect on acetone stripping efficiency was detergent use, with a value of -2.5%. A negative effect indicated that acetone's stripping efficiencies tended to decrease for wash cycles. Finally, the main effect with water temperature was -2.0%, indicating that stripping efficiencies for acetone tended to decrease slightly with increasing temperature. In fact, as expected, stripping efficiencies increased for two of four experiments when water temperature was increased, and decreased in the other two experiments when water temperature was increased.

Dishwasher Experiments 2, 4, and 8 were replicated. Through comparison of the acetone stripping efficiencies for these three experiments, the following relative differences were calculated: 28% for Experiments 2 and 2 replicate, 11% for Experiments 4 and 4 replicate, and 7.8% for Experiments 8 and 8 replicate.

Stripping efficiencies for toluene ranged from 96% to 98%, with an average value of 97%. Similarly, stripping efficiencies for ethylbenzene ranged from 97% to 98%, also with an average value of

97%. This narrow range in stripping efficiencies did not allow for the use of a factorial analysis, such that no trends related to operating conditions and stripping efficiencies could be identified. However, stripping efficiencies for toluene and ethylbenzene were consistently greater than acetone, which has a lower Henry's law constant.

The relative differences in toluene stripping efficiencies between replicate experiments were 1.0% for Experiments 2 and 2 replicate, 1.0% for Experiments 4 and 4 replicate, and 0% for Experiments 8 and 8 replicate. Similarly, for ethylbenzene, relative differences were 1.0% for Experiments 2 and 2 replicate, Experiments 4 and 4 replicate, and Experiments 8 and 8 replicate, respectively.

Finally, 100% of cyclohexane volatilized for every experiment. In fact, 100% volatilization of cyclohexane was achieved within the first minute of almost all experiments. At the temperatures listed in Table 5-3, cyclohexane had Henry's law constants between $11 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ (Experiment 4 replicate with a temperature of 38°C) and $18 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ (Experiments 5, 6, and 8 replicate with a temperature of 55°C). Although no operating condition impacts could be identified, chemical stripping efficiencies did consistently increase for chemicals with increasing Henry's law constant.

Because cyclohexane achieved 100% volatilization for every experiment, the relative difference for replicate experiments was consistently 0%.

The chemical stripping efficiency results suggest that, for chemicals with a Henry's law constant greater than that for toluene, there will be nearly complete removal from the water whenever a dishwasher is used. This phenomenon is significant for many gasoline constituents, trichloroethene, tetrachloroethene, and radon. For lower volatility chemicals, stripping efficiency is defined by Henry's law.

5.4.3. K_LA Values

Values of K_LA for each chemical tracer are reported in Tables 5-4 to 5-7, respectively. Different tables were used for each chemical to show the factorial main effect analysis on each

Table 5-4. Acetone K_LA values for dishwasher experiments

Experiment #	Liquid temp.	Cycle type	Dish loading pattern	K_LA (L/min)	Dishes effect ^a (L/min)	Detergent effect ^b (L/min)	Liq. temp. effect ^c (L/min)
1	43	Rinse	Empty	7	2	1.9	1.2
2	42	Rinse	Full	4.2	2	3.1	3.3
2 replicate	39	Rinse	Full	5.8			
3	43	Wash	Empty	5.1	3.0	1.9	2.5
4	45	Wash	Full	6.8	3.0	3.1	3.0
4 replicate	38	Wash	Full	9.4			
5	55	Rinse	Empty	8.2	6.5	0.60	1.2
6	55	Rinse	Full	1.7	6.5	3.4	3.3
7	54	Wash	Empty	7.6	2.5	0.6	2.5
8	55	Wash	Full	4.9	2.5	3.4	3.0
8 replicate	53	Wash	Full	5.2			
				Average =	2.0	! 1.0	! 0.65

^a Dishes effect from full to none.

^b Detergent effect from full to none.

^c Liquid temperature effect from water heat off to water heat on.

Table 5-5. Toluene K_LA values for dishwasher experiments

Experiment #	Liquid temp.	Cycle type	Dish-loading pattern	K_LA (L/min)	Dishes effect ^a (L/min)	Detergent effect ^b (L/min)	Liq. temp. effect ^c (L/min)
1	43	Rinse	Empty	33	2.0	3.0	6
2	42	Rinse	Full	30	2	3.0	2
2 replicate	39	Rinse	Full	32			
3	43	Wash	Empty	30	4.0	3.0	8
4	45	Wash	Full	33	4.0	3.0	1.0
4 replicate	38	Wash	Full	34			
5	55	Rinse	Empty	39	6.0	1	6
6	55	Rinse	Full	33	6.0	0	2
7	54	Wash	Empty	38	5.0	1	8
8	55	Wash	Full	31	5	0	1.0
8 replicate	53	Wash	Full	35			
				Average =	2.3	0.25	! 3.8

^a Dishes effect from full to none.

^b Detergent effect full to none.

^c Liquid temperature effect from water heat off to water heat on.

Table 5-6. Ethylbenzene K_LA values for dishwasher experiments

Experiment #	Liquid temp.	Cycle type	Dish-loading pattern	K_LA (L/min)	Dishes effect ^a (L/min)	Detergent effect ^b (L/min)	Liq. temp. effect ^c (L/min)
1	43	Rinse	Empty	31	3.0	2.0	11
2	42	Rinse	Full	32	3.0	2.0	2
2 replicate	39	Rinse	Full	35			
3	43	Wash	Empty	33	3.0	2.0	8
4	45	Wash	Full	35	3.0	2.0	0
4 replicate	38	Wash	Full	36			
5	55	Rinse	Empty	42	6.0	1.0	11
6	55	Rinse	Full	36	6.0	0	2
7	54	Wash	Empty	41	5.0	1.0	8
8	55	Wash	Full	34	5	0	0
8 replicate	53	Wash	Full	37			
				Average =	1.3	! 0.80	5.3

^a Dishes effect from full to none.

^b Detergent effect from full to none.

^c Liquid temperature effect from water heat off to water heat on.

Table 5-7. Cyclohexane K_LA values for dishwasher experiments

Experiment #	Liquid temp.	Cycle type	Dish-loading pattern	K_LA (L/min)	Dishes effect ^a (L/min)	Detergent effect ^b (L/min)	Liq. temp. effect ^c (L/min)
1	43	Rinse	Empty	45	9.0	6.0	12
2	42	Rinse	Full	49	9	2	2
2 replicate	39	Rinse	Full	58			
3	43	Wash	Empty	51	5.0	6.0	1
4	45	Wash	Full	50	5	2	5
4 replicate	38	Wash	Full	62			
5	55	Rinse	Empty	57	1.0	7.0	12
6	55	Rinse	Full	56	1.0	5.0	2
7	54	Wash	Empty	50	1.0	7.0	1
8	55	Wash	Full	47	1	5	5
8 replicate	53	Wash	Full	55			
				Average =	! 3.5	1.0	2

^a Dishes effect from full to none.

^b Detergent effect from full to none.

^c Liquid temperature effect from water heat off to water heat on.

combination of operating conditions (see Section 3.7 and 5.4.2 for methodology). The three factors of the dishwasher two-level factorial arrays were liquid temperature, use of detergent, and dish-loading pattern. As shown in Tables 5-4 to 5-7, the difference in experimental response was listed twice, once for each corresponding experiment. Duplicating the listing of each difference in response, however, does not affect the average value for each variable. The experimental results for Experiments 2 and 2 replicate, 4 and 4 replicate, and 8 and 8 replicate were averaged, respectively, before applying factorial analyses.

As shown in Table 5-4, values of $K_L A$ for acetone ranged from 1.7 to 9.5 L/minute, with an overall average value of 6.0 L/minute. The highest value corresponded to the experimental conditions of a wash cycle with dishes present, and water heat option.

The largest main effect on values of $K_L A$ for acetone was 2.0 L/minute for the presence of dishes. In a manner similar to stripping efficiency results, values of $K_L A$ were grouped according to the presence of dishes resulting in the following average values: 7.0 L/minute for experiments using no dishes and 5.5 L/minute for experiments using dishes.

Although a value of $K_L A$ was roughly estimated for acetone based on the first three liquid-phase data points, experimental results clearly show acetone reached an equilibrium condition within the dishwasher headspace. Figure 5-4 shows the ratios of gas-phase and liquid-phase concentrations measured during each experiment. The shaded portion of the graph shows the range of Henry's law constants for acetone calculated based on the correlation given in Section 3.2.1 for all experiments. As shown in Figure 5-4, C_g/C_l values measured at or after 90 seconds are within or above the shaded region. A possible reason that measured C_g/C_l values exceed the given range of Henry's law constants is the potential inaccuracy of the Henry's law constant for acetone at elevated temperatures. Also, experimental error in the liquid standard calibration or gas standard calibration could lead to higher predictions of C_g/C_l . Thus, results suggest that an assumption of rapid and dynamic equilibrium is valid

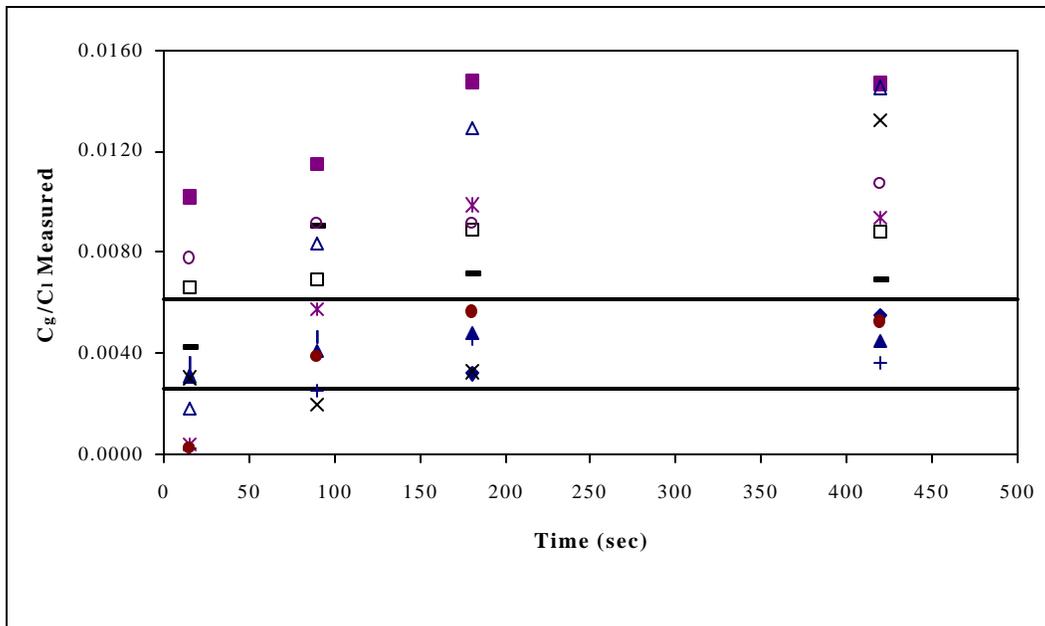


Figure 5-4. Comparison of measured C_g/C_i to predicted Henry's law constant for acetone.

for lower volatility chemicals, for example, many disinfection by-products. Unfortunately, Henry's law constants are lacking for many chemicals at elevated temperatures, a fact that currently hinders accurate predictions of dishwasher emissions.

Values of K_LA for toluene ranged from 30 to 39 L/minute, with an overall average of 33 L/minute. Despite this relatively narrow range of values, a factorial main effect analysis was also completed for toluene. The results are presented in Table 5-5 for each set of experimental conditions. The highest main effect was for water temperature, with a value of 3.8 L/minute. Grouping values of K_LA according to water temperature and averaging them gave the following results: 32 L/minute for regular hot water (~41°C) and 35 L/minute for water additionally heated by a dishwasher heating element (~54°C).

Replicate experiments had the following relative differences between values of K_LA for toluene: 6.5% for Experiments 2 and 2 replicate, 3.0% for Experiments 4 and 4 replicate, and 12% for Experiments 8 and 8 replicate.

Toluene results for Experiment 8 are presented in Figure 5-5. The best-fit K_LA value for this experiment was 31 L/minute. The Henry's law constant for toluene for Experiment 8 (temperature = 55°C) was $0.62 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$. Figure 5-5 illustrates the initial drop in liquid-phase concentration followed by steady-state conditions. Steady-state conditions were reached because of the dishwasher ventilation rate. In general, the ratio of C_g/C_l for measured data occurring after 100 seconds was equivalent or slightly greater than the predicted Henry's law constant for that temperature. To further illustrate this approach to equilibrium, the y-axis of Figure 5-5 is shown magnified in Figure 5-6.

Values of K_LA for ethylbenzene were slightly higher than those for toluene, with values from 31 to 42 L/minute, with an overall average of 36 L/minute. For the temperatures listed in Table 5-6, ethylbenzene had Henry's law constants ranging from $0.64 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ and $1.4 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ compared with $0.40 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ and $0.62 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$ for toluene. The factorial main effects listed in Table 5-6 for ethylbenzene were also similar to those for toluene, with the highest value being 4.0 L/minute for liquid temperature. Grouping ethylbenzene K_LA values according to liquid temperature resulted in an average value of 34 L/minute for experiments with water heat off (~ 41°C), and 38 L/minute for water heated by dishwasher heating element (~ 54°C).

Replicate experiments had the following relative differences between values of K_LA for ethylbenzene: 9.0% for Experiments 2 and 2 replicate, 2.8% for Experiments 4 and 4 replicate, and 8.5% for Experiments 8 and 8 replicate.

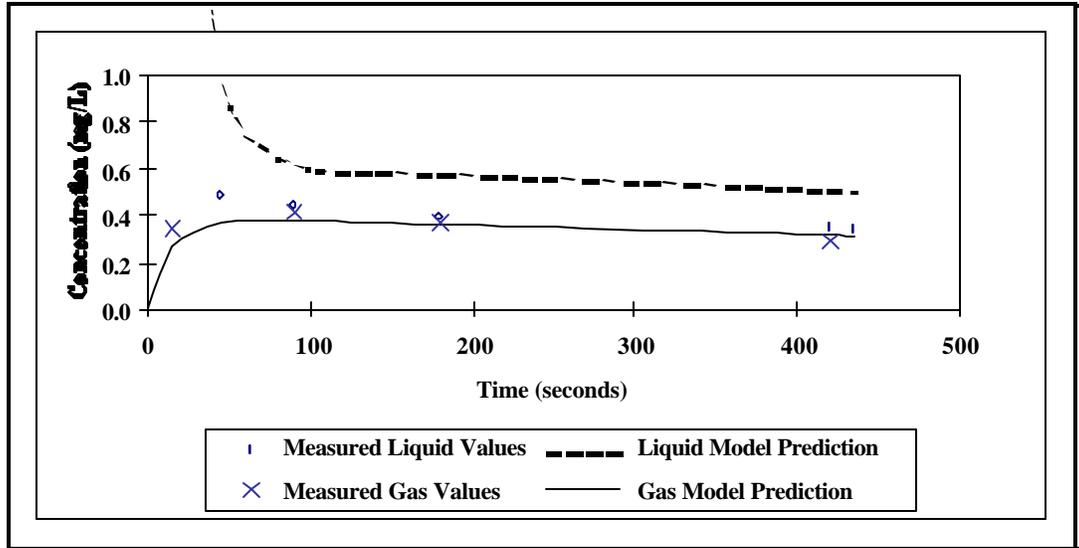


Figure 5-6. Amplitude of Figure 5-5 to illustrate for Equilibrium conditions for toluene.

Ethylbenzene results for Experiment 8 are plotted in Figure 5-7. This plot is similar to that of toluene, except the Henry's law constant for ethylbenzene at this temperature is $1.4 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$. Thus, at equilibrium, liquid-phase concentrations were less than gas-phase concentrations; that is, the gas and liquid concentration lines crossed.

Finally, values of $K_L A$ for cyclohexane ranged from 45 to 62 L/minute, with an overall average value of 53 L/minute (see Table 5-7). As expected from its relatively high Henry's law constant, cyclohexane consistently had the highest $K_L A$ value of all tracers for each experiment. Interestingly, cyclohexane had a slightly larger main effect of -3.5 L/minute associated with dish-loading pattern compared to 2.0 L/minute for liquid temperature.

Cyclohexane data for Experiment 8 are presented in Figure 5-8, which shows that cyclohexane has completely volatilized by 60 seconds into the experiment.

Replicate experiments had the following relative differences between values of $K_L A$ for cyclohexane: 17% for Experiments 2 and 2 replicate, 21% for Experiments 4 and 4 replicate, and 16% for Experiments 8 and 8 replicate.

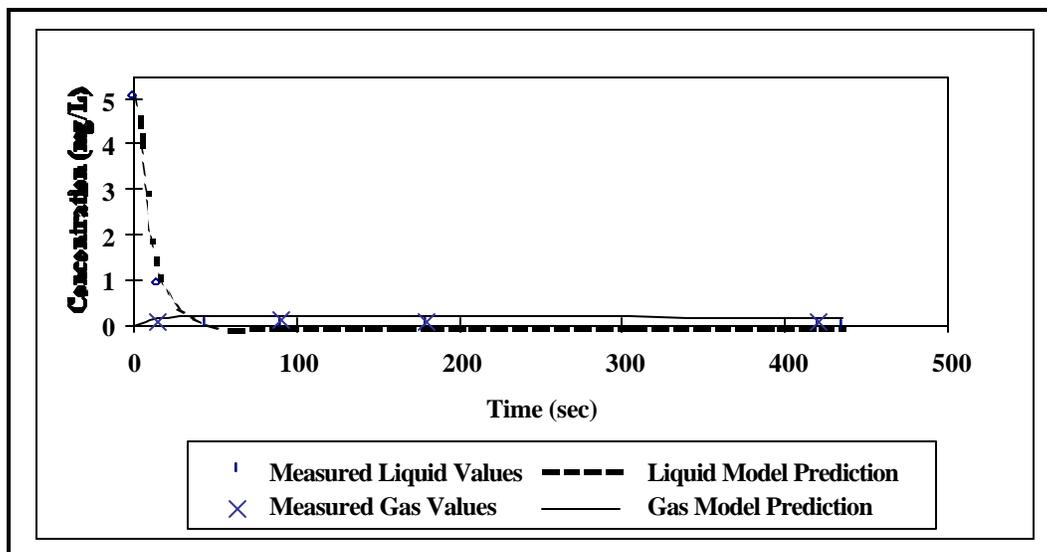


Figure 5-3. Ethylbenzene concentrations for Experiment 8.

The sensitivity of toluene's Henry's law constant on predicted emissions was also analyzed. The Henry's law constant of toluene would have to be reduced by 70% to reduce the predicted gas-phase concentrations of Experiment 8 by 10%. Thus, there is a critical value ($\approx 0.2 \text{ m}^3_{\text{liq}}/\text{m}^3_{\text{gas}}$) above which the accuracy of Henry's law is not as important to the estimation of chemical emissions from dishwasher use. In this case, even though equilibrium is reached, the volume of gas is large relative to the volume of liquid such that essentially all of the chemical mass is transferred to the gas.

5.4.4. Liquid- and Gas-Phase Mass Transfer Coefficients

The extent of chemical mass transfer in a dishwasher is dictated by chemical volatility. A chemical with a relatively high Henry's law constant will completely volatilize from the dishwasher, whereas a chemical with a lower Henry's law constant will be prevented from completely volatilizing because of equilibrium limitations. For lower volatility compounds, knowledge of gas-phase resistance to mass transfer is needed only for determining the time required to reach equilibrium. For higher volatility chemicals, the time to approach complete stripping is dictated by the liquid-phase mass transfer coefficient.

Because of the rapid approach to equilibrium for all chemicals except cyclohexane, it was not possible to determine values of k_gA during dishwasher experiments. The rate of mass transfer for cyclohexane is dominated by liquid-phase resistance such that Equation 2.5 may be simplified to

$$K_LA \cong k_lA \quad (5-2)$$

Values of k_lA for any chemical of interest may be predicted using cyclohexane data and Equation 2.12. The average value of k_lA for cyclohexane based on dishwasher experiments was 53 L/minute.

5.4.5. Mass Closure

An important goal for all experiments was to achieve adequate mass closure. For dishwasher experiments, mass closure was determined for separate experimental periods. An experimental period was defined when both a liquid-phase sample and a gas-phase sample were collected. Poor mixing in the initial seconds of a dishwasher experiment tended to lower the percent mass recovered for each chemical tracer in that mass closure period. Mass closure for this initial period was also difficult to assess because of gas sampling limitations. For the remaining three experimental periods, mass closure was consistent for all chemicals and was always in the range of 84% to 124%. All mass closure values for dishwasher experiments are reported in the database in the Appendix.